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(54) Title: BIO-BASED POLYMERS AND METHODS OF PRODUCING THEREOF

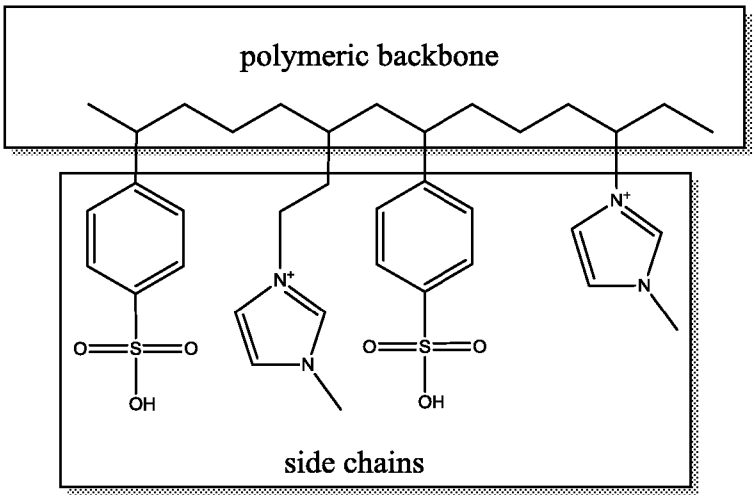

FIG. 1

(57) Abstract: Provided herein are bio-based polymers in which at least one component is derived partially or completely from bio-mass, and methods of producing such bio-based polymers. The bio-derived components can be obtained by degrading biomass using the catalysts described herein to produce a mixture of sugars, and the sugars can be converted into one or more components of the bio-based polymers.

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BIO-BASED POLYMERS AND METHODS OF PRODUCING THEREOF

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 61/637,370, filed April 24, 2012, and U.S. Provisional Application No. 61/743,931, filed September 14, 2012, both of which are incorporated herein by reference in their entireties.

FIELD

[0002] The present disclosure relates generally to bio-based polymers and methods of producing such polymers, and more specifically to bio-based polymers that contain components that are derived partially or completely from biomass using the polymer catalysts described herein.

BACKGROUND

[0003] Conventional plastics, such as those used in the manufacture of packaging materials, films, textiles, molded parts, and many other consumer products, are polymers currently made using chemical monomers derived from petroleum refining processes. Due to the rising cost of oil, the greenhouse gas emissions associated with petrochemicals, and mounting consumer demand for environmentally-responsible manufacturing, a need exists for replacing these oil-based monomers with equivalent monomers that are derived from non-petroleum sources.

[0004] One such method would be to develop processes for making the chemical monomers from renewable sources, such as biomass. Biomass is cellulosic material that is not suitable for food production and can contain, for example, a combination of cellulose, hemicellulose, and lignin. Hydrolysis of biomass to constituent sugars can be followed by chemical or fermentation processes to convert the sugars to the monomers from which plastics are derived.

[0005] Exemplary monomers that are currently converted into plastics include ethylene glycol. One use of ethylene glycol is to produce polyethylene terephthalate by polymerizing ethylene glycol (MEG) with terephthalic acid (PTA). Polyethylene terephthalate (PET) is widely used in, for example, bottles and containers for beverages and food. Another monomer that is ubiquitously incorporated into plastics is propylene, which is chemically polymerized into polypropylene. Polypropylene is used, for example, in making films, labels, trays, carpeting, automotive parts, and many other common plastic components.

[0006] Recent attention has focused on bio-based plastics, or plastics in which some to all of the petroleum-drived monomers are replaced by equivalent monomers derived from renewable sources, such as biomass. However, processes currently known for liberating sugars from biomass are inefficient on a commercial scale based on the sugar yields, as well as water and energy usage. Thus, there is an ongoing need for processes to efficiently obtain sugars from biomass on a commercially-viable scale, and convert these sugars to monomers for plastics production. These monomers will enable replacement of petroleum-based monomers to make bio-based polymers and commercial plastic products.

SUMMARY

[0007] The present disclosure addresses this need by providing methods to produce bio-based polymers, in which at least one component of the polymer is derived from a renewable source, such as biomass.

[0008] In one aspect, provided is a method of producing an ethylene glycol compound, by: a) providing a cellulosic material; b) contacting the cellulosic material with a polymer catalyst, c) degrading at least a portion of the cellulosic material to produce a saccharide composition; and d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture that includes an ethylene glycol compound. In other embodiments, the method further includes isolating the ethylene glycol compound from the fermentation product mixture. In yet other embodiments, the method further includes purifying the isolated ethylene glycol compound.

[0009] In one embodiment, provided herein is a method of producing an ethylene glycol compound, comprising:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers

comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone;

c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition comprises at least one of glucose, galactose, fructose, xylose, and arabinose; and

d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture comprising an ethylene glycol compound or a chemical intermediate between the saccharide composition and the ethylene glycol compound, or a mixture thereof.

[0010] The method can also include isolating the ethylene glycol compound from the fermentation product mixture. The ethylene glycol compound can be selected from monoethylene glycol, diethylene glycol, and polyethylene glycol.

[0011] Disclosed herein is a method of producing an ethylene glycol-containing compound, comprising: combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising the ethylene glycol-containing compound, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose.

[0012] In some embodiments, the saccharide composition can include one or more of glucose, galactose, fructose, xylose, and arabinose. In some embodiments, the saccharide composition can include two or more of these sugars. In other embodiments, the saccharide composition can include xylose and the chemical intermediate is selected from xylonate, 2-dehydro-3-deoxy-D-pentonate, and glycoaldehyde.

[0013] Provided is also an ethylene glycol compound produced according to any of the methods described above. In some embodiments, the ethylene glycol compound is monoethylene glycol, diethylene glycol, or polyethylene glycol. In one embodiment, the ethylene glycol compound is monoethylene glycol.

[0014] In yet another aspect, provided is a method of producing a propylene-containing compound, by: a) providing a cellulosic material; b) contacting the cellulosic material with a polymer catalyst, c) degrading at least a portion of the cellulosic material to produce a saccharide composition; and d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture that includes one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol; and e) converting the one or more compounds to the propylene-containing compound.

[0015] In yet another aspect, provided is a method of producing a propylene-containing compound, by:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone;

c) degrading at least a portion of the cellulosic material to produce a saccharide composition;

d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture that can include one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more compounds;

e) isolating the one or more compounds from the fermentation mixture; and

f) converting the one or more compounds to the propylene-containing compound.

[0016] In one embodiment, the method further includes producing polypropylene from propylene.

[0017] Disclosed herein is a method of producing a propylene-containing compound, comprising:

a) combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more compounds, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose, and

b) converting the one or more compounds to the propylene-containing compound.

[0018] In one aspect, provided is a method of producing a bio-based polymer that has a terephthalate component and an ethylene glycol component, by: a) providing a terephthalate component; b) providing an ethylene glycol component; and c) reacting the terephthalate component and the ethylene glycol component to produce a bio-based polymer, wherein at least about 1 wt% of the ethylene glycol component is bio-derived. In some embodiments, the terephthalate component comprises terephthalic acid, dimethylterephthalate, isophthalic acid, or a combination thereof. In other embodiments, at least a portion of the ethylene glycol component is produced from cellulosic material. The ethylene glycol component can be selected from monoethylene glycol, diethylene glycol, and polyethylene glycol.

[0019] In another aspect, provided is a method of producing a bio-based polymer that has a polypropylene component, by: a) providing a propylene component, wherein at least 1 wt% of the propylene component is bio-derived; and b) reacting the propylene component to produce a bio-based polymer that has a polypropylene component. The propylene reaction to form polypropylene can be, for example, a direct polymerization reaction or an indirect method, such as a process involving one or more intermediates. Such reactions are well known in the art. *See, e.g.,* Moore, E.P. Polypropylene Handbook. Polymerization, Characterization, Properties, Processing, Applications. Hanser Publishers: New York, 1996.

[0020] In some embodiments, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the ethylene glycol component is bio-derived. In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the ethylene glycol component is derived from cellulosic material (*e.g.*, biomass) degraded by a polymer catalyst.

[0021] In some embodiments, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the ethylene glycol component is bio-derived. In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the propylene component is derived from cellulosic material (*e.g.*, biomass) degraded by a polymer catalyst.

[0022] In some embodiments, the polymer catalyst is a solid-supported acid catalyst or a polymeric acid catalyst. In certain embodiments, the solid-supported acid catalyst can include a support and a plurality of acidic groups attached to the support. In certain embodiments, the support is selected from biochar, carbon, amorphous carbon, activated carbon, silica, silica gel, and alumina, or a combination thereof. In certain embodiments, the acidic groups at each

occurrence are independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid.

[0023] In other embodiments, the polymer catalyst can include a support and a plurality of acidic groups and cationic groups attached to the support. In certain embodiments, the support is selected from biochar, carbon, amorphous carbon, activated carbon, silica, silica gel, and alumina, or a combination thereof. In certain embodiments, the acidic groups at each occurence are independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid. In certain embodiments, the ionic groups at each occurence are independently selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium, phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, triphenyl phosphonium and trifluoro phosphonium.

[0024] In other embodiments, the polymer catalyst is a polymeric acid catalyst. In certain embodiments, the polymeric acid catalyst has acidic monomers that are connected to form a polymeric backbone, in which each acidic monomer has at least one Bronsted-Lowry acid. In other embodiments, the polymeric acid catalyst has acidic monomers and ionic monomers that are connected to form a polymeric backbone, in which each acidic monomer has at least one Bronsted-Lowry acid, and each ionic monomer independently has at least one nitrogen-containing cationic group or phosphorous-containing cationic group. In some embodiments, the Bronsted-Lowry acid at each occurrence is independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid. In certain embodiments, the Bronsted-Lowry acid at each occurrence is independently sulfonic acid or phosphonic acid. In one embodiment, the Bronsted-Lowry acid at each occurrence is sulfonic acid. In some embodiments, the nitrogen-containing cationic group at each occurrence is independently selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium. In one embodiment, the nitrogen-containing cationic group is imidazolium. In some embodiments, the phosphorous-containing cationic group at each occurrence is independently selected from triphenyl phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, and

trifluoro phosphonium. In one embodiment, the phosphorous-containing cationic group is triphenyl phosphonium.

[0025] In some embodiments, the one or more of the acidic monomers are directly connected to the polymeric backbone. In other embodiments, the one or more of the acidic monomers each further include a linker connecting the Bronsted-Lowry acid to the polymeric backbone. In certain embodiments, some of the Bronsted-Lowry acids are directly connected to the polymeric backbone, while other the Bronsted-Lowry acids are connected to the polymeric backbone by a linker. In some embodiments, the one or more of the ionic monomers are directly connected to the polymeric backbone. In other embodiments, the one or more of the ionic monomers each further include a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone. In certain embodiments, some of the cationic groups are directly connected to the polymeric backbone, while other cationic groups are connected to the polymeric backbone by a linker.

[0026] In some embodiments, the ethylene glycol component includes monoethylene glycol, diethylene glycol, or polyethylene glycol. In other embodiments, the bio-based polymer is polyethylene terephthalate, or copolyesters thereof. In some embodiments, the bio-based polymer is a polypropylene compound. In yet other embodiments, the bio-based polymer is recyclable, at least partially bio-degradable, or a combination thereof.

[0027] Provided is also a bio-based polymer produced according to any of the methods described herein.

[0028] In some embodiments, the saccharide composition includes at least one C5 saccharide and at least one C6 saccharide. In other embodiments, the at least one C5 saccharide and the at least one C6 saccharide are present in the saccharide composition in a ratio suitable for fermentation to produce the ethylene glycol compound. In yet other embodiments, the ratio of the at least one C5 saccharide and the at least one C6 saccharide is further suitable to feed the fermentation host producing the ethylene glycol compound. In one embodiment, the saccharide composition includes xylose, glucose and arabinose. In another embodiment, the xylose, glucose and arabinose is present in the saccharide composition in a ratio of about 20 to 1 to 1.

[0029] In some embodiments, the fermentation host is genetically modified to convert xylose to the ethylene glycol compound. In certain embodiments, the fermentation host is

genetically modified to convert xylose to ribulose, and ribulose to the ethylene glycol compound. In one embodiment, the fermentation host is a genetically modified *E. coli* strain.

[0030] In some embodiments, the fermentation host is genetically modified to convert the saccharide composition into one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. These intermediates can be converted to propylene via methods well known in the art. In one embodiment, the fermnentation host is a genetically modified bacterial strain selected from *Citrobacter freundii, Clostridium propionicum, Clostribdium butyricum, Escherichia coli, Lactobacillus buchneri, Lactobacillus brevis, Pichia stipites, Saccharomyces cerevisiae, Salmonello entericia, and Carnobacterium maltaromaticurn.* In one embodiment, the fermentation host is a genetically modified *E. coli* strain.

[0031] In yet another aspect, provided is a method of producing a bio-based polymer that includes a terephthalate component and a diol component, by: a) providing a terephthalate component; b) providing a diol component that includes an ethylene glycol compound, wherein at least a portion of the ethylene glycol compound is produced according to any of the methods described above; and c) reacting the terephthalate component and the diol component to produce a bio-based polymer.

[0032] In some embodiments, the terephthalate component includes terephthalic acid, dimethylterephthalate, and isophthalic acid, or a combination thereof. In other embodiments, at least a portion of the terephthalate component is derived from cellulosic material (*e.g.*, biomass). In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the terephthalate component is derived from cellulosic material. In other embodiments, of the terephthalate component is bio-derived.

[0033] In other embodiments, the diol component further includes cyclohexane dimethanol. In yet other embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the ethylene glycol component is derived from cellulosic material (*e.g.*, biomass). In certain embodiments, at least about 1 wt%, at least

about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the ethylene glycol compound in the diol component is produced according to any of the methods described above. In other embodiments, the ethylene glycol component is derived from cellulosic material degraded by a polymer catalyst.

[0034] In yet another aspect, provided is a method of producing a bio-based polymer that includes a polypropylene component, by: a) providing a propylene component wherein at least a portion of the propylene-containing compound is produced according to any of the methods described above; and b) reacting the propylene component to produce a bio-based polymer that has a polypropylene component.

[0035] In some embodiments, at least a portion of the propylene component is derived from cellulosic material (*e.g.*, biomass). In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the propylene component is derived from cellulosic material (*e.g.*, biomass). In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the propylene component is produced according to any of the methods described herein. In other embodiments, the propylene component is derived from cellulosic material degraded by a polymer catalyst.

[0036] In yet another aspect, provided is a method of producing a saccharide composition suitable for use in preparing monoethylene glycol, by: a) providing a cellulosic material; b) contacting the cellulosic material with a polymer catalyst, wherein the polymeric catalyst includes acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently have at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers have a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently have at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers have a linker connecting the nitrogen-containing

cationic group or the phosphorous-containing cationic group to the polymeric backbone; and c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition has at least one C5 saccharide and at least one C6 saccharide in a ratio suitable for fermentation to produce monoethylene glycol.

[0037] In some embodiments, the method further includes combining the saccharide composition with a fermentation host to produce a fermentation product mixture that includes monoethylene glycol. In other embodiments, the method further includes reacting the monoethylene glycol with a terephthalate component to produce a bio-based polymer.

[0038] In yet another aspect, provided is a method of producing a saccharide composition suitable for use in preparing suitable for use in preparing one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, by:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst, wherein the polymer catalyst includes acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently have at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers have a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently have at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers have a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone; and

c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition has at least one C5 saccharide and at least one C6 saccharide in a ratio suitable for fermentation to produce one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol.

[0039] In some embodiments, the method further includes d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture that includes one or more compounds selected from compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. In some embodiments, the method further includes e) isolating the one or more compounds from the fermentation mixture. In other embodiments, the method further includes converting the one or more compounds

selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol to propylene, and producing a polypropylene-containing compound from said propylene.

[0040] Provided herein is a composition comprising the saccharide composition and a fermentation host under conditions such that one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol are capable of being produced.

[0041] In some embodiments, the at least one C5 saccharide and the at least one C6 saccharide are present in the saccharide composition in a ratio suitable for fermentation to produce the monoethylene glycol. In other embodiments, the at least one C5 saccharide is xylose and arabinose, and the at least one C6 saccharide is glucose. In one embodiment, the xylose, glucose and arabinose is present in the saccharide composition in a ratio of about 20 to 1 to 1.

[0042] In some embodiments, the Bronsted-Lowry acid at each occurrence is independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid. In certain embodiments, the Bronsted-Lowry acid at each occurrence is independently sulfonic acid or phosphonic acid. In one embodiment, the Bronsted-Lowry acid at each occurrence is sulfonic acid. In some embodiments, the nitrogen-containing cationic group at each occurrence is independently selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium. In one embodiment, the nitrogen-containing cationic group is imidazolium. In some embodiments, the phosphorous-containing cationic group at each occurrence is independently selected from triphenyl phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, and trifluoro phosphonium. In one embodiment, the phosphorous-containing cationic group is triphenyl phosphonium.

[0043] In some embodiments, the linker at each occurrence is independently selected from unsubstituted or substituted alkylene, unsubstituted or substituted cycloalkylene, unsubstituted or substituted alkenylene, unsubstituted or substituted arylene, unsubstituted or substituted heteroarylene, unsubstituted or substituted alkylene ether, unsubstituted or substituted alkylene ester, and unsubstituted or substituted alkylene carbamate. In certain embodiments, the linker at each occurence is independently unsubstituted or substituted arylene, unsubstituted or substituted

heteroarylene. In certain embodiments, the linker is unsubstituted or substituted arylene. In one embodiment, the linker is phenylene. In another embodiment, the linker is hydroxyl-substituted phenylene.

[0044] Provided is also a saccharide composition produced according to any of the methods described above. In one embodiment, provided herein are compositions having a saccharide composition and a fermentation host under conditions suitable to produce ethylene glycol. In one embodiment, provided herein are compositions having a saccharide composition and a fermentation host under conditions such that one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol are capable of being produced.

[0045] The following description sets forth exemplary compositions, methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments. All references disclosed herein are incorporated by reference in their entirety.

DESCRIPTION OF THE FIGURES

[0046] The following description sets forth exemplary compositions, methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

[0047] FIG. **1** illustrates a portion of an exemplary polymer that has a polymeric backbone and side chains.

[0048] FIG. **2** illustrates a portion of an exemplary polymer, in which a side chain with the acidic group is connected to the polymeric backbone by a linker and in which a side chain with the cationic group is connected directly to the polymeric backbone.

[0049] FIG. **3A** illustrates a portion of an exemplary polymer, in which the monomers are randomly arranged in an alternating sequence.

[0050] FIG. **3B** illustrates a portion of an exemplary polymer, in which the monomers are arranged in blocks of monomers, and the block of acidic monomers alternates with the block of ionic monomers.

[0051] FIGS. **4A** and **4B** illustrate a portion of exemplary polymers with cross-linking within a given polymeric chain.

[0052] FIGS. **5A**, **5B**, **5C** and **5D** illustrate a portion of exemplary polymers with cross-linking between two polymeric chains.

[0053] FIG. **6A** illustrates a portion of an exemplary polymer with a polyethylene backbone.

[0054] FIG. **6B** illustrates a portion of an exemplary polymer with a polyvinylalcohol backbone.

[0055] FIG. **6C** illustrates a portion of an exemplary polymer with an ionomeric backbone.

[0056] FIG. **7A** illustrates two side chains in an exemplary polymer, in which there are three carbon atoms between the side chain with the Bronsted-Lowry acid and the side chain with the cationic group.

[0057] FIG. **7B** illustrates two side chains in another exemplary polymer, in which there are zero carbons between the side chain with the Bronsted-Lowry acid and the side chain with the cationic group.

[0058] FIG. **8** illustrates several non-limiting exemplary series of transformations of biomass to produce propylene.

[0059] FIG. **9** illustrates metabolic pathways from several sugars that can be produced by the methods described herein through one or more intermediates to reach 2-dihydroxyacetone phosphate (DHAP) and glycoaldehyde.

[0060] FIG. **10** illustrates metabolic pathways from DHAP and glycoaldehyde to precursor compounds of propylene, such as propanol and propanoate.

[0061] FIG. **11** illustrates metabolic pathways from 1,2-propanediol and DHAP to precursor compounds of propylene, such as 1,3-propanediol and 3-hydroxypropanoate.

DETAILED DESCRIPTION

[0062] The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

[0063] While specific embodiments of the present disclosure have been discussed, the specification is illustrative and not restrictive. Many variations of this disclosure will become apparent to those skilled in the art upon review of this specification. The full scope of the disclosure should be determined by reference to the claims, along with their full scope of equivalents, and the specification, along with such variations.

[0064] When ranges are used herein for physical properties, such as molecular weight, or chemical properties, such as chemical formulae, all combinations and subcombinations of ranges and specific embodiments therein are intended to be included. Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." The term "about" when referring to a number or a numerical range means that the number or numerical range referred to is an approximation within experimental variability (or within statistical experimental error), and thus the number or numerical range can vary from, for example, but not limited to, between 0.1% and 15% of the stated number or numerical range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure.

[0065] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this specification pertains.

[0066] As used in the specification and claims, the singular form "a", "an" and "the" includes plural references unless the context clearly dictates otherwise.

[0067] "Bronsted-Lowry acid" refers to a molecule, or substituent thereof, in neutral or ionic form that is capable of donating a proton (hydrogen cation, H^+).

[0068] "Homopolymer" refers to a polymer having at least two monomer units, and where all the units contained within the polymer are derived from the same monomer in the same

manner. A non-limiting example is polyethylene, where ethylene monomers are linked to form a uniform repeating chain (-CH_2-CH_2-CH_2-). Another non-limiting example is polyvinyl chloride, having a structure (-CH_2-CHCl-CH_2-CHCl-) where the -CH_2-CHCl- repeating unit is derived from the H_2C=CHCl monomer.

[0069] "Heteropolymer" refers to a polymer having at least two monomer units, and where at least one monomeric unit differs from the other monomeric units in the polymer. Heteropolymer also refers to polymers having difunctionalized, or trifunctionalized, monomer units that can be incorporated in the polymer in different ways. The different monomer units in the polymer can be in a random order, in an alternating sequence of any length of a given monomer, or in blocks of monomers. A non-limiting example is polyethyleneimidazolium, where if in an alternating sequence, would be the polymer depicted in FIG. **6C**. Another non-limiting example is polystyrene-co-divinylbenzene, where if in an alternating sequence, could be (-CH_2-CH(phenyl)-CH_2-CH(4-ethylenephenyl)-CH_2-CH(phenyl)-CH_2-CH(4-ethylenephenyl)-). Here, the ethenyl functionality could be at the 2, 3, or 4position on the phenyl ring.

[0070] As used herein, the terms "plastic" and "plastics" refer to any synthetic or semi-synthetic organic solid that is moldable. In many instances, a plastic contains one or more organic polymers, such as a homopolymer or heteropolymer. These polymers can have a backbone chain with repeating monomer units, and optionally, functional groups attached to the backbone as side chains. Attachment can be directly to the backbone or through a linker as described herein. In addition to the organic solid, the plastic can contain one or more additives that are separate entities from the polymer content. Such additives include, but are not limited to, antimicrobials, antioxidants, plasticizers, lubricants, fillers, light and heat stabilizers, fragrances, and pigments.

[0071] Plastics are catergorized as either thermoplastics or thermosetting polymers. Thermoplastics do not ondergo chemical change when heated and can be remolded. Polypropylene is an example of a thermoplastic. Thermosetting polymers melt during an irreversible chemical process to form a plastic shape which can not be remolded. Vulcanization of rubber is an example of a thermosetting polymer. Plastics can also be characterized by their biodegradability, elastomeric capability, electrical conductance, tensile strength, crystallinity and density.

[0072] As used herein, the terms "ethylene glycol compound", "ethylene glycol-containing compound" and "ethylene glycol component" refer to any of monoethylene glycol, diethylene glycol, or polyethylene glycol. The term "ethylene glycol" refers specifically to monoethylene glycol.

[0073] As used herein, the term "propylene" refers to the compound CH_3-CH_2=CH_2. The terms "propylene compound", "propylene-containing compound" and "propylene component" refer to CH_3-CH_2=CH_2, as well as any of ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol that can be converted to to propylene.

[0074] As used herein, the term "polypropylene" or "polypropylene-containing compound" refers to any addition polymer made from the propylene monomer. Polypropylenes can have thermoplastic and/or isotactic properties. Polypropylene can be atactic, syndiotactic, or a mixture thereof. Generally, there are three types of polypropylene, homopolymer, random copolymer and block copolymer. One common method of polymerization of propylene to afford polypropylene uses one or more of the Ziegler-Natta family of catalysts.

[0075] As used herein, ~~~~ denotes a generic polymeric backbone to which one or more substitutents or sidechains can be attached, as denoted by a straight perpendicular line descending from the ~~~~ mark.

[0076] When a range of values is listed, it is intended to encompass each value and sub–range within the range. For example "C_{1-6} alkyl" is intended to encompass, C_1, C_2, C_3, C_4, C_5, C_6, C_{1-6}, C_{1-5}, C_{1-4}, C_{1-3}, C_{1-2}, C_{2-6}, C_{2-5}, C_{2-4}, C_{2-3}, C_{3-6}, C_{3-5}, C_{3-4}, C_{4-6}, C_{4-5}, and C_{5-6} alkyl.

[0077] "Alkyl" refers to a straight or branched hydrocarbon chain group consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to ten carbon atoms (*e.g.*, C_1-C_{10} alkyl, 1-10C, C1-C10 or C1-10). Whenever it appears herein, a numerical range such as "1 to 10" refers to each integer in the given range; *e.g.*, "1 to 10 carbon atoms" means that the alkyl group can consist of 1 carbon atom, 2 carbon atoms, 3 carbon atoms, etc., up to and including 10 carbon atoms, although the present definition also covers the occurrence of the term "alkyl" where no numerical range is designated. In some embodiments, it is a C_1-C_6 alkyl group. In some embodiments, alkyl groups have 1 to 10, 1 to 6, or 1 to 3 carbon atoms. Representative saturated straight chain alkyls include -methyl, -ethyl, -n-propyl, -n-butyl, -n-pentyl, and -n-hexyl; while saturated branched alkyls include -isopropyl, -sec-butyl, -isobutyl, -tert-butyl, -isopentyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 2-

methylhexyl, 3-methylhexyl, 4-methylhexyl, 5-methylhexyl, 2,3-dimethylbutyl, and the like. The alkyl is attached to the rest of the molecule by a single bond, for example, methyl (Me), ethyl (Et), *n*-propyl, 1-methylethyl (*iso*-propyl), *n*-butyl, *n*-pentyl, 1,1-dimethylethyl (*t*-butyl), 3-methylhexyl, 2-methylhexyl, and the like. When an alkyl residue having a specific number of carbons is named, all geometric isomers having that number of carbons are intended to be encompassed and described; thus, for example, "butyl" is meant to include *n*-butyl, *sec*-butyl, *iso*-butyl, and *tert*-butyl; "propyl" includes *n*-propyl, and *iso*-propyl. As used herein, "alkylene" refers to the same residues as alkyl, but having bivalency. Examples of alkylene include methylene (-CH_2-), ethylene (-CH_2CH_2-), propylene (-$CH_2CH_2CH_2$-), butylene (-$CH_2CH_2CH_2CH_2$-).Unless stated otherwise in the specification, an alkyl group is optionally substituted by one or more of substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, -OR_a, -SR_a, -$N(R_a)_2$, -$C(O)R_a$, -$C(O)N(R_a)_2$, -$N(R_a)C(O)R_a$, -$N(R_a)S(O)tR_a$ (where t is 1 or 2), and -$S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0078] "Perhaloalkyl" refers to an alkyl group in which all of the hydrogen atoms have been replaced with a halogen selected from fluoro, chloro, bromo, and iodo. In some embodiments, all of the hydrogen atoms are each replaced with fluoro. In some embodiments, all of the hydrogen atoms are each replaced with chloro. Examples of perhaloalkyl groups include –CF_3, –CF_2CF_3, –$CF_2CF_2CF_3$, –CCl_3, –$CFCl_2$, –CF_2Cl and the like.

[0079] "Alkylaryl" refers to an -(alkyl)aryl group where aryl and alkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for aryl and alkyl respectively. The "alkylaryl" is bonded to the parent molecular structure through the alkyl group.

[0080] The term "alkoxy" refers to the group -O-alkyl, including from 1 to 10 carbon atoms of a straight, branched, cyclic configuration and combinations thereof, attached to the parent molecular structure through an oxygen atom. Examples include methoxy, ethoxy, propoxy, isopropoxy, cyclopropyloxy, cyclohexyloxy and the like. "Lower alkoxy" refers to alkoxy groups containing one to six carbons. In some embodiments, C_1-C_4 alkoxy is an alkoxy group which encompasses both straight and branched chain alkyls of from 1 to 4 carbon atoms. Unless

stated otherwise in the specification, an alkoxy group is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0081] "Alkenyl" refers to a straight or branched hydrocarbon chain group consisting solely of carbon and hydrogen atoms, containing at least one double bond, and having from two to ten carbon atoms (i.e., C2-C10 alkenyl). Whenever it appears herein, a numerical range such as "2 to 10" refers to each integer in the given range; e.g., "2 to 10 carbon atoms" means that the alkenyl group can consist of 2 carbon atoms, 3 carbon atoms, etc., up to and including 10 carbon atoms. In certain embodiments, an alkenyl comprises two to eight carbon atoms. In other embodiments, an alkenyl comprises two to five carbon atoms (e.g., C2-C5 alkenyl). When an alkenyl residue having a specific number of carbons is named, all geometric isomers having that number of carbons are intended to be encompassed and described; thus, for example, "butenyl" is meant to include *n*-butenyl, *sec*-butenyl, and *iso*-butenyl. Examples of alkenyl can include $–CH=CH_2$, $–CH_2-CH=CH_2$ and $–CH_2-CH=CH-CH=CH_2$. The alkenyl is attached to the parent molecular structure by a single bond, for example, ethenyl (i.e., vinyl), prop 1 enyl (i.e., allyl), but 1 enyl, pent 1 enyl, penta 1,4 dienyl, and the like. The one or more carbon–carbon double bonds can be internal (such as in 2–butenyl) or terminal (such as in 1–butenyl). Examples of C2–4 alkenyl groups include ethenyl (C2), 1–propenyl (C3), 2–propenyl (C3), 1–butenyl (C4), 2–butenyl (C4), butadienyl (C4) and the like. Examples of C2–6 alkenyl groups include the aforementioned C2–4 alkenyl groups as well as pentenyl (C5), pentadienyl (C5), hexenyl (C6) and the like. Additional examples of alkenyl include heptenyl (C7), octenyl (C8), octatrienyl (C8) and the like. As used herein, "alkenylene" refers to the same residues as alkenyl, but having bivalency. Examples of alkenylene include ethylene (-CH=CH-), propylene ($-CH_2-CH=CH-$) and butylene ($-CH_2-CH=CH-CH_2-$). Alkenyl contains only C and H when unsubstituted. Unless stated otherwise in the specification, an alkenyl group is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, -

$C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0082] "Amino" or "amine" refers to a $-N(R^b)_2$, $-N(R^b)R^b-$, or $-R_bN(R_b)R_b-$ group, where each R^b is independently selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein. When a $-N(R^b)_2$ group has two R^b other than hydrogen, they can be combined with the nitrogen atom to form a 3-, 4-, 5-, 6-, or 7-membered ring. For example, $-N(R^b)_2$ is meant to include, but not be limited to, 1-pyrrolidinyl and 4-morpholinyl. Unless stated otherwise in the specification, an amino group is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0083] The term "amino" also refers to N-oxides of the groups $-N^+(H)(R^a)O^-$, and $-N^+(R^a)(R^{a)}O-$, R^a as described above, where the N-oxide is bonded to the parent molecular structure through the N atom. N-oxides can be prepared by treatment of the corresponding amino group with, for example, hydrogen peroxide or m-chloroperoxybenzoic acid. The person skilled in the art is familiar with reaction conditions for carrying out the N-oxidation.

[0084] "Amide" or "amido" refers to a chemical moiety with formula $-C(O)N(R^b)_2$ or $-NR^bC(O)R^b$, where R^b is independently selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein. In some embodiments, this group is a C_1-C_4 amido or amide group, which includes the amide carbonyl in the total number of

carbons in the group. When a $-C(O)N(R^b)_2$ has two R^b other than hydrogen, they can be combined with the nitrogen atom to form a 3-, 4-, 5-, 6-, or 7-membered ring. For example, $N(R^b)_2$ portion of a $-C(O)N(R^b)_2$ group is meant to include, but not be limited to, 1-pyrrolidinyl and 4-morpholinyl. Unless stated otherwise in the specification, an amido R^b group is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0085] "Aromatic" or "aryl" refers to a group with six to ten ring atoms (*e.g.,* C_6-C_{10} aromatic or C_6-C_{10} aryl) which has at least one ring having a conjugated pi electron system which is carbocyclic (*e.g.,* phenyl, fluorenyl, and naphthyl). The aromatic carbocyclic group can have a single ring (*e.g.*, phenyl) or multiple condensed rings (*e.g.*, naphthyl or anthryl), which condensed rings may or may not be aromatic. For example, bivalent radicals formed from substituted benzene derivatives and having the free valences at ring atoms are named as substituted phenylene radicals. In other embodiments, bivalent radicals derived from univalent polycyclic hydrocarbon radicals whose names end in "-yl" by removal of one hydrogen atom from the carbon atom with the free valence are named by adding "-idene" to the name of the corresponding univalent radical, *e.g.,* a naphthyl group with two points of attachment is termed naphthylidene. An aryl group having more than one ring where at least one ring is non-aromatic can be connected to the parent structure at either an aromatic ring position or at a non-aromatic ring position. Whenever it appears herein, a numerical range such as "6 to 10 aryl" refers to each integer in the given range; *e.g.,* "6 to 10 ring atoms" means that the aryl group can consist of 6 ring atoms, 7 ring atoms, etc., up to and including 10 ring atoms. The term includes monocyclic or fused-ring polycyclic (*i.e.,* rings which share adjacent pairs of ring atoms) groups. Examples of aryl can include phenyl, phenol, and benzyl. Unless stated otherwise in the specification, an aryl moiety can be optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is

independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0086] "Aralkyl" or "arylalkyl" refers to an (aryl)alkyl— group where aryl and alkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for aryl and alkyl respectively. The "aralkyl/arylalkyl" is bonded to the parent molecular structure through the alkyl group. The terms "aralkenyl/arylalkenyl" and "aralkynyl/arylalkynyl" mirror the above description of "aralkyl/arylalkyl" wherein the "alkyl" is replaced with "alkenyl" or "alkynyl" respectively, and the "alkenyl" or "alkynyl" terms are as described herein.

[0087] "Azide" refers to a $-N_3$ radical.

[0088] "Carbamate" refers to any of the following groups: $-O-(C=O)-NR^b-$, $-O-(C=O)-N(R^b)_2$, $-N(R^b)-(C=O)-O-$, and $-N(R^b)-(C=O)-OR^b$, wherein each R^b is independnently selected from alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein.

[0089] "Cyano" refers to a –CN group.

[0090] "Cycloalkyl" refers to a monocyclic or polycyclic group that contains only carbon and hydrogen, and can be saturated, or partially unsaturated. Partially unsaturated cycloalkyl groups can be termed "cycloalkenyl" if the carbocycle contains at least one double bond, or "cycloalkynyl" if the carbocycle contains at least one triple bond. The cycloalkyl can consist of one ring, such as cyclohexyl, or multiple rings, such as adamantyl. A cycloalkyl with more than one ring can be fused, spiro or bridged, or combinations thereof. Cycloalkyl groups include groups having from 3 to 10 ring atoms (*i.e.,* C_3-C_{10} cycloalkyl). Whenever it appears herein, a numerical range such as "3 to 10" refers to each integer in the given range; *e.g.,* "3 to 10 carbon atoms" means that the cycloalkyl group can consist of 3 carbon atoms, 4 carbon atoms, 5 carbon atoms, etc., up to and including 10 carbon atoms. The term "cycloalkyl" also includes bridged and spiro-fused cyclic structures containing no heteroatoms. The term also includes monocyclic or fused-ring polycyclic (*i.e.,* rings which share adjacent pairs of ring atoms) groups. In some embodiments, it is a C_3-C_8 cycloalkyl group. In some embodiments, it is a C_3-C_5 cycloalkyl

group. Illustrative examples of cycloalkyl groups include, but are not limited to the following moieties: C_{3-6} carbocyclyl groups include, without limitation, cyclopropyl (C_3), cyclobutyl (C_4), cyclopentyl (C_5), cyclopentenyl (C_5), cyclohexyl (C_6), cyclohexenyl (C_6), cyclohexadienyl (C_6) and the like. Examples of C_{3-8} carbocyclyl groups include the aforementioned C_{3-6} carbocyclyl groups as well as cycloheptyl (C_7), cycloheptadienyl (C_7), cycloheptatrienyl (C_7), cyclooctyl (C_8), bicyclo[2.2.1]heptanyl, bicyclo[2.2.2]octanyl, and the like. Examples of C_{3-10} carbocyclyl groups include the aforementioned C_{3-8} carbocyclyl groups as well as octahydro–1*H*–indenyl, decahydronaphthalenyl, spiro[4.5]decanyl and the like. As used herein, "cycloalkylene" refers to the same residues as cycloalkyl, but having bivalency. Unless stated otherwise in the specification, a cycloalkyl group is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0091] "Ether" refers to a $–R^b-O-R^b-$ group where each R^b is independently selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein.

[0092] "Halo", "halide", or, alternatively, "halogen" means fluoro, chloro, bromo or iodo. The terms "haloalkyl," "haloalkenyl," "haloalkynyl" and "haloalkoxy" include alkyl, alkenyl, alkynyl and alkoxy structures that are substituted with one or more halo groups or with combinations thereof. For example, the terms "fluoroalkyl" and "fluoroalkoxy" include haloalkyl and haloalkoxy groups, respectively, in which the halo is fluorine, such as, but not limited to, trifluoromethyl, difluoromethyl, 2,2,2-trifluoroethyl, 1-fluoromethyl-2-fluoroethyl, and the like. Each of the alkyl, alkenyl, alkynyl and alkoxy groups can be optionally substituted as defined herein.

[0093] "Heteroalkyl" includes optionally substituted alkyl, alkenyl and alkynyl groups, respectively, and which have one or more skeletal chain atoms selected from an atom other than

carbon, *e.g.,* oxygen, nitrogen, sulfur, phosphorus or combinations thereof. A numerical range can be given, *e.g.,* C_1-C_4 heteroalkyl which refers to the chain length in total, which in this example is 4 atoms long. For example, a $–CH_2OCH_2CH_3$ group is referred to as a "C_4" heteroalkyl, which includes the heteroatom center in the atom chain length description. Connection to the rest of the parent molecular strucuture can be through either a heteroatom or a carbon in the heteroalkyl chain. Exemplary heteroalkyl groups include, without limitation, ethers such as methoxyethanyl ($–CH_2CH_2OCH_3$), ethoxymethanyl ($–CH_2OCH_2CH_3$), (methoxymethoxy)ethanyl ($–CH_2CH_2OCH_2OCH_3$), (methoxymethoxy)methanyl ($–CH_2OCH_2OCH_3$) and (methoxyethoxy)methanyl ($–CH_2OCH_2$ CH_2OCH_3) and the like; amines such as $–CH_2CH_2NHCH_3$, $–CH_2CH_2N(CH_3)_2$, $–CH_2NHCH_2CH_3$, $–CH_2N(CH_2CH_3)(CH_3)$ and the like. A heteroalkyl group can be optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0094] "Heteroaryl" or, alternatively, "heteroaromatic" refers to a refers to a group of a 5–18 membered monocyclic or polycyclic (*e.g.,* bicyclic or tricyclic) aromatic ring system (*e.g.,* having 6, 10 or 14 π electrons shared in a cyclic array) having ring carbon atoms and 1–6 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen ,phosphorous and sulfur ("5–18 membered heteroaryl"). A heteroaryl group may have a single ring (*e.g.*, pyridyl, pyridinyl, imidazolyl) or multiple condensed rings (*e.g.*, indolizinyl, benzothienyl) which condensed rings may or may not be aromatic. A heteroaryl group having more than one ring where at least one ring is non-aromatic can be connected to the parent structure at either an aromatic ring position or at a non-aromatic ring position. In one variation, a heteroaryl group having more than one ring where at least one ring is non-aromatic is connected to the parent structure at an aromatic ring position. Heteroaryl polycyclic ring systems can include one or more heteroatoms in one or both rings. Whenever it appears herein, a numerical range such as "5 to 18" refers to each integer in the given range; *e.g.,* "5 to 18 ring atoms" means that the heteroaryl group can consist of 5 ring atoms, 6 ring atoms, etc., up to and including 18 ring atoms. For example, bivalent radicals derived from univalent heteroaryl radicals whose names end in "-yl" by removal of one hydrogen atom from the atom

with the free valence are named by adding "-idene" to the name of the corresponding univalent radical, *e.g.,* a pyridyl group with two points of attachment is a pyridylidene.

[0095] For example, an N-containing "heteroaromatic" or "heteroaryl" moiety refers to an aromatic group in which at least one of the skeletal atoms of the ring is a nitrogen atom. One or more heteroatom(s) in the heteroaryl group can be optionally oxidized. One or more nitrogen atoms, if present, are optionally quaternized. "Heteroaryl" also includes ring systems substituted with one or more oxide (-O-) substituents, such as pyridinyl N-oxides. The heteroaryl is attached to the parent molecular structure through any atom of the ring(s).

[0096] "Heteroaryl" also includes ring systems wherein the heteroaryl ring, as defined above, is fused with one or more aryl groups wherein the point of attachment is either on the aryl or on the heteroaryl ring, or wherein the heteroaryl ring, as defined above, is fused with one or more carbocycyl or heterocycyl groups wherein the point of attachment is on the heteroaryl ring. For polycyclic heteroaryl groups wherein one ring does not contain a heteroatom (*e.g.,* indolyl, quinolinyl, carbazolyl and the like) the point of attachment can be on either ring, *i.e.,* either the ring bearing a heteroatom (*e.g.,* 2–indolyl) or the ring that does not contain a heteroatom (*e.g.,* 5–indolyl). In some embodiments, a heteroaryl group is a 5–10 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, phosphorous, and sulfur ("5–10 membered heteroaryl"). In some embodiments, a heteroaryl group is a 5–8 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, phosphorous, and sulfur ("5–8 membered heteroaryl"). In some embodiments, a heteroaryl group is a 5–6 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, phosphorous, and sulfur ("5–6 membered heteroaryl"). In some embodiments, the 5–6 membered heteroaryl has 1–3 ring heteroatoms selected from nitrogen, oxygen, phosphorous, and sulfur. In some embodiments, the 5–6 membered heteroaryl has 1–2 ring heteroatoms selected from nitrogen, oxygen, phosphorous, and sulfur. In some embodiments, the 5–6 membered heteroaryl has 1 ring heteroatom selected from nitrogen, oxygen, phosphorous, and sulfur.

[0097] Examples of heteroaryls include, but are not limited to, azepinyl, acridinyl, benzimidazolyl, benzindolyl, 1,3-benzodioxolyl, benzofuranyl, benzooxazolyl,

benzo[d]thiazolyl, benzothiadiazolyl, benzo[*b*][1,4]dioxepinyl, benzo[b][1,4]oxazinyl, 1,4-benzodioxanyl, benzonaphthofuranyl, benzoxazolyl, benzodioxolyl, benzodioxinyl, benzoxazolyl, benzopyranyl, benzopyranonyl, benzofuranyl, benzofuranonyl, benzofurazanyl, benzothiazolyl, benzothienyl (benzothiophenyl), benzothieno[3,2-d]pyrimidinyl, benzotriazolyl, benzo[4,6]imidazo[1,2-a]pyridinyl, carbazolyl, cinnolinyl, cyclopenta[d]pyrimidinyl, 6,7-dihydro-5H-cyclopenta[4,5]thieno[2,3-d]pyrimidinyl, 5,6-dihydrobenzo[h]quinazolinyl, 5,6-dihydrobenzo[h]cinnolinyl, 6,7-dihydro-5H-benzo[6,7]cyclohepta[1,2-c]pyridazinyl, dibenzofuranyl, dibenzothiophenyl, furanyl, furazanyl, furanonyl, furo[3,2-c]pyridinyl, 5,6,7,8,9,10-hexahydrocycloocta[d]pyrimidinyl, 5,6,7,8,9,10-hexahydrocycloocta[d]pyridazinyl, 5,6,7,8,9,10-hexahydrocycloocta[d]pyridinyl,isothiazolyl, imidazolyl, indazolyl, indolyl, indazolyl, isoindolyl, indolinyl, isoindolinyl, isoquinolyl, indolizinyl, isoxazolyl, 5,8-methano-5,6,7,8-tetrahydroquinazolinyl, naphthyridinyl, 1,6-naphthyridinonyl, oxadiazolyl, 2-oxoazepinyl, oxazolyl, oxiranyl, 5,6,6a,7,8,9,10,10a-octahydrobenzo[h]quinazolinyl, 1-phenyl-1*H*-pyrrolyl, phenazinyl, phenothiazinyl, phenoxazinyl, phthalazinyl, pteridinyl, purinyl, pyranyl, pyrrolyl, pyrazolyl, pyrazolo[3,4-d]pyrimidinyl, pyridinyl, pyrido[3,2-d]pyrimidinyl, pyrido[3,4-d]pyrimidinyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyrrolyl, quinazolinyl, quinoxalinyl, quinolinyl, isoquinolinyl, tetrahydroquinolinyl, 5,6,7,8-tetrahydroquinazolinyl, 5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidinyl, 6,7,8,9-tetrahydro-5H-cyclohepta[4,5]thieno[2,3-d]pyrimidinyl, 5,6,7,8-tetrahydropyrido[4,5-c]pyridazinyl, thiazolyl, thiadiazolyl, thiapyranyl, triazolyl, tetrazolyl, triazinyl, thieno[2,3-d]pyrimidinyl, thieno[3,2-d]pyrimidinyl, thieno[2,3-c]pridinyl, and thiophenyl (*i.e.,* thienyl). Unless stated otherwise in the specification, a heteroaryl moiety is optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, $-OR_a$, $-SR_a$, $-N(R_a)_2$, $-C(O)R_a$, $-C(O)N(R_a)_2$, $-N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[0098] "Heterocyclyl", "heterocycloalkyl" or 'heterocarbocyclyl" refer to any 3- to 18-membered non-aromatic monocyclic or polycyclic moiety comprising at least one heteroatom selected from nitrogen, oxygen, phosphorous and sulfur. A heterocyclyl group can be a monocyclic, bicyclic, tricyclic or tetracyclic ring system, wherein the polycyclic ring systems

can be a fused, bridged or spiro ring system. Heterocyclyl polycyclic ring systems can include one or more heteroatoms in one or both rings. A heterocyclyl group can be saturated or partially unsaturated. Partially unsaturated heterocycloalkyl groups can be termed "heterocycloalkenyl" if the heterocyclyl contains at least one double bond, or "heterocycloalkynyl" if the heterocyclyl contains at least one triple bond. Whenever it appears herein, a numerical range such as "3 to 18" refers to each integer in the given range; *e.g.,* "5 to 18 ring atoms" means that the heterocyclyl group can consist of 5 ring atoms, 6 ring atoms, etc., up to and including 18 ring atoms. For example, bivalent radicals derived from univalent heterocyclyl radicals whose names end in "-yl" by removal of one hydrogen atom from the atom with the free valence are named by adding "-idene" to the name of the corresponding univalent radical, *e.g.,* a piperidine group with two points of attachment is a piperidylidene.

[0099] An N-containing heterocyclyl moiety refers to an non-aromatic group in which at least one of the skeletal atoms of the ring is a nitrogen atom. The heteroatom(s) in the heterocyclyl group is optionally oxidized. One or more nitrogen atoms, if present, are optionally quaternized. "Heterocyclyl" also includes ring systems substituted with one or more oxide (-O-) substituents, such as piperidinyl N-oxides. The heterocyclyl is attached to the parent molecular structure through any atom of the ring(s).

[00100] "Heterocyclyl" also includes ring systems wherein the heterocycyl ring, as defined above, is fused with one or more carbocycyl groups wherein the point of attachment is either on the carbocycyl or heterocyclyl ring, or ring systems wherein the heterocyclyl ring, as defined above, is fused with one or more aryl or heteroaryl groups, wherein the point of attachment is on the heterocyclyl ring. In some embodiments, a heterocyclyl group is a 5–10 membered non–aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen and sulfur ("5–10 membered heterocyclyl"). In some embodiments, a heterocyclyl group is a 5–8 membered non–aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen and sulfur ("5–8 membered heterocyclyl"). In some embodiments, a heterocyclyl group is a 5–6 membered non–aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen and sulfur ("5–6 membered heterocyclyl"). In some embodiments, the 5–6 membered heterocyclyl has 1–3 ring heteroatoms selected from nitrogen, oxygen and sulfur. In some embodiments, the 5–6 membered heterocyclyl has 1–2 ring heteroatoms selected from

nitrogen, oxygen and sulfur. In some embodiments, the 5–6 membered heterocyclyl has 1 ring heteroatom selected from nitrogen, oxygen and sulfur.

[00101] Exemplary 3–membered heterocyclyls containing 1 heteroatom include, without limitation, azirdinyl, oxiranyl, thiorenyl. Exemplary 4–membered heterocyclyls containing 1 heteroatom include, without limitation, azetidinyl, oxetanyl and thietanyl. Exemplary 5–membered heterocyclyls containing 1 heteroatom include, without limitation, tetrahydrofuranyl, dihydrofuranyl, tetrahydrothiophenyl, dihydrothiophenyl, pyrrolidinyl, dihydropyrrolyl and pyrrolyl–2,5–dione. Exemplary 5–membered heterocyclyls containing 2 heteroatoms include, without limitation, dioxolanyl, oxathiolanyl and dithiolanyl. Exemplary 5–membered heterocyclyls containing 3 heteroatoms include, without limitation, triazolinyl, oxadiazolinyl, and thiadiazolinyl. Exemplary 6–membered heterocyclyl groups containing 1 heteroatom include, without limitation, piperidinyl, tetrahydropyranyl, dihydropyridinyl, and thianyl. Exemplary 6–membered heterocyclyl groups containing 2 heteroatoms include, without limitation, piperazinyl, morpholinyl, dithianyl, dioxanyl. Exemplary 6–membered heterocyclyl groups containing 2 heteroatoms include, without limitation, triazinanyl. Exemplary 7–membered heterocyclyl groups containing 1 heteroatom include, without limitation, azepanyl, oxepanyl and thiepanyl. Exemplary 8–membered heterocyclyl groups containing 1 heteroatom include, without limitation, azocanyl, oxecanyl and thiocanyl. Exemplary bicyclic heterocyclyl groups include, without limitation, indolinyl, isoindolinyl, dihydrobenzofuranyl, dihydrobenzothienyl, tetrahydrobenzothienyl, tetrahydrobenzofuranyl, tetrahydroindolyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, decahydroquinolinyl, decahydroisoquinolinyl, octahydrochromenyl, octahydroisochromenyl, decahydronaphthyridinyl, decahydro–1,8–naphthyridinyl, octahydropyrrolo[3,2–b]pyrrole, indolinyl, phthalimidyl, naphthalimidyl, chromanyl, chromenyl, 1H–benzo[e][1,4]diazepinyl, 1,4,5,7–tetrahydropyrano[3,4–b]pyrrolyl, 5,6–dihydro–4H–furo[3,2–b]pyrrolyl, 6,7–dihydro–5H–furo[3,2–b]pyranyl, 5,7–dihydro–4H–thieno[2,3–c]pyranyl, 2,3–dihydro–1H–pyrrolo[2,3–b]pyridinyl, 2,3–dihydrofuro[2,3–b]pyridinyl, 4,5,6,7–tetrahydro–1H–pyrrolo[2,3–b]pyridinyl, 4,5,6,7–tetrahydrofuro[3,2–c]pyridinyl, 4,5,6,7–tetrahydrothieno[3,2–b]pyridinyl, 1,2,3,4–tetrahydro–1,6–naphthyridinyl, and the like.

[00102] Unless stated otherwise, heterocyclyl moieties are optionally substituted by one or more substituents which independently include: alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano,

halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, -OR_a, -SR_a, -$S(O)_tR_a$, -$N(R_a)_2$, -$C(O)R_a$, -$C(O)N(R_a)_2$, -$N(R_a)C(O)R_a$, -$N(R_a)S(O)tR_a$ (where t is 1 or 2), and -$S(O)_tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[00103] "Imino" refers to the "-(C=N)-R^b" group where R^b is selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein.

[00104] "Moiety" refers to a specific segment or functional group of a molecule. Chemical moieties are often recognized chemical entities embedded in or appended to a molecule.

[00105] "Nitro" refers to the $-NO_2$ group.

[00106] As used herein, the term "unsubstituted" means that for carbon atoms, only hydrogen atoms are present besides those valencies linking the atom to the parent molecular group. A non-limiting example is propyl (-CH_2-CH_2-CH_3). For nitrogen atoms, valencies not linking the atom to the parent molecular group are either hydrogen or an electron pair. For sulfur atoms, valencies not linking the atom to the parent molecular group are either hydrogen, oxygen or electron pair(s).

[00107] As used herein, the term "substituted" or "substitution" means that at least one hydrogen present on a group (*e.g.*, a carbon or nitrogen atom) is replaced with a permissible substituent, *e.g.*, a substituent which upon substitution for the hydrogen results in a stable compound, e.g., a compound which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, or other reaction. Unless otherwise indicated, a "substituted" group can have a substituent at one or more substitutable positions of the group, and when more than one position in any given structure is substituted, the substituent is either the same or different at each position. Substituents include one or more group(s) individually and independently selected from alkyl, alkoxy, alkylaryl, cycloalkyl, aralkyl, aryl, aryloxy, amino, amido, carbamate, carbonyl, heteroalkyl, heteroaryl, heterocycloalkyl, cyano, halo, haloalkoxy, haloalkyl, ether, thio, alkylthio, arylthio, -OR_a, -SR_a, -$N(R_a)_2$, -$C(O)R_a$, -$C(O)N(R_a)_2$, -

$N(R_a)C(O)R_a$, $-N(R_a)S(O)tR_a$ (where t is 1 or 2), and $-S(O)tN(R_a)_2$ (where t is 1 or 2), where each R_a is independently hydrogen, alkyl, haloalkyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl, or heteroaryl and each of these moieties can be optionally substituted as defined herein.

[00108] "Sulfanyl", "sulfide", and "thio" each refer to the groups: $-S-R^b$, wherein R^b is selected from alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein. For instance, an 'alkylthio" refers to the "alkyl-S-" group, and "arylthio" refers to the "aryl-S-" group, each of which are bound to the parent molecular group through the S atom. The terms "thiol", "mercapto", and "mercaptan" each refer to the group $-R^cSH$.

[00109] "Sulfinyl" refers to the $-S(O)-R^b$ group, wherein R^b is selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein.

[00110] "Sulfonyl" refers to the $-S(O_2)-R^b$ group, wherein R^b is selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein.

[00111] "Sulfonamidyl" or "sulfonamido" refers to a $-S(=O)_2-NR^bR^b$ or $-N(R^b)-S(=O)_2-$ group, where each R^b is independently selected from hydrogen, alkyl, alkenyl, alkynyl, haloalkyl, heteroalkyl (bonded through a chain carbon), cycloalkyl, cycloalkylalkyl, aryl, aralkyl, heterocycloalkyl (bonded through a ring carbon), heterocycloalkylalkyl, heteroaryl (bonded through a ring carbon) or heteroarylalkyl, unless stated otherwise in the specification, each of which moiety can itself be optionally substituted as described herein. The R^b groups in $-NR^bR^b$ of the $-S(=O)_2-NR^bR^b$ group can be taken together with the nitrogen to which they are attached to form a 4-, 5-, 6-, or 7-membered ring. In some embodiments, the term designates a C_1-C_4

sulfonamido, wherein each R in sulfonamido contains 1 carbon, 2 carbons, 3 carbons, or 4 carbons total.

[00112] "Sulfoxyl" refers to a $-S(=O)_2OH$ group.

[00113] Where substituent groups are specified by their conventional chemical formulae, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, *e.g.*, $-CH_2O-$ is equivalent to $-OCH_2-$.

[00114] Described herein are methods to produce bio-based polymers that are partially or completely derived from cellulosic material (*e.g.*, biomass). The cellulosic material can be at least partially degraded using a polymer catalyst to produce a saccharide composition, which can undergo fermentation to produce bio-based polymers or one or more precursors suitable for use in producing the bio-based polymers. Such precursors can include, for example, alcohols (*e.g.*, ethylene glycol, 1,3-propanediol, 1,4-butanediol), carboxylic acids (*e.g.*, succinic acid, adipic acid, pimelic acid), hydroxyacids (*e.g.*, glycolic acid, 3-hydroxypropanoic acid) and amines (*e.g.*, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane). In one embodiment, the precursor produced from fermentation of sugars liberated from cellulosic material is ethylene glycol, which can be used as a building block for the production of polyethylene terephthalate, or copolyesters thereof. In another embodiment, the precursors produced from fermentation of sugars liberated from cellulosic material can be used as a building block for the production of propylene and polypropylene.

Degradation of Cellulosic Materials to Sugars

[00115] Cellulosic materials can be contacted with the polymer catalysts described herein to render the cellulosic material more susceptible to hydrolysis. In some instances, the cellulosic material can also be hydrolyzed into sugars suitable for use in producing bio-based polymers.

a) Cellulosic Materials

[00116] Cellulosic materials can include any material containing cellulose and/or hemicellulose. In certain embodiments, cellulosic materials can be lignocellulosic materials that contain lignin in addition to cellulose and/or hemicellulose. Cellulose is a polysaccharide that includes a linear chain of beta-(1-4)-D-glucose units. Hemicellulose is also a polysaccharide; however, unlike cellulose, hemicellulose is a branched polymer that typically includes shorter

chains of sugar units. Hemicellulose can include a diverse number of sugar monomers including, for example, xylans, xyloglucans, arabinoxylans, and mannans.

[00117] Cellulosic materials can typically be found in biomass. In some embodiments, the cellulosic materials used with the polymer catalysts described herein contains a substantial proportion of cellulosic material, such as about 5%, about 10%, about 15%, about 20%, about 25%, about 50%, about 75%, about 90% or greater than about 90% cellulose. In some embodiments, the cellulosic material can include herbaceous materials, agricultural residues, forestry residues, municipal solid waste, waste paper, and pulp and paper mill residues. In other embodiments, the cellulosic material includes corns, natural fibers, sugarcanes, beets, citrus fruits, woody plants, potatoes, plant oils, other polysaccharides such as pectin, chitin, levan, or pullulan, or a combination thereof. In certain embodiments, the cellulosic material is corn stover, corn fiber, or corn cob. In other embodiments, the cellulosic material is bagasse, rice straw, wheat straw, switch grass or miscanthus. In yet other embodiments, the cellulosic material can also include chemical cellulose (*e.g.*, Avicel®), industrial cellulose (*e.g.*, paper or paper pulp), bacterial cellulose, or algal cellulose. As described herein and known in the art, the cellulosic materials can be used as obtained from the source, or can be subjected to one or pretreatments. For example, pretreated corn stover ("PCS") is a cellulosic material derived from corn stover by treatment with heat and/or dilute sulfuric acid, and is suitable for use with the polymer catalysts described herein.

[00118] Several different crystalline structures of cellulose are known in the art. For example, crystalline cellulose are forms of cellulose where the linear beta-(1-4)-glucan chains can be packed into a three-dimensional superstructure. The aggregated beta-(1-4)-glucan chains are typically held together via inter- and intra-molecular hydrogen bonds. Steric hindrance resulting from the structure of crystalline cellulose can impede access of the reactive species, such as enzymes or chemical catalysts, to the beta-glycosidic bonds in the glucan chains. In contrast, non-crystalline cellulose and amorphous cellulose are forms of cellulose in which individual beta-(1-4)-glucan chains are not appreciably packed into a hydrogen-bonded super-structure, where access of reactive species to the beta-glycosidic bonds in the cellulose is hindered.

[00119] One of skill in the art would recognize that natural sources of cellulose can include a mixture of crystalline and non-crystalline domains. The regions of a beta-(1-4)-glucan chain where the sugar units are present in their crystalline form are referred to herein as the "crystalline

domains" of the cellulosic material. Generally, the beta-(1-4)-glucan chains present in natural cellulose exhibit a number average degree of polymerization between about 1,000 and about 4,000 anhydroglucose ("AHG") units (*i.e.*, about 1,000-4,000 glucose molecules linked via beta-glycosidic bonds), while the number average degree of polymerization for the crystalline domains is typically between about 200 and about 300 AHG units. *See e.g.*, R. Rinaldi, R. Palkovits, and F. Schüth, *Angew.* Chem. *Int. Ed.*, 47, 8047 –8050 (2008); Y.-H. P. Zhang and L.R. Lynd, *Biomacromolecules,* 6, 1501-1515 (2005).

[00120] Typically, cellulose has multiple crystalline domains that are connected by non-crystalline linkers that can include a small number of anhydroglucose units. One of skill in the art would recognize that traditional methods to digest biomass, such as dilute acidic conditions, can digest the non-crystalline domains of natural cellulose, but not the crystalline domains. Dilute acid treatment does not appreciably disrupt the packing of individual beta-(1-4)-glucan chains into a hydrogen-bonded super-structure, nor does it hydrolyze an appreciable number of glycosidic bonds in the packed beta-(1-4)-glucan chains. Consequently, treatment of natural cellulosic materials with dilute acid reduces the number average degree of polymerization of the input cellulose to approximately 200-300 anhydroglucose units, but does not further reduce the degree of polymerization of the cellulose to below about 150-200 anhydroglucose units (which is the typical size of the crystalline domains).

[00121] In certain embodiments, the polymer catalysts described herein can be used to digest natural cellulosic materials. The polymer catalysts can be used to digest crystalline cellulose by a chemical transformation in which the average degree of polymerization of cellulose is reduced to a value less than the average degree of polymerization of the crystalline domains. Digestion of crystalline cellulose can be detected by observing reduction of the average degree of polymerization of cellulose. In certain embodiments, the polymer catalysts can reduce the average degree of polymerization of cellulose from at least about 300 AGH units to less than about 200 AHG units.

[00122] It should be understood that the polymer catalysts described herein can be used to digest crystalline cellulose, as well as microcrystalline cellulose. One of skill in the art would recognize that crystalline cellulose typically has a mixture of crystalline and amorphous or non-crystalline domains, whereas microcrystalline cellulose typically refers to a form of cellulose where the amorphous or non-crystalline domains have been removed by chemical processing such that the residual cellulose substantially has only crystalline domains.

[00123] Moreover, in some embodiments, the polymer catalysts described herein can be used with cellulosic material that has been pretreated. In other embodiments, the polymer catalysts described herein can be used with cellulosic material before pretreatment.

[00124] Any pretreatment process known in the art can be used to disrupt plant cell wall components of cellulosic materials, including, for example, chemical or physical pretreatment processes. *See, e.g.*, Chandra *et al.*, Substrate pretreatment: The key to effective enzymatic hydrolysis of lignocellulosics?, *Adv. Biochem. Engin./Biotechnol.*, 108: 67-93 (2007); Galbe and Zacchi, Pretreatment of lignocellulosic materials for efficient bioethanol production, *Adv. Biochem. Engin./Biotechnol.*, 108: 41-65 (2007); Hendriks and Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, *Bioresource Technol.*, 100: 10-18 (2009); Mosier *et al.*, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technol.*, 96: 673-686 (2005); Taherzadeh and Karimi, Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review, *Int. J. of Mol. Sci.*, 9: 1621-1651 (2008); Yang and Wyman, Pretreatment: the key to unlocking low-cost cellulosic ethanol, *Biofuels Bioproducts and Biorefining (Biofpr)*, 2: 26-40 (2008). Examples of suitable pretreatment methods are described by Schell *et al.* (*Appl. Biochem. and Biotechnol.*, 105-108: 69-85 (2003) and Mosier *et al.* (*Bioresource Technol.*, 96: 673-686 (2005), and in U.S. Patent Application No. 2002/0164730.

[00125] Suitable pretreatments can include, for example, washing, solvent-extraction, solvent-swelling, comminution, milling, steam pretreatment, explosive steam pretreatment, dilute acid pretreatment, hot water pretreatment, alkaline pretreatment, lime pretreatment, wet oxidation, wet explosion, ammonia fiber explosion, organosolvent pretreatment, biological pretreatment, ammonia percolation, ultrasound, electroporation, microwave, supercritical CO2, supercritical H2O, ozone, and gamma irradiation, or a combination thereof. One of skill in the art would recognize the conditions suitable to pretreat biomass. *See e.g.,* U.S. Patent Application No. 2002/0164730; Schell et al., Appl. Biochem. Biotechnol., 105-108: 69-85 (2003); Mosier et al., Bioresource Technol., 96: 673-686 (2005); Duff and Murray, Bioresource Technol., 855: 1-33 (1996); Galbe and Zacchi, Appl. Microbiol. Biotechnol., 59: 618-628 (2002); Ballesteros et al., Appl. Biochem. Biotechnol., 129-132: 496-508 (2006); Varga et al., Appl. Biochem. Biotechnol., 113-116: 509-523 (2004); Sassner et al., Enzyme Microb. Technol., 39: 756-762 (2006); Schell et al., Bioresource Technol., 91: 179-188 (2004); Lee et al., Adv. Biochem. Eng. Biotechnol., 65: 93-115 (1999); Wyman et al., Bioresource Technol., 96: 1959-1966 (2005);

Mosier et al., Bioresource Technol., 96: 673-686 (2005); Schmidt and Thomsen, Bioresource Technol., 64: 139-151 (1998); Palonen et al., Appl. Biochem. Biotechnol., 117: 1-17 (2004); Varga et al., Biotechnol. Bioeng., 88: 567-574 (2004); Martin et al., J. Chem. Technol. Biotechnol., 81: 1669-1677 (2006); WO 2006/032282; Gollapalli et al., Appl. Biochem. Biotechnol., 98: 23-35 (2002); Chundawat et al., Biotechnol. Bioeng., 96: 219-231 (2007); Alizadeh et al., Appl. Biochem. Biotechnol., 121: 1133-1141 (2005); Teymouri et al., Bioresource Technol., 96: 2014-2018 (2005); Pan et al., Biotechnol. Bioeng., 90: 473-481 (2005); Pan et al., Biotechnol. Bioeng., 94: 851-861 (2006); Kurabi et al., Appl. Biochem. Biotechnol., 121: 219-230 (2005); Hsu, T.-A., Pretreatment of Biomass, in Handbook on Bioethanol: Production and Utilization, Wyman, C. E., ed., Taylor & Francis, Washington, D.C., 179-212 (1996); Ghosh and Singh, Physicochemical and biological treatments for enzymatic/microbial conversion of cellulosic biomass, Adv. Appl. Microbiol., 39: 295-333 (1993); McMillan, J. D., Pretreating lignocellulosic biomass: a review, in Enzymatic Conversion of Biomass for Fuels Production, Himmel, M. E., Baker, J. O., and Overend, R. P., eds., ACS Symposium Series 566, American Chemical Society, Washington, D.C., Chapter 15 (1994); Gong, C. S., Cao, N. J., Du, J., and Tsao, G. T., Ethanol production from renewable resources, in Advances in Biochemical Engineering/Biotechnology, Scheper, T., ed., Springer-Verlag Berlin Heidelberg, Germany, 65: 207-241 (1999); Olsson and Hahn-Hagerdal, Fermentation of lignocellulosic hydrolysates for ethanol production, Enz. Microb. Tech., 18: 312-331 (1996); and Vallander and Eriksson, Production of ethanol from lignocellulosic materials: State of the art, Adv. Biochem. Eng./Biotechnol., 42: 63-95(1990).

[00126] In other embodiments, the polymer catalysts described herein can be used with cellulosic material that has not been pretreated. Further, the cellulosic material can also be subjected to other processes instead of or in addition to pretreatment including, for example, particle size reduction, pre-soaking, wetting, washing, or conditioning.

[00127] Moreover, the use of the term "pretreatment" does not imply or require any specific timing of the steps of the methods described herein. For example, the cellulosic material can be pretreated before hydrolysis. Alternatively, the pretreatment can be carried out simultaneously with hydrolysis. In some embodiments, the pretreatment step itself results in some conversion of cellulosic material to sugars (for example, even in the absence of the polymer catalysts described herein).

[00128] Several common methods that can be used to pretreat cellulose materials for use with the polymer catalysts are described below.

Steam Pretreatment

[00129] Cellulosic material can be heated to disrupt the plant cell wall components (*e.g.*, lignin, hemicellulose, cellulose) to make the cellulose and/or hemicellulose more accessible to enzymes. Cellulosic material is typically passed to or through a reaction vessel, where steam is injected to increase the temperature to the required temperature and pressure is retained therein for the desired reaction time.

[00130] In certain embodiments where steam pretreatment is employed to pretreat the cellulosic materials, the pretreatment can be performed at a temperature between about 140°C and about 230°C, between about 160°C and about 200°C, or between about 170°C and about 190°C. It should be understood, however, that the optimal temperature range for steam pretreatment can vary depending on the polymer catalyst used.

[00131] In certain embodiments, the residence time for the steam pretreatment is about 1 to about 15 minutes, about 3 to about 12 minutes, or about 4 to about 10 minutes. It should be understood, however, that the optimal residence time for steam pretreatment can vary depending on the temperature range and the polymer catalyst used.

[00132] In some embodiments, steam pretreatment can be combined with an explosive discharge of the material after the pretreatment, which is known as steam explosion—a rapid flashing to atmospheric pressure and turbulent flow of the material to increase the accessible surface area by fragmentation. *See, e.g.,* Duff and Murray, *Bioresource Technol.*, 855: 1-33 (1996); Galbe and Zacchi, *Appl. Microbiol. Biotechnol.*, 59: 618-628 (2002); U.S. Patent Application No. 2002/0164730.

[00133] During steam pretreatment, acetyl groups in hemicellulose can be cleaved, and the resulting acid can autocatalyze the partial hydrolysis of the hemicellulose to monosaccharides and/or oligosaccharides. One of skill in the art would recognize, however, that lignin (when present in the cellulosic material) is removed to only a limited extent. Thus, in certain embodiments, a catalyst such as sulfuric acid (typically about 0.3% to about 3% w/w) can be added prior to steam pretreatment, to decrease the time and temperature, increase the recovery, and improve enzymatic hydrolysis. *See, e.g.,* Ballesteros *et al.*, *Appl. Biochem. Biotechnol.*, 129-

132: 496-508 (2006); Varga *et al.*, *Appl. Biochem. Biotechnol.*, 113-116: 509-523 (2004); Sassner *et al.*, *Enzyme Microb. Technol.*, 39: 756-762 (2006).

Chemical Pretreatment

[00134] Chemical pretreatment of cellulosic materials can promote the separation and/or release of cellulose, hemicellulose, and/or lignin by chemical processes. Examples of suitable chemical pretreatment processes include, for example, dilute acid pretreatment, lime pretreatment, wet oxidation, ammonia fiber/freeze explosion (AFEX), ammonia percolation (APR), and organosolvent pretreatments.

[00135] In one embodiment, dilute or mild acid pretreatment can be employed. Cellulosic material can be mixed with a dilute acid and water to form a slurry, heated by steam to a certain temperature, and after a residence time flashed to atmospheric pressure. Suitable acids for this pretreatment method can include, for example, sulfuric acid, acetic acid, citric acid, nitric acid, phosphoric acid, tartaric acid, succinic acid, hydrogen chloride, or mixtures thereof. In one variation, sulfuric acid is used. The dilute acid treatment can be conducted in a pH range of about 1-5, a pH range of about 1-4, or a pH range of about 1-3. The acid concentration can be in the range from about 0.01 to about 20 wt % acid, about 0.05 to about 10 wt % acid, about 0.1 to about 5 wt % acid, or about 0.2 to about 2.0 wt % acid. The acid is contacted with cellulosic material, and can be held at a temperature in the range of about 160-220°C, or about 165-195°C, for a period of time ranging from seconds to minutes (e.g., about 1 second to about 60 minutes). The dilute acid pretreatment can be performed with a number of reactor designs, including for example plug-flow reactors, counter-current reactors, and continuous counter-current shrinking bed reactors. *See, e.g.,* Duff and Murray (1996), supra; Schell et al., Bioresource Technol., 91: 179-188 (2004); Lee et al., Adv. Biochem. Eng. Biotechnol., 65: 93-115 (1999).

[00136] In another embodiment, an alkaline pretreatment can be employed. Examples of suitable alkaline pretreatments include, for example, lime pretreatment, wet oxidation, ammonia percolation (APR), and ammonia fiber/freeze explosion (AFEX). Lime pretreatment can be performed with calcium carbonate, sodium hydroxide, or ammonia at temperatures of about 85°C to about 150°C, and at residence times from 1 hour to several days. *See, e.g.,* Wyman *et al.*, *Bioresource Technol.*, 96: 1959-1966 (2005); Mosier *et al.*, *Bioresource Technol.*, 96: 673-686 (2005).

[00137] In yet another embodiment, wet oxidation can be employed. Wet oxidation is a thermal pretreatment that can be performed, for example, at about 180°C to about 200°C for about 5-15 minutes with addition of an oxidative agent such as hydrogen peroxide or over-pressure of oxygen. *See, e.g.,* Schmidt and Thomsen, *Bioresource Technol.*, 64: 139-151 (1998); Palonen *et al.*, *Appl. Biochem. Biotechnol.*, 117: 1-17 (2004); Varga *et al.*, *Biotechnol. Bioeng.*, 88: 567-574 (2004); Martin *et al.*, *J. Chem. Technol. Biotechnol.*, 81: 1669-1677 (2006). Wet oxidation can be performed, for example, at about 1-40% dry matter, about 2-30% dry matter, or about 5-20% dry matter, and the initial pH can also be increased by the addition of alkali (*e.g.*, sodium carbonate). A modification of the wet oxidation pretreatment method, known as wet explosion—a combination of wet oxidation and steam explosion, can handle dry matter up to about 30%. In wet explosion, the oxidizing agent can be introduced during pretreatment after a certain residence time, and the pretreatment can end by flashing to atmospheric pressure. *See, e.g.,* WO 2006/032282.

[00138] In yet another embodiment, pretreatment methods using ammonia can be employed. *See, e.g.*, WO 2006/110891; WO 2006/11899; WO 2006/11900; and WO 2006/110901. For example, ammonia fiber explosion (AFEX) involves treating cellulosic material with liquid or gaseous ammonia at moderate temperatures (*e.g.*, about 90-100°C) and at high pressure (*e.g.*, about 17-20 bar) for a given duration (*e.g.*, about 5-10 minutes), where the dry matter content can be in some instances as high as about 60%. *See, e.g.,* Gollapalli *et al.*, *Appl. Biochem. Biotechnol.*, 98: 23-35 (2002); Chundawat *et al.*, *Biotechnol. Bioeng.*, 96: 219-231 (2007); Alizadeh *et al.*, *Appl. Biochem. Biotechnol.*, 121: 1133-1141 (2005); Teymouri *et al.*, *Bioresource Technol.*, 96: 2014-2018 (2005). AFEX pretreatment can depolymerize cellulose, partial hydrolyze hemicellulose, and, in some instances, cleave some lignin-carbohydrate complexes.

Organosolvent Pretreatment

[00139] An organosolvent solution can be used to delignify cellulosic material. In one embodiment, an organosolvent pretreatment involves extraction using aqueous ethanol (e.g., about 40-60% ethanol) at an elevated temperature (e.g., about 160-200°C) for a period of time (e.g., about 30-60 minutes). *See, e.g.,* Pan et al., Biotechnol. Bioeng., 90: 473-481 (2005); Pan et al., Biotechnol. Bioeng., 94: 851-861 (2006); Kurabi et al., Appl. Biochem. Biotechnol., 121: 219-230 (2005). In one variation, sulfuric acid is added to the organosolvent solution as a

catalyst to delignify the cellulosic material. One of skill in the art would recognize that an organosolvent pretreatment can typically breakdown the majority of hemicellulose

.Physical Pretreatment

[00140] Physical pretreatment of cellulosic materials can promote the separation and/or release of cellulose, hemicellulose, and/or lignin by physical processes. Examples of suitable physical pretreatment processes can involve irradiation (*e.g.*, microwave irradiation), steaming/steam explosion, hydrothermolysis, and combinations thereof.

[00141] Physical pretreatment can involve high pressure and/or high temperature. In one embodiment, the physical pretreatment is steam explosion. In some variations, high pressure refers to a pressure in the range of about 300-600 psi, about 350-550 psi, or about 400-500 psi, or about 450 psi. In some variations, high temperature refers to temperatures in the range of about 100-300°C, or about 140- 235°C.

[00142] In another embodiment, the physical pretreatment is a mechanical pretreatment. Suitable examples of mechanical pretreatment can include various types of grinding or milling (*e.g.*, dry milling, wet milling, or vibratory ball milling). In some variations, mechanical pretreatment is performed in a batch-process, such as in a steam gun hydrolyzer system that uses high pressure and high temperature (*e.g.,* a Sunds Hydrolyzer available from Sunds Defibrator AB, Sweden).

Combined Physical and Chemical Pretreatment

[00143] In some embodiments, cellulosic material can be pretreated both physically and chemically. For instance, in one variation, the pretreatment step can involve dilute or mild acid treatment and high temperature and/or pressure treatment. It should be understood that the physical and chemical pretreatments can be carried out sequentially or simultaneously. In other variation, the pretreatment can also include a mechanical pretreatment, in addition to chemical pretreatment.

Biological Pretreatment

[00144] Biological pretreatment techniques can involve applying lignin-solubilizing microorganisms. *See, e.g.*, Hsu, T.-A., Pretreatment of Biomass, in Handbook on Bioethanol: Production and Utilization, Wyman, C. E., ed., Taylor & Francis, Washington, D.C., 179-212

(1996); Ghosh and Singh, Physicochemical and biological treatments for enzymatic/microbial conversion of cellulosic biomass, *Adv. Appl. Microbiol.*, 39: 295-333 (1993); McMillan, J. D., Pretreating lignocellulosic biomass: a review, in Enzymatic Conversion of Biomass for Fuels Production, Himmel, M. E., Baker, J. O., and Overend, R. P., eds., ACS Symposium Series 566, American Chemical Society, Washington, D.C., chapter 15 (1994); Gong, C. S., Cao, N. J., Du, J., and Tsao, G. T., Ethanol production from renewable resources, in Advances in Biochemical Engineering/Biotechnology, Scheper, T., ed., Springer-Verlag Berlin Heidelberg, Germany, 65: 207-241 (1999); Olsson and Hahn-Hagerdal, Fermentation of lignocellulosic hydrolysates for ethanol production, *Enz. Microb. Tech.*, 18: 312-331 (1996); and Vallander and Eriksson, Production of ethanol from lignocellulosic materials: State of the art, *Adv. Biochem. Eng./Biotechnol.*, 42: 63-95(1990). In some embodiments, pretreatment can be performed in an aqueous slurry. In other embodiments, the cellulosic material is present during pretreatment in amounts between about 10-80 wt %, between about 20-70 wt %, or between about 30-60 wt %, or about 50 wt %. Furthermore, after pretreatment, the pretreated cellulosic material can be unwashed or washed using any method known in the art (*e.g.*, washed with water) before hydrolysis to produce one or more sugars or use with the polymer catalyst.

b) Polymer catalysts

[00145] Various types of polymer catalysts can be used in the methods described herein. In some embodiments, the polymer catalyst is capable of degrading at least a portion of the cellulosic material into a saccharide composition, which can include monosaccharides, disaccharides and other oligosaccharides. In other embodiments, the polymer catalyst is capable of reducing the degree of crystallization of the cellulosic material. In yet other embodiments, the polymer catalyst is capable of break down at least a portion of the crystalline domains of the cellulose in the cellulosic material.

[00146] In some embodiments, the polymer catalyst used in the methods described herein is a solid-supported acid catalyst that includes a support and a plurality of acidic groups attached to the support. In other embodiments, the solid-supported acid catalyst can also include a plurality of cationic groups attached to the support, in addition to the plurality of acidic groups attached to the support. Any suitable supports can be used for the polymer catalyst, including for example biochar, carbon, amorphous carbon, activated carbon, silica, silica gel, and alumina, or a combination thereof. Any suitable acidic groups can be attached to the support in the polymer catalyst, including for example sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and

boronic acid. Any suitable cationic groups can be attached to the support in the polymer catalyst, including for example pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium, phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, triphenyl phosphonium and trifluoro phosphonium.

[00147] In yet other embodiments, the polymer catalyst is a polymeric acid catalyst. In certain embodiments, the polymeric acid catalyst has acidic monomers that are connected to form a polymeric backbone, in which each acidic monomer has at least one Bronsted-Lowry acid. In yet other embodiments, the polymeric acid catalyst has acidic monomers and ionic monomers (which are also known as "ionomers") that are connected to form a polymeric backbone, in which each acidic monomer has at least one Bronsted-Lowry acid, and each ionic monomer independently has at least one nitrogen-containing cationic group or phosphorous-containing cationic group.

[00148] Some of the acidic and ionic monomers can also include a linker that connects the Bronsted-Lowry acid and cationic group, respectively, to the polymeric backbone. For the acidic monomers, the Bronsted-Lowry acid and the linker together form a side chain. Similarly, for the ionic monomers, the cationic group and the linker together form a side chain. With reference to the portion of the exemplary catalyst depicted in FIG. **1**, the side chains are pendant from the polymeric backbone.

[00149] In some embodiments, the catalyst described herein contain monomers that have at least one Bronsted-Lowry acid and at least one cationic group. The Bronsted-Lowry acid and the cationic group can be on different monomers or on the same monomer.

[00150] In some embodiments, the acidic monomers can have one Bronsted-Lowry acid. In other embodiments, the acidic monomers can have two or more Bronsted-Lowry acids, as is chemically feasible. When the acidic monomers have two or more Bronsted-Lowry acids, the acids can be the same or different.

[00151] Suitable Bronsted-Lowry acids can include any Bronsted-Lowry acid that can form a covalent bond with a carbon. The Bronsted-Lowry acids can have a pK value of less than about 7, less than about 6, less than about 5, less than about 4, less than about 3, less than about 2, less than about 1, or less than zero. In some embodiments, the Bronsted-Lowry acid at each

occurrence can be independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid.

[00152] The acidic monomers in the catalyst can either all have the same Bronsted-Lowry acid, or can have different Bronsted-Lowry acids. In an exemplary embodiment, each Bronsted-Lowry acid in the catalyst is sulfonic acid. In another exemplary embodiment, each Bronsted-Lowry acid in the catalyst is phosphonic acid. In yet another exemplary embodiment, the Bronsted-Lowry acid in some monomers of the catalyst is sulfonic acid, while the Bronsted-Lowry acid in other monomers of the catalyst is phosphonic acid.

[00153] In some embodiments, the ionic monomers can have one cationic group. In other embodiments, the ionic monomers can have two or more cationic groups, as is chemically feasible. When the ionic monomers have two or more cationic groups, the cationic groups can be the same or different.

[00154] Suitable cationic groups can include any nitrogen-containing cationic group or a phosphorus-containing cationic group. In some embodiments, the nitrogen-containing cationic group at each occurrence can be independently selected from ammonium, pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium. In other embodiments, the phosphorous-containing cationic group at each occurrence can be independently selected from triphenyl phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, and trifluoro phosphonium.

[00155] The ionic monomers can either all have the same cationic group, or can have different cationic groups. In some embodiments, each cationic group in the catalyst is a nitrogen-containing cationic group. In other embodiments, each cationic group in the catalyst is a phosphorous-containing cationic group. In yet other embodiments, the cationic group in some monomers of the catalyst is a nitrogen-containing cationic group, whereas the cationic group in other monomers of the catalyst is a phosphorous-containing cationic group. In an exemplary embodiment, each cationic group in the catalyst is imidazolium. In another exemplary embodiment, the cationic group in some monomers of the catalyst is imidazolium, while the cationic group in other monomers of the catalyst is pyridinium. In yet another exemplary embodiment, each cationic group in the catalyst is a substituted phosphonium. In yet another

exemplary embodiment, the cationic group in some monomers of the catalyst is triphenyl phosphonium, while the cationic group in other monomers of the catalyst is imidazolium.

[00156] In some embodiments, the cationic group can coordinate with a counterion. For example, the counterion can be a halide (*e.g.*, bromide, chloride, iodide, and fluoride), nitrate (NO_3^-), sulfate (SO_4^{2-}), formate ($HCOO^-$), acetate (H_3COO^-), or an organosulfonate ($R\text{-}SO_3^-$; where R is an organic functional group, *e.g.*, methyl, phenyl).

[00157] In other embodiments, the cationic group can coordinate with a Bronsted-Lowry acid in the catalyst. At least a portion of the Bronsted-Lowry acids and the cationic groups in the catalyst can form inter-monomer ionic associations. Inter-monomeric ionic associations result in salts forming between monomers in the catalyst, rather than with external counterions. In some exemplary embodiments, the ratio of acidic monomers engaged in inter-monomer ionic associations to the total number of acidic monomers can be at most about 90% internally-coordinated, at most about 80% internally-coordinated, at most about 70% internally-coordinated, at most about 60% internally-coordinated, at most about 50% internally-coordinated, at most about 40% internally-coordinated, at most about 30% internally-coordinated, at most about 20% internally-coordinated, at most about 10% internally-coordinated, at most about 5% internally-coordinated, at most about 1% internally-coordinated, or less than about 1% internally-coordinated. It should be understood that internally-coordinates sites are less likely to exchange with an ionic solution that is brought into contact with the catalyst.

[00158] Some of the monomers in the catalyst contain both the Bronsted-Lowry acid and the cationic group in the same monomer. Such monomers are referred to as "acidic-ionic monomers". In exemplary embodiments, a side chain of an acidic-ionic monomer can contain imidazolium and acetic acid, or pyridinium and boronic acid.

[00159] With reference to the portion of an exemplary catalyst depicted in FIG. **2**, the Bronsted-Lowry acid and the cationic group in the side chains of the monomers can be directly connected to the polymeric backbone or connected to the polymeric backbone by a linker.

[00160] Suitable linkers can include, for example, unsubstituted or substituted alkylene, unsubstituted or substituted cycloalkylene, unsubstituted or substituted alkenylene, unsubstituted or substituted arylene, and unsubstituted or substituted heteroarylene, where the terms unsubstituted and substituted have the meanings as disclosed herein.. In some embodiments, the

linker is an unsubstituted or substituted C5 or C6 arylene. In certain embodiments, the linker is an unsubstituted or substituted phenylene. In one exemplary embodiment, the linker is unsubstituted phenylene. In another exemplary embodiment, the linker is substituted phenylene (*e.g.*, hydroxy-substituted phenylene).

[00161] Further, it should be understood that some or all of the acidic monomers connected to the polymeric backbone by a linker can have the same linker, or independently have different linkers. Similarly, some or all of the ionic monomers connected to the polymeric backbone by a linker can have the same linker, or independently have different linkers. Further, some or all of the acidic monomers connected to the polymeric backbone by a linker can have the same or different linkers as some or all of the ionic monomers connected to the polymeric backbone by a linker.

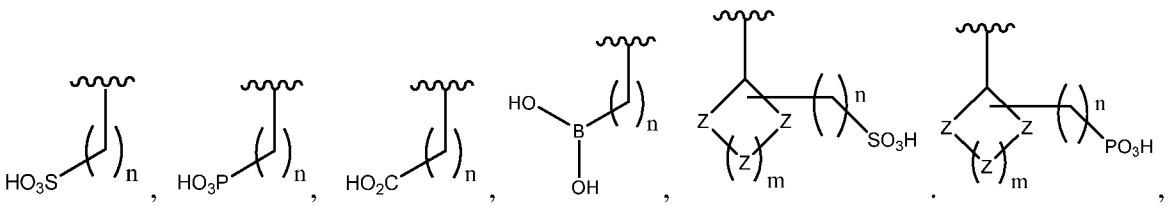
[00162] Disclosed herein are polymers that include acidic monomers and ionic monomers connected to form a polymeric backbone,

wherein a plurality of acidic monomers independently comprises at least one Bronsted-Lowry acid, wherein at least one of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone,

wherein each ionic monomer independently comprises at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and

wherein at least one of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone.

[00163] In some embodiments, the acidic monomers can be selected from Formulas IA-VIA:



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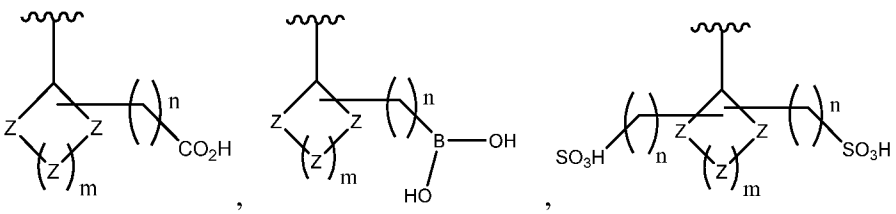

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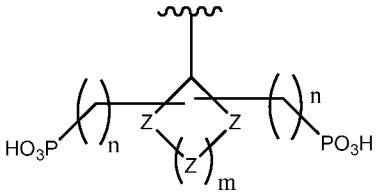

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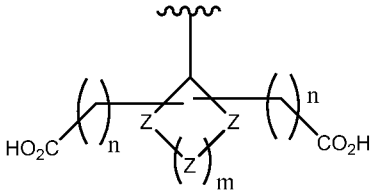

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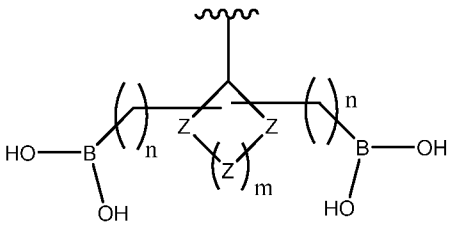

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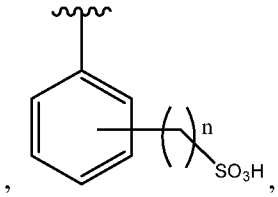

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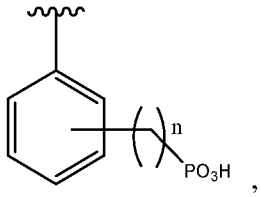

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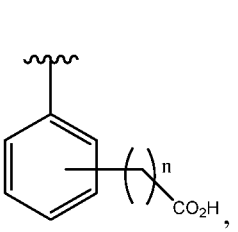
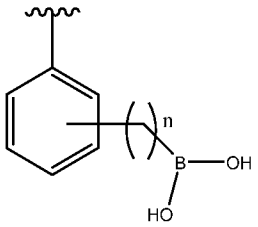
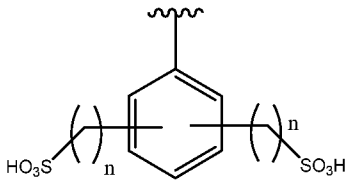


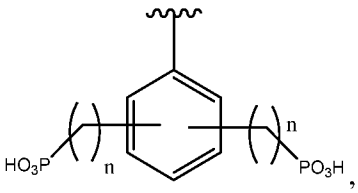
IVA



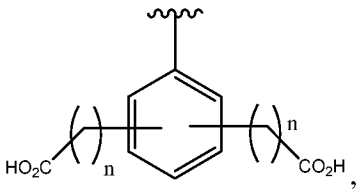
IVB



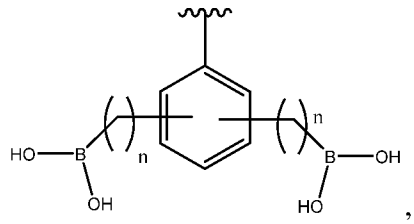
IVC



IVD



VA

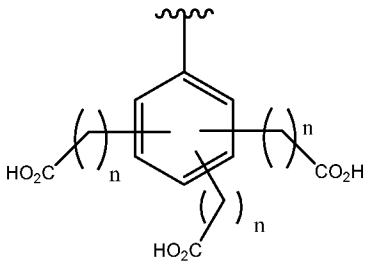


VB

VC

VD

and



VIA

wherein each Z is independently selected from $C(R^2)(R^3)$, $N(R^4)$, S, $S(R^5)(R^6)$, $S(O)(R^5)(R^6)$, SO_2, and O, where any two adjacent Z can be joined by a double bond;

each m is independently selected from 0, 1, 2, and 3;

each n is independently selected from 0, 1, 2, and 3;

each R^2, R^3, and R^4 is independently selected from hydrogen, alkyl, heteroalkyl, cycloalkyl, heterocyclyl, aryl, and heteroaryl;

each R^5 and R^6 is independently selected from alkyl, heteroalkyl, cycloalkyl, heterocyclyl, aryl, and heteroaryl; and

where any two adjacent Z can be taken together to form a group selected from cycloalkyl, heterocycloalkyl, aryl and heteroaryl.

[00164] In some embodiments, the polymer can be selected from Formulas IA, IB, IVA, and IVB. In other embodiments, the polymer can be selected from Formulas IIA, IIB, IIC, IVA, IVB, and IVC. In other embodiments, the polymer can be selected from IIIA, IIIB, and IIIC. In some embodiments, the polymer can be selected from VA, VB, and VC. In some embodiments, the polymer can be selected from IA. In other embodiments, the polymer can be selected from IB.

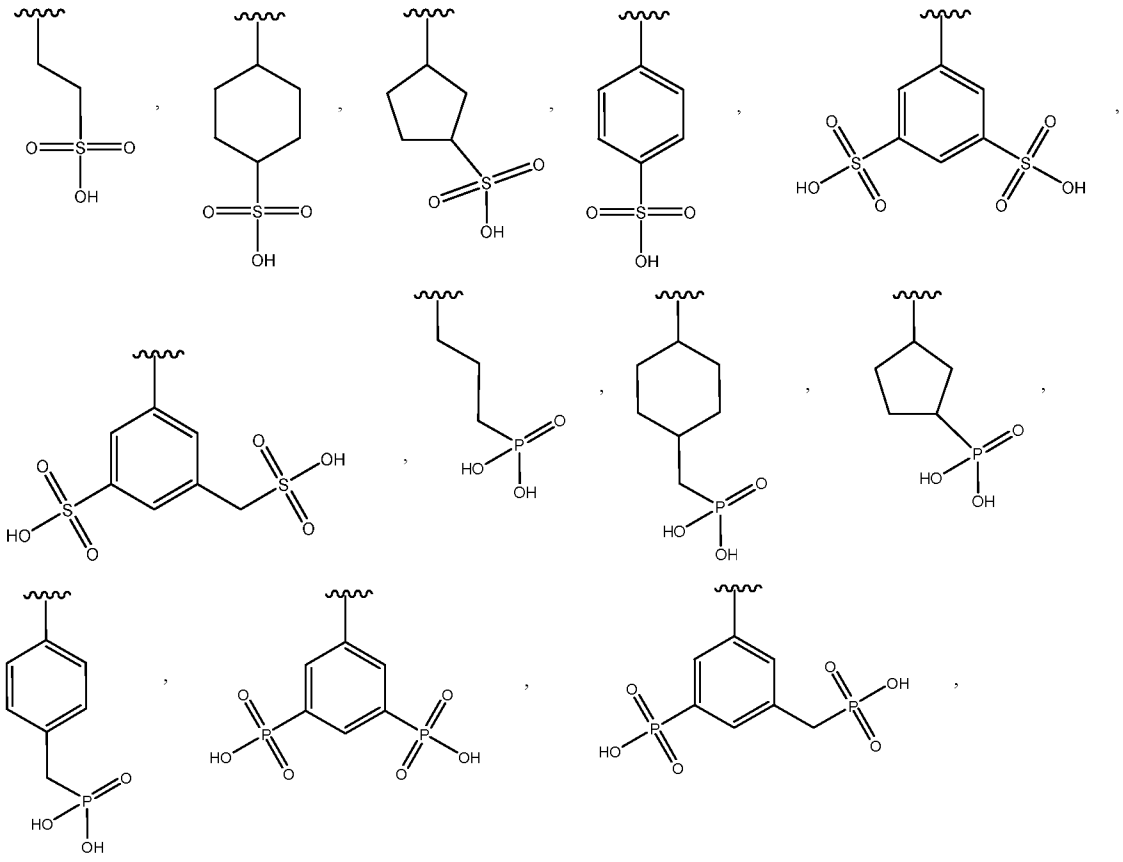
[00165] In some embodiments, Z can be chosen from $C(R_2)(R_3)$, $N(R_4)$, SO_2, and O. In some embodiments, any two adjacent Z can be taken together to form a group selected from a heterocycloalkyl, aryl, and heteroaryl. In other embodiments, any two adjacent Z can be joined by a double bond. Any combination of these embodiments is also contemplated.

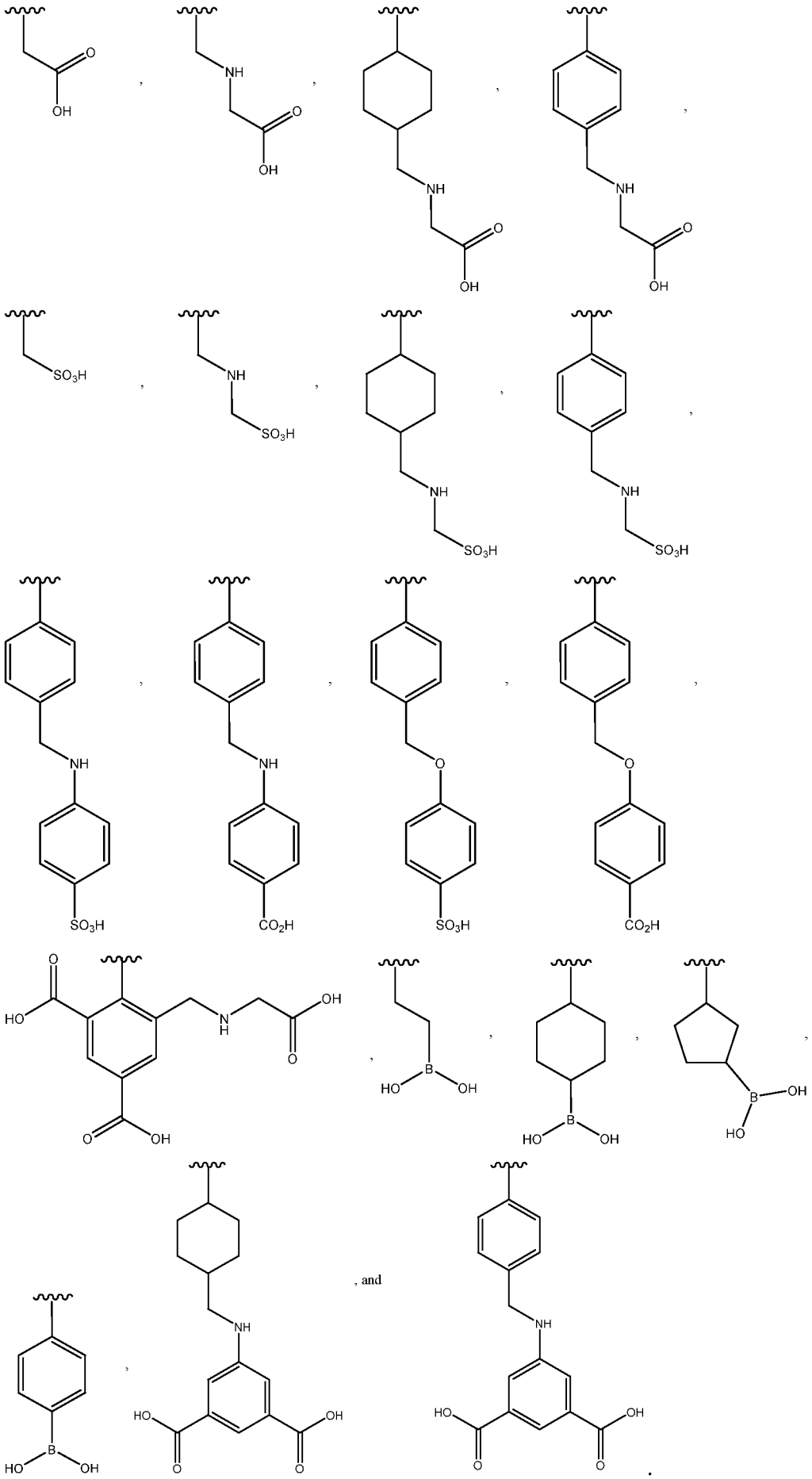
[00166] In some embodiments, m is selected from 2 or 3, such as 3. In other embodiments, n is selected from 1, 2, and 3, such as 2 or 3. In some embodiments, R^1 can be selected from hydrogen, alkyl and heteroalkyl. In some embodiments, R^1 can be selected from hydrogen, methyl, or ethyl. In some embodiments, each R^2, R^3, and R^4 can be independently selected from hydrogen, alkyl, heterocyclyl, aryl, and heteroaryl. In other embodiments, each R^2, R^3 and R^4 can be independently selected from heteroalkyl, cycloalkyl, heterocyclyl, and heteroaryl. In some embodiments, each R^5 and R^6 can be independently selected from alkyl, heterocyclyl, aryl, and heteroaryl. In another embodiment, any two adjacent Z can be taken together to form a group selected from cycloalkyl, heterocycloalkyl, aryl and heteroaryl.

[00167] In some embodiments, the polymer catalyst described herein contains monomers that have at least one Bronsted-Lowry acid and at least one cationic group. The Bronsted-Lowry acid and the cationic group can be on different monomers or on the same monomer.

[00168] In one aspect, provided is a polymer having acidic monomers and ionic monomers that are connected to form a polymeric backbone, in which each acidic monomer has at least one Bronsted-Lowry acid, and each ionic monomer independently has at least one nitrogen-containing cationic group or phosphorous-containing cationic group. In some embodiments, each acidic monomer has one Bronsted-Lowry acid. In other embodiments, some of the acidic monomers have one Bronsted-Lowry acid, while others have two Bronsted-Lowry acids. In some embodiments, each ionic monomer has one nitrogen-containing cationic group or phosphorous-containing cationic group. In other embodiments, some of the ionic monomers have one nitrogen-containing cationic group or phosphorous-containing cationic group, while others have two nitrogen-containing cationic groups or phosphorous-containing cationic groups.

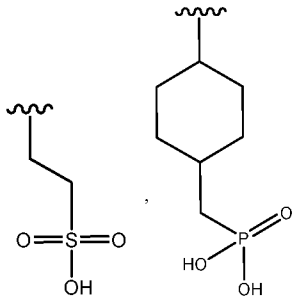
[00169] In certain embodiments, the acidic monomers can have a side chain with a Bronsted-Lowry acid that is connected to the polymeric backbone by a linker. Side chains with one or more Bronsted-Lowry acids connected by a linker can include, for example,

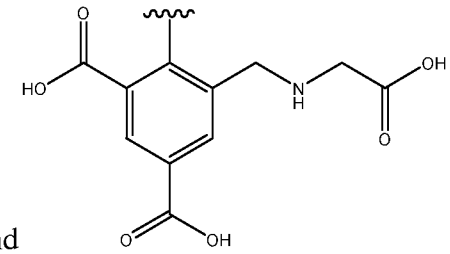




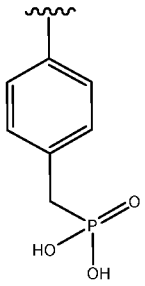
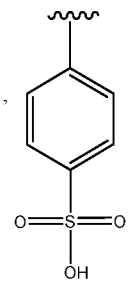
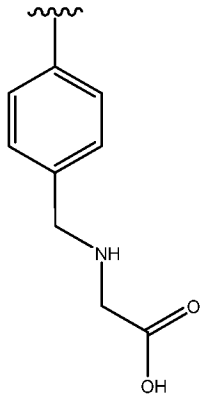
, and

[00170] In some embodiments, the acidic side chain can be selected from

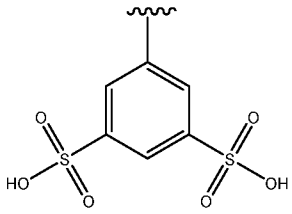
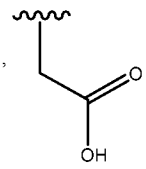
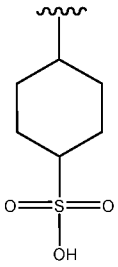


and  .

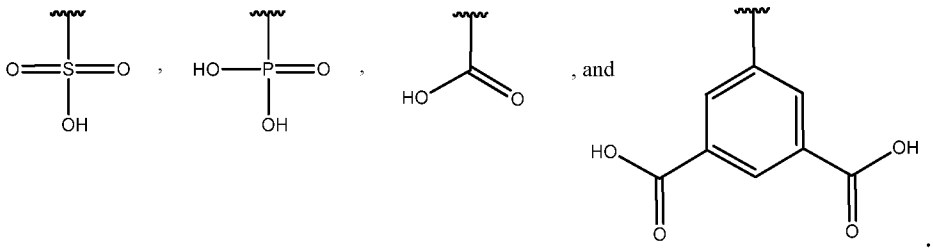
[00171] In some embodiments, the acidic side chain can be selected from




and .

[00172] In some embodiments, the acidic side chain can be selected from



and  .

[00173] In other embodiments, the acidic monomers can have a side chain with a Bronsted-Lowry acid that is directly connected to the polymeric backbone. Side chains with a Bronsted-Lowry acid directly connected to the polymeric backbone can include, for example,



[00174] In some embodiments, the ionic monomers can have one cationic group. In other embodiments, the ionic monomers can have two or more cationic groups, as is chemically feasible. When the ionic monomers have two or more cationic groups, the cationic groups can be the same or different.

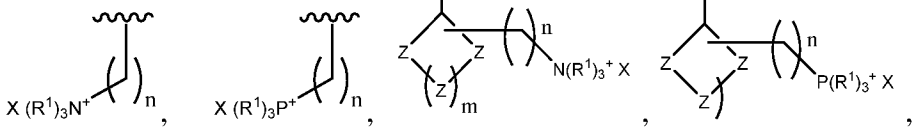
[00175] In some embodiments, each cationic group in the polymer catalyst is a nitrogen-containing cationic group. In other embodiments, each cationic group in the polymer catalyst is a phosphorous-containing cationic group. In yet other embodiments, the cationic group in some monomers of the polymer catalyst is a nitrogen-containing cationic group, whereas the cationic group in other monomers of the polymer catalyst is a phosphorous-containing cationic group. In an exemplary embodiment, each cationic group in the polymer catalyst is imidazolium. In another exemplary embodiment, the cationic group in some monomers of the polymer catalyst is imidazolium, while the cationic group in other monomers of the polymer catalyst is pyridinium. In yet another exemplary embodiment, each cationic group in the polymer catalyst is a substituted phosphonium. In yet another exemplary embodiment, the cationic group in some monomers of the polymer catalyst is triphenyl phosphonium, while the cationic group in other monomers of the polymer catalyst is imidazolium.

[00176] In some embodiments, the nitrogen-containing cationic group at each occurrence can be independently selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium. In other embodiments, the nitrogen-containing cationic group at each occurrence can be independently selected from imidazolium, pyridinium, pyrimidinium, morpholinium, piperidinium, and piperizinium. In some embodiments, the nitrogen-containing cationic group can be imidazolium.

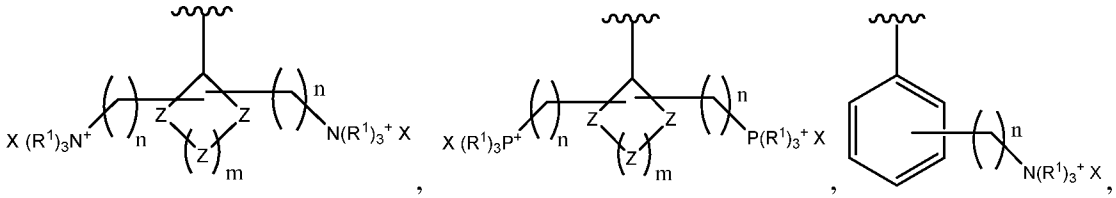
[00177] In some embodiments, the phosphorous-containing cationic group at each occurrence can be independently selected from triphenyl phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, and

trifluoro phosphonium. In other embodiments, the phosphorous-containing cationic group at each occurrence can be independently selected from triphenyl phosphonium, trimethyl phosphonium, and triethyl phosphonium. In other embodiments, the phosphorous-containing cationic group can be triphenyl phosphonium.

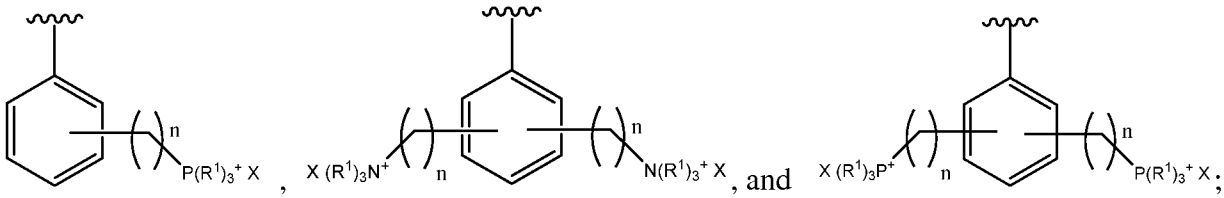
[00178] In some embodiments, each ionic monomer is independently selected from Formulas VIIA-XIB:



VIIA VIIB VIIIA VIIIB



IXA IXB XA



XB XIA XIB

wherein each Z is independently selected from $C(R^2)(R^3)$, $N(R^4)$, S, $S(R^5)(R^6)$, $S(O)(R^5)(R^6)$, SO_2, and O, where any two adjacent Z may be joined by a double bond;

each X is independently selected from F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, $R^7SO_4^-$, $R^7CO_2^-$, PO_4^{2-}, $R^7PO_3^-$, and $R^7PO_2^-$, where SO_4^{2-} and PO_4^{2-} are each independently associated with at least two cationic groups at any X position on any ionic monomer, and

each m is independently selected from 0, 1, 2, and 3;

each n is independently selected from 0, 1, 2, and 3;

each R^1, R^2, R^3 and R^4 is independently selected from hydrogen, alkyl, heteroalkyl, cycloalkyl, heterocyclyl, aryl, and heteroaryl;

each R^5 and R^6 is independently selected from alkyl, heteroalkyl, cycloalkyl, heterocyclyl, aryl, and heteroaryl;

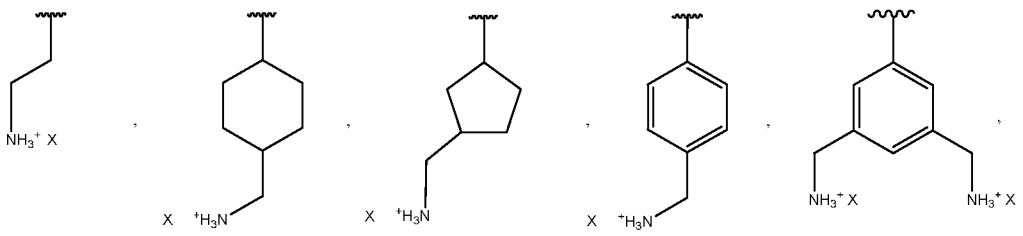
where any two adjacent Z can be taken together to form a group selected from cycloalkyl, heterocycloalkyl, aryl and heteroaryl; and

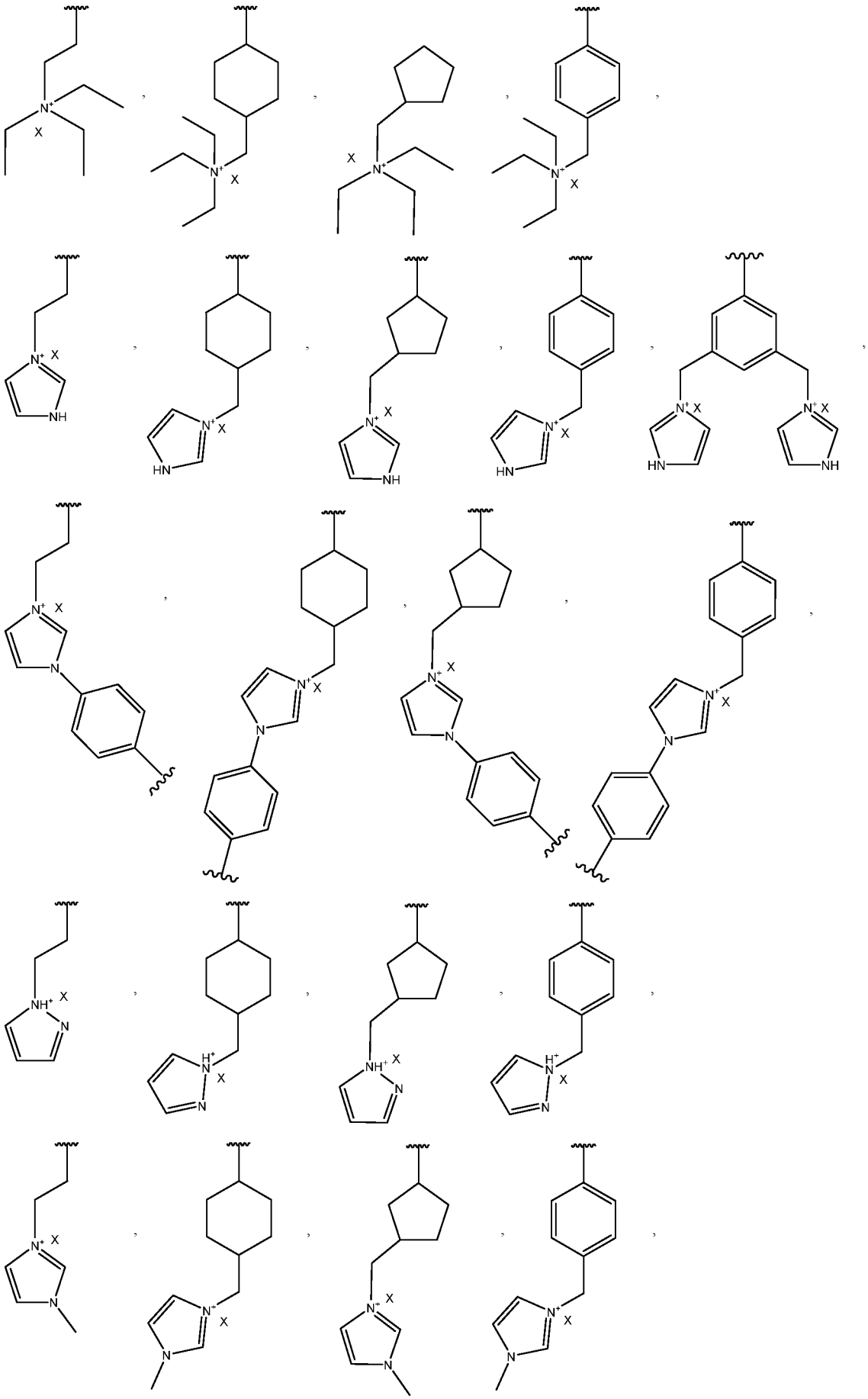
each R^7 is independently selected from hydrogen, C_{1-4}alkyl, and C_{1-4}heteroalkyl.

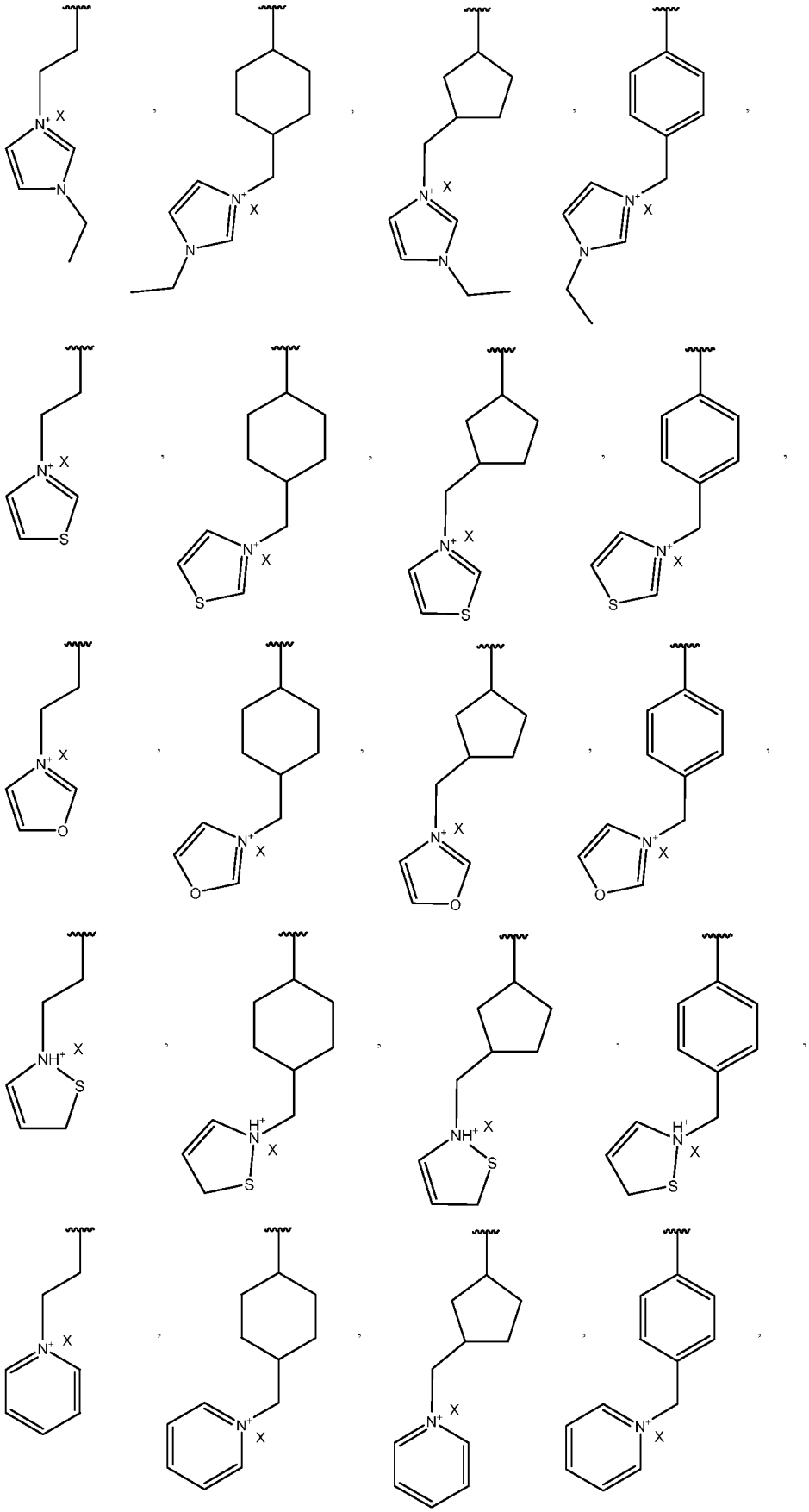
[00179] In some embodiments, Z can be chosen from $C(R^2)(R^3)$, $N(R^4)$, SO_2, and O. In some embodiments, any two adjacent Z can be taken together to form a group selected from a heterocycloalkyl, aryl and heteroaryl. In other embodiments, any two adjacent Z can be joined by a double bond. In some embodiments, each X can be selected from Cl^-, NO_3^-, SO_4^{2-}, $R^7SO_4^-$, and $R^7CO_2^-$, where R^7 can be selected from hydrogen and C_{1-4}alkyl. In another embodiment, each X can be selected from Cl^-, Br^-, I^-, HSO_4^-, HCO_2^-, $CH_3CO_2^-$, and NO_3^-. In other embodiments, X is acetate. In other embodiments, X is bisulfate. In other embodiments, X is chloride. In other embodiments, X is nitrate.

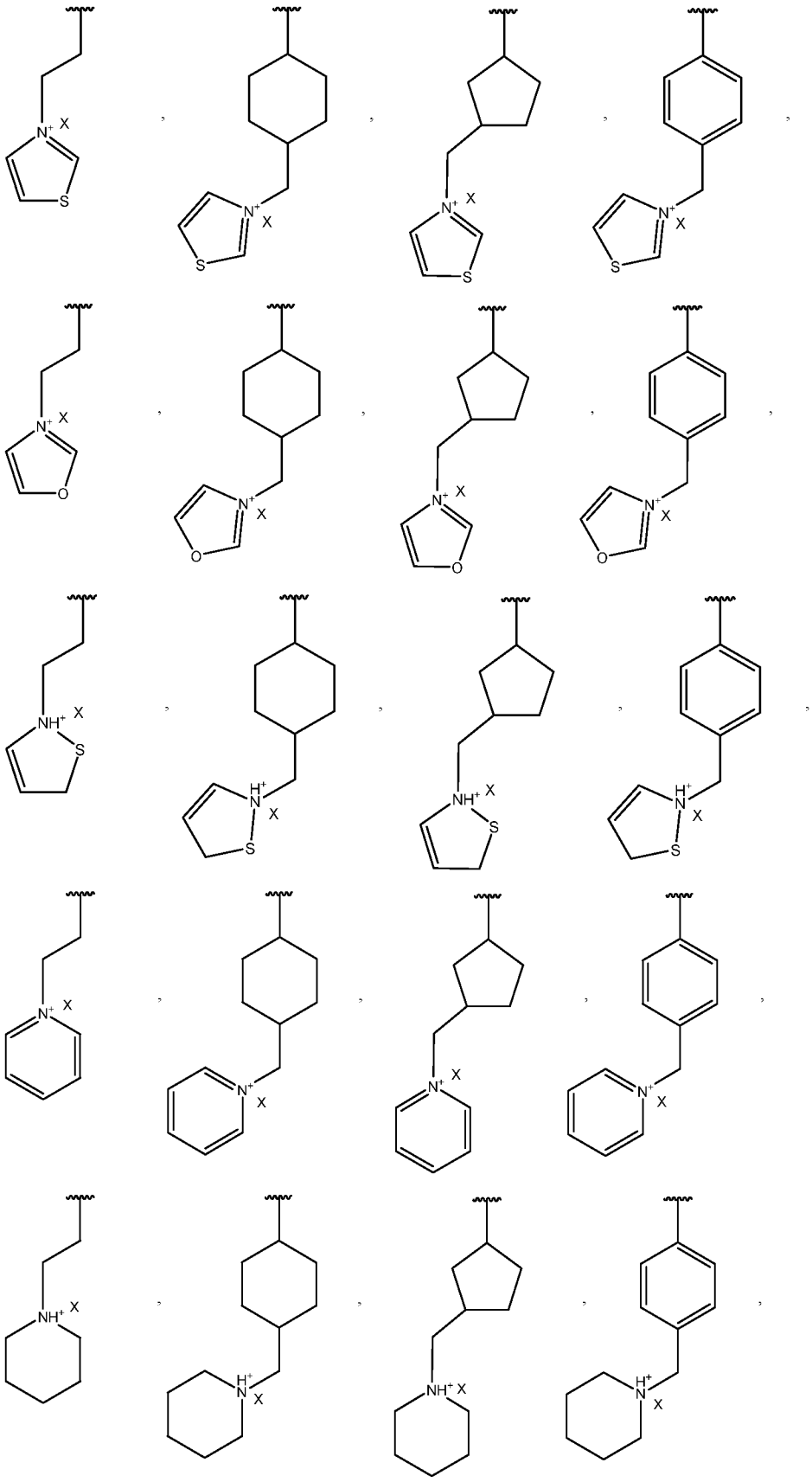
[00180] In some embodiments, m is selected from 2 or 3, such as 3. In other embodiments, n is selected from 1, 2, and 3, such as 2 or 3. In some embodiments, R^1 can be selected from hydrogen, alkyl, and heteroalkyl. In some embodiments, R^1 can be selected from hydrogen, methyl, or ethyl. In some embodiments, each R^2, R^3, and R^4 can be independently selected from hydrogen, alkyl, heterocyclyl, aryl, and heteroaryl. In other embodiments, each R^2, R^3 and R^4 can be independently selected from heteroalkyl, cycloalkyl, heterocyclyl, and heteroaryl. In some embodiments, each R^5 and R^6 can be independently selected from alkyl, heterocyclyl, aryl, and heteroaryl. In another embodiment, any two adjacent Z can be taken together to form a group selected from cycloalkyl, heterocycloalkyl, aryl and heteroaryl.

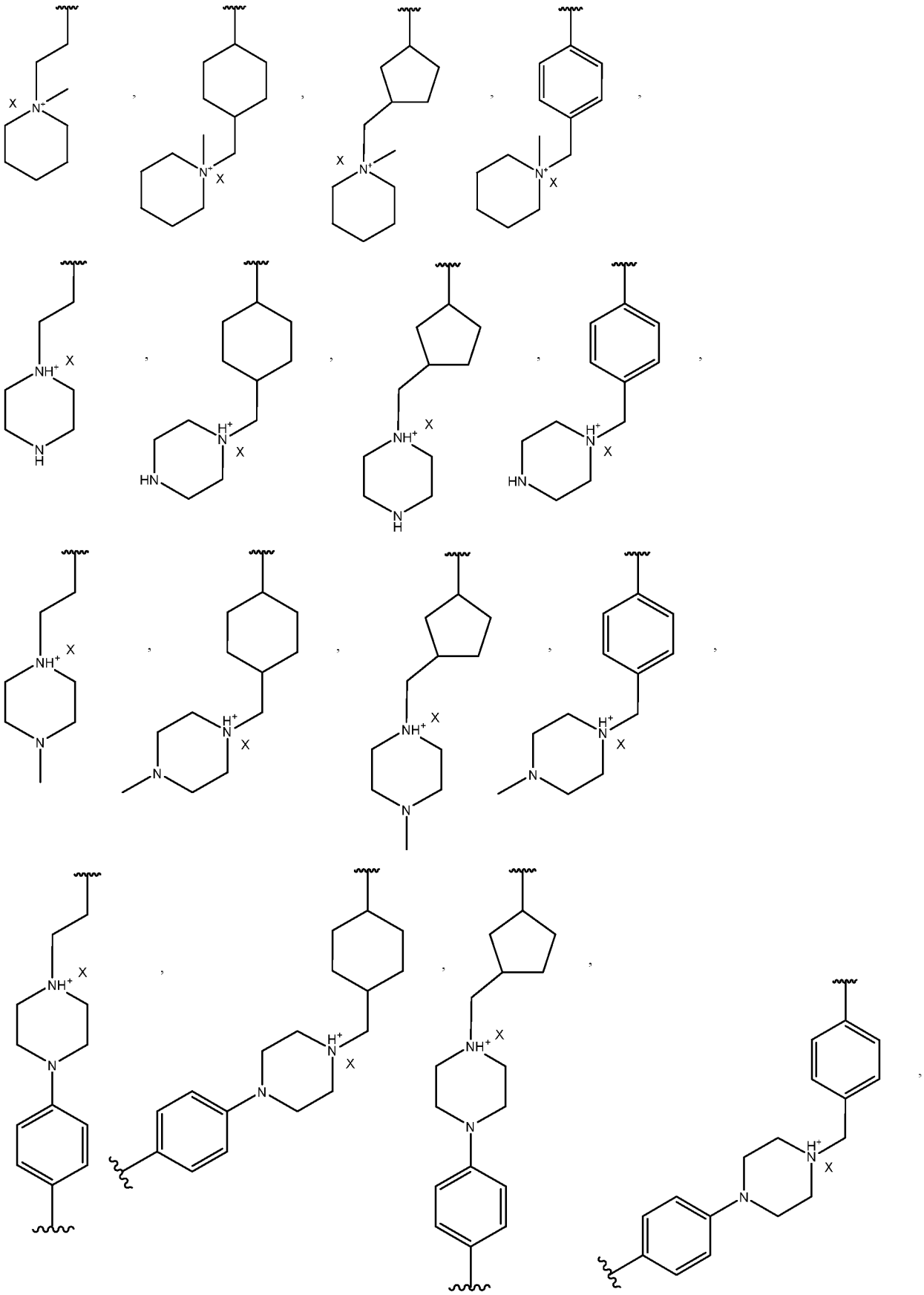
[00181] In certain embodiments, the ionic monomers can have a side chain with a cationic group that is connected to the polymeric backbone by a linker. Side chains with one or more cationic groups connected by a linker can include, for example,

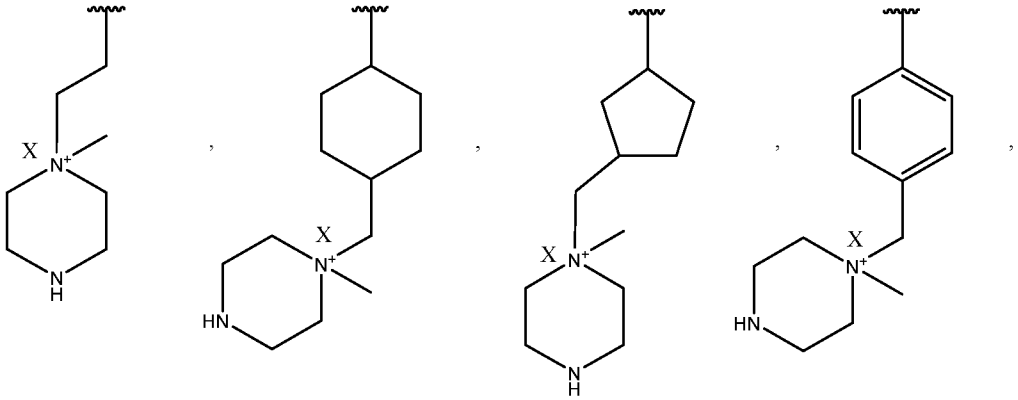


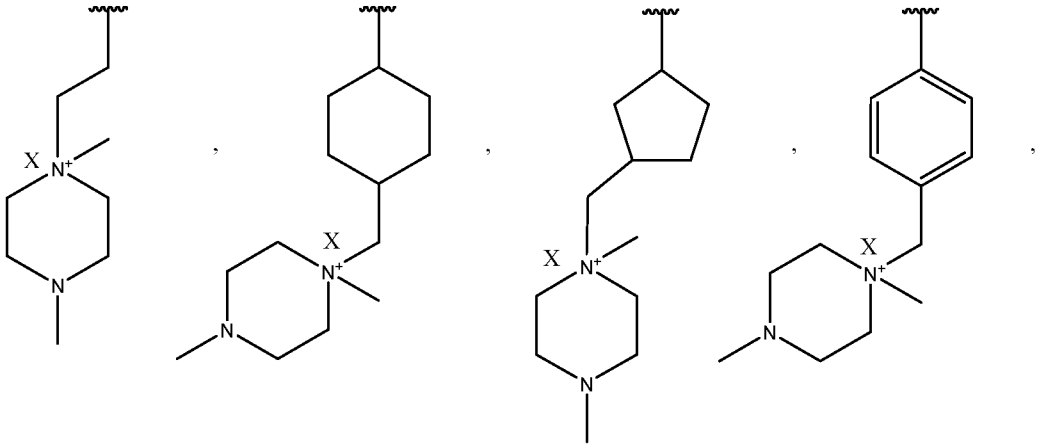


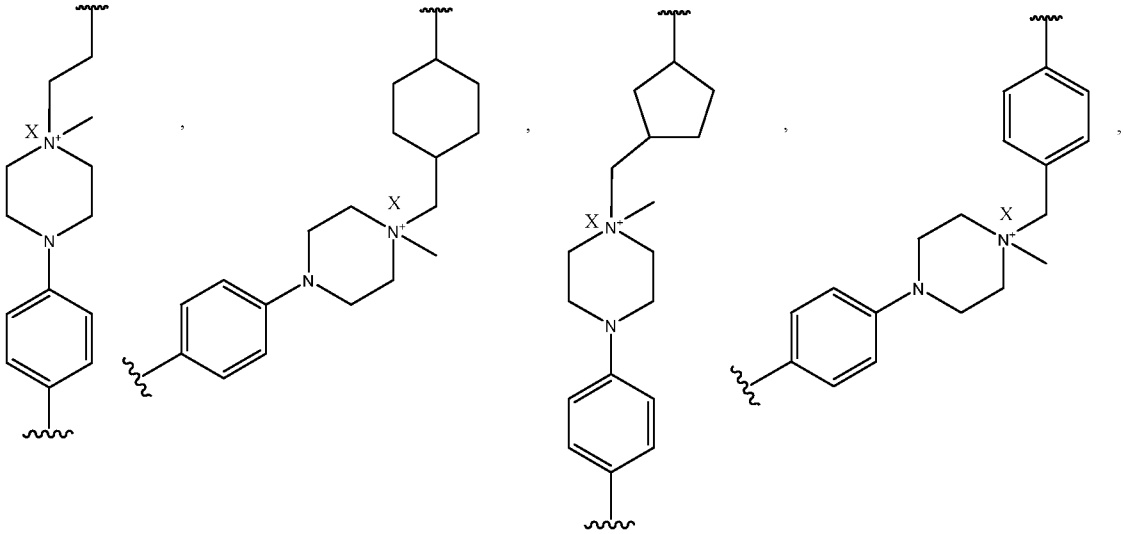


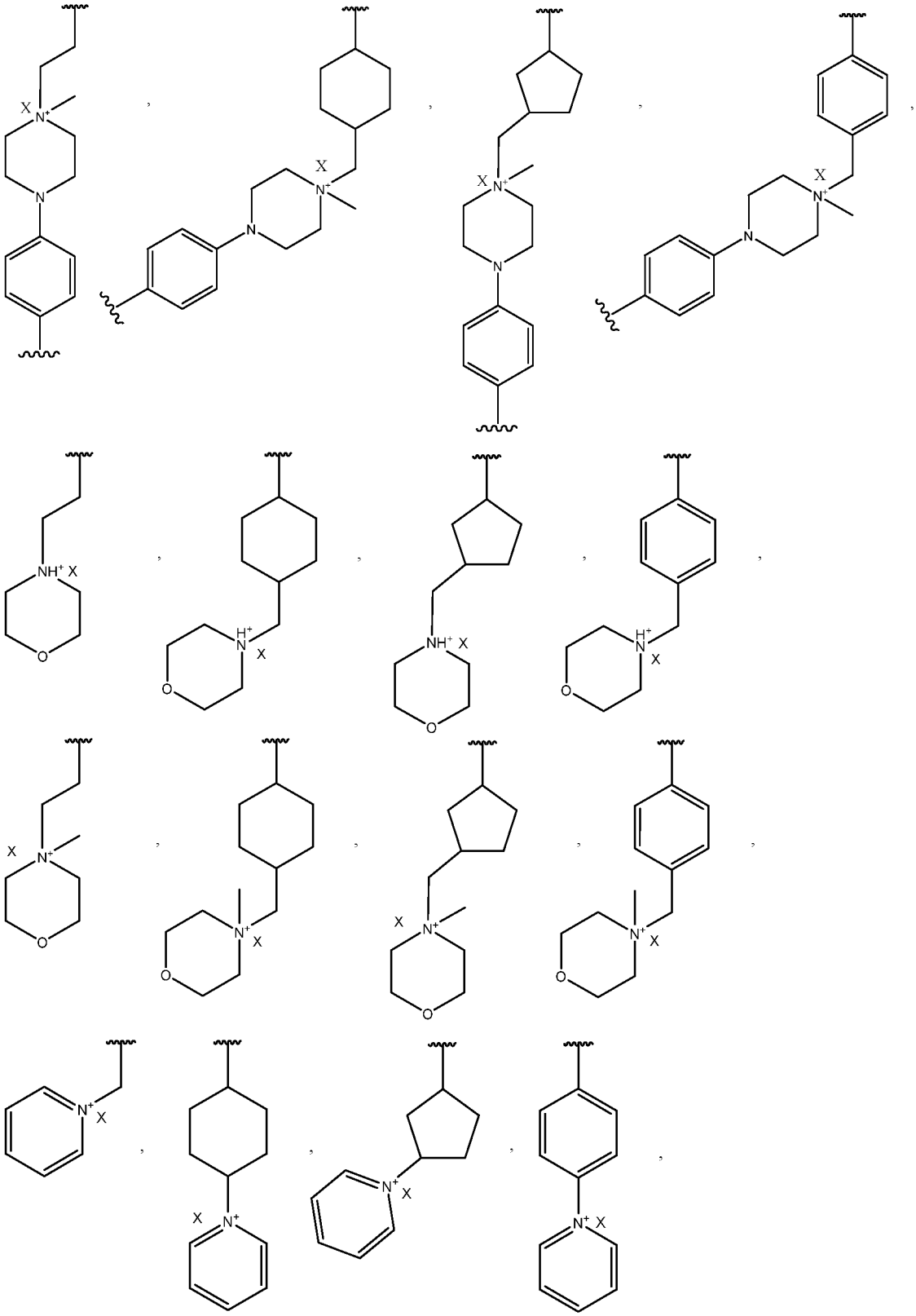


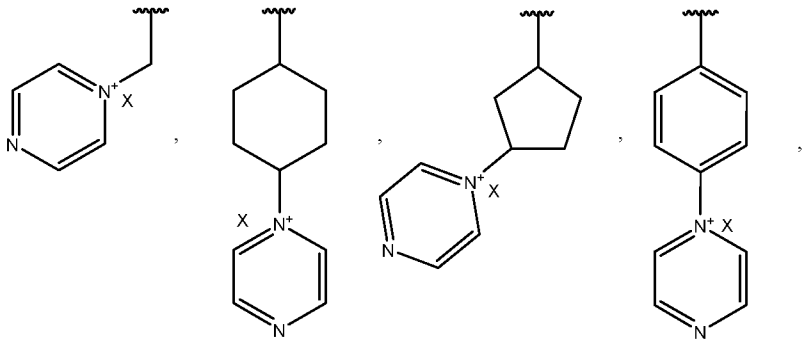


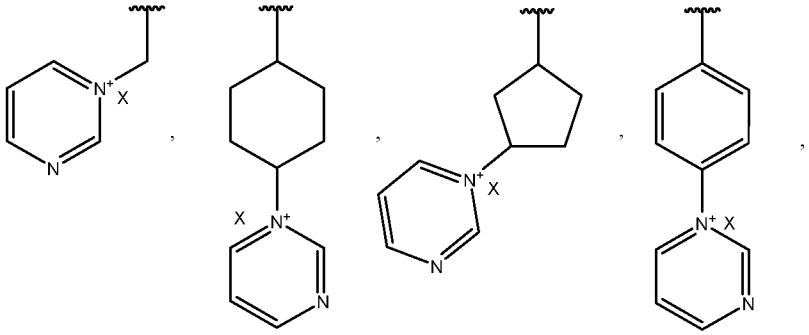


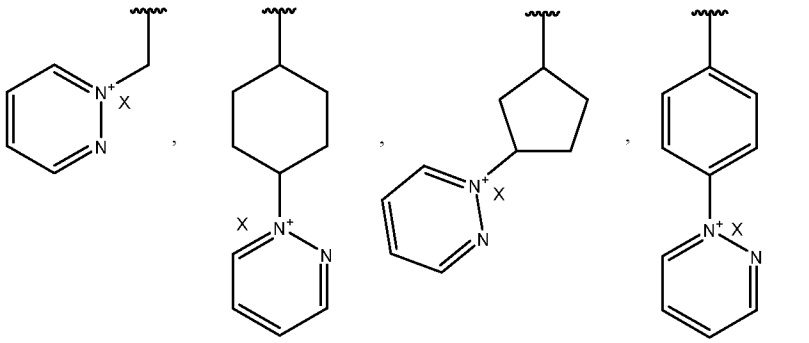


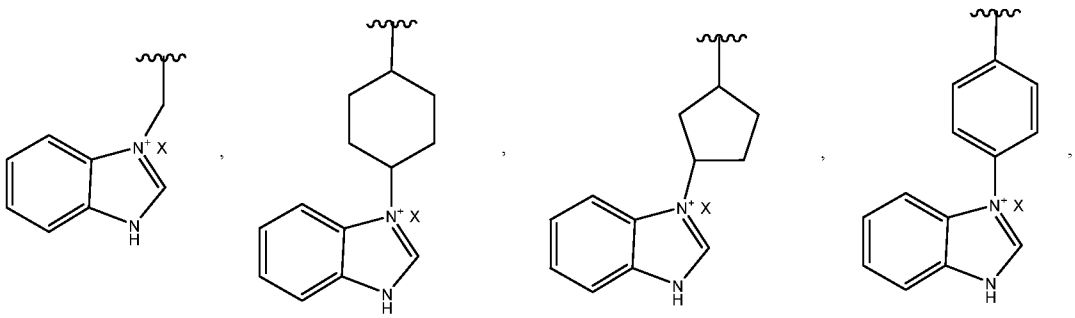


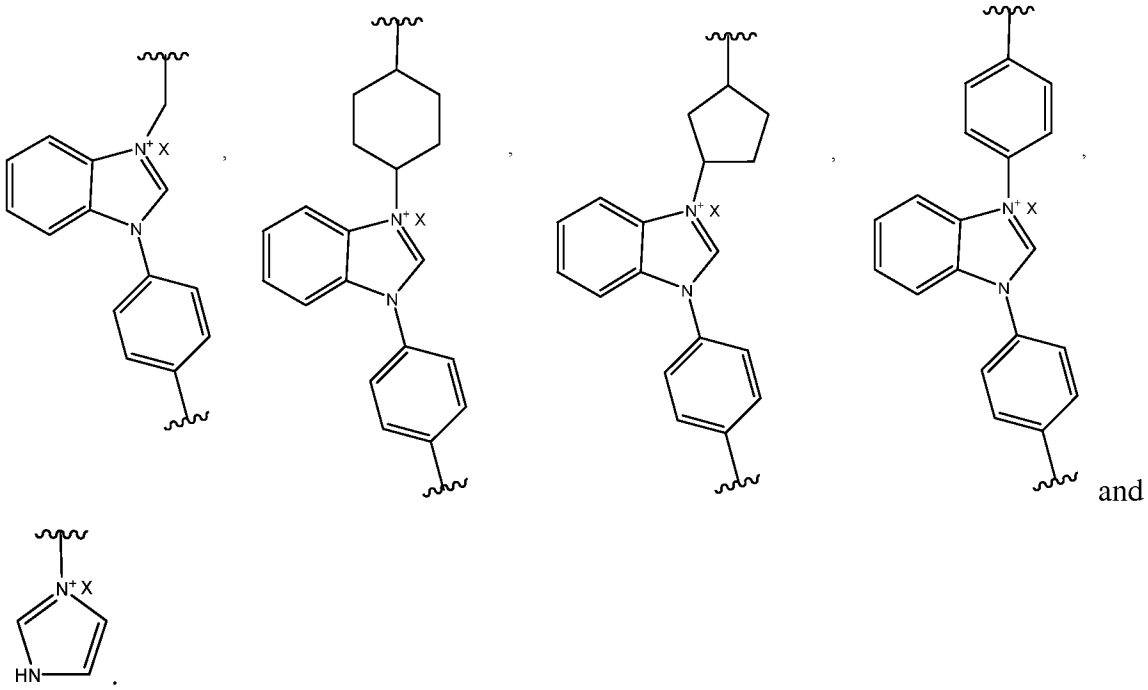




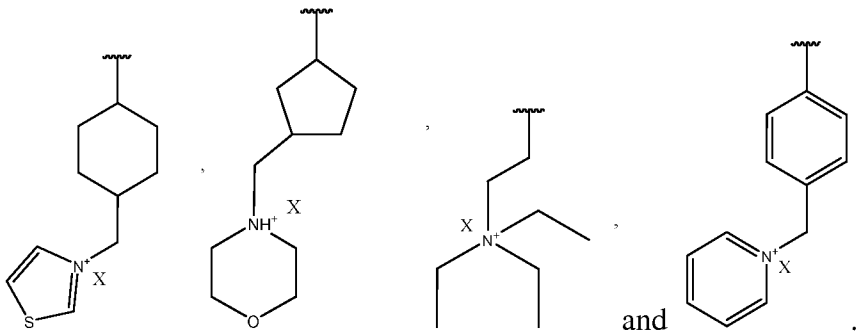




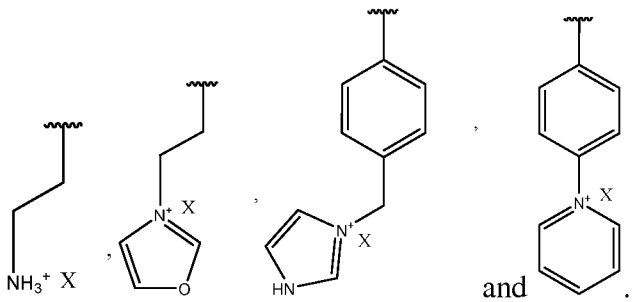




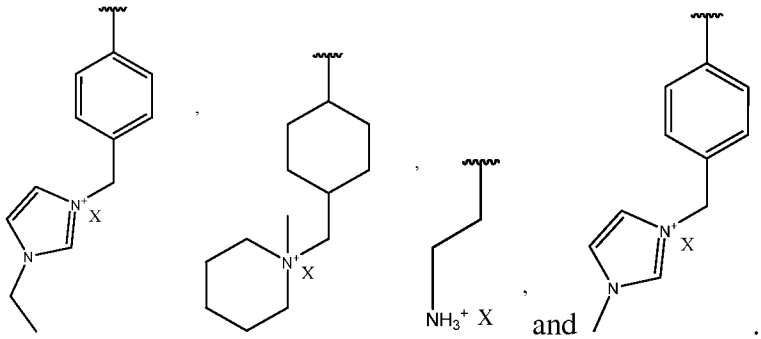
[00182] In some embodiments, the nitrogen-containing side chain is independently selected from



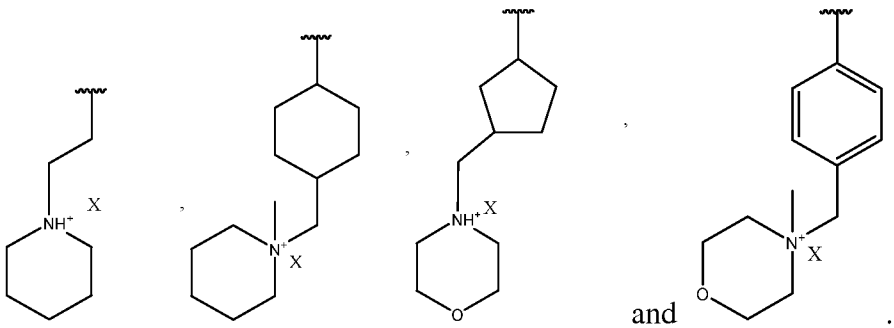
[00183] In some embodiments, the nitrogen-containing side chain is independently selected from



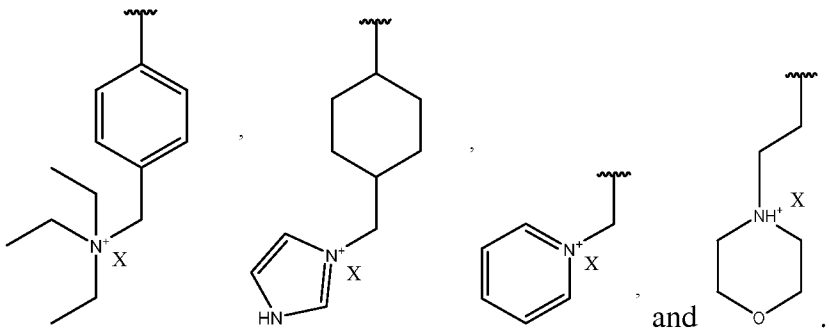
[00184] In some embodiments, the nitrogen-containing side chain is independently selected from



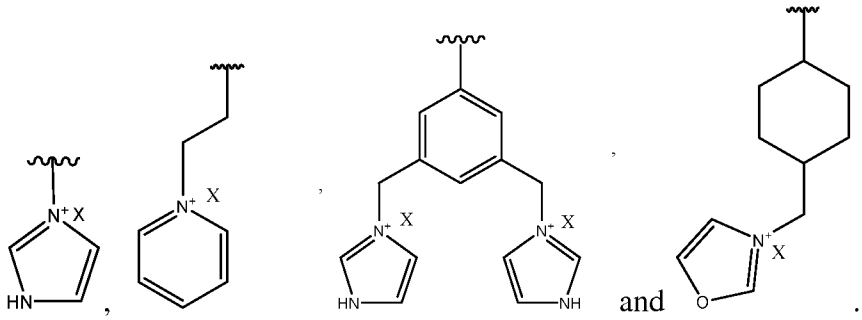
[00185] In some embodiments, the nitrogen-containing side chain is independently selected from



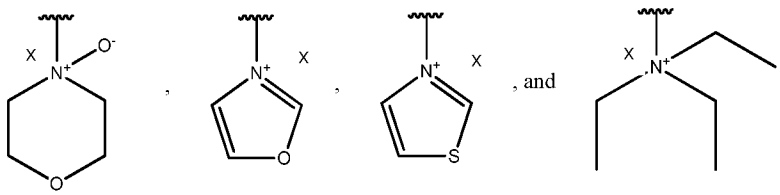
[00186] In some embodiments, the nitrogen-containing side chain is independently selected from



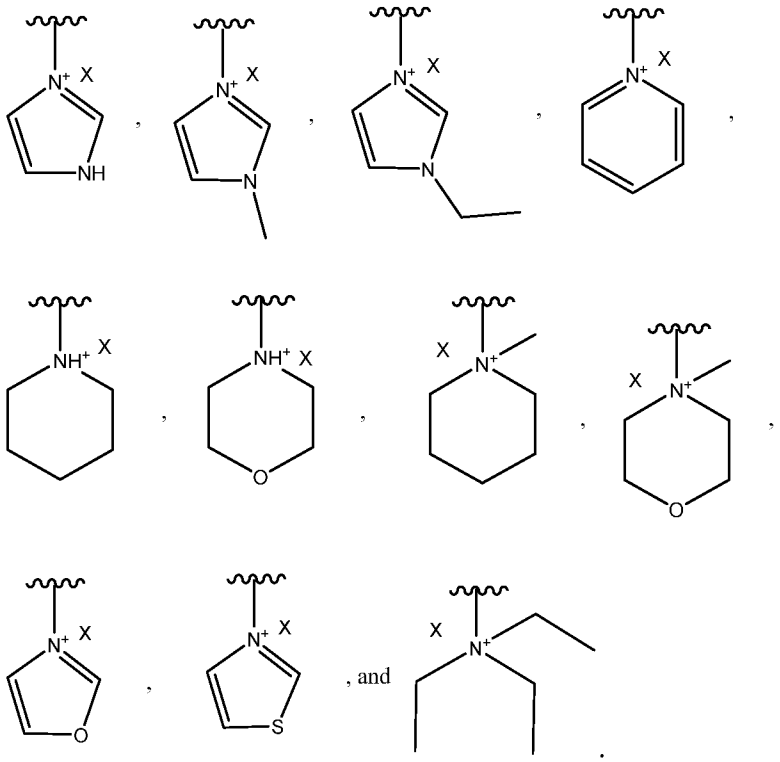
[00187] In some embodiments, the nitrogen-containing side chain is independently selected from



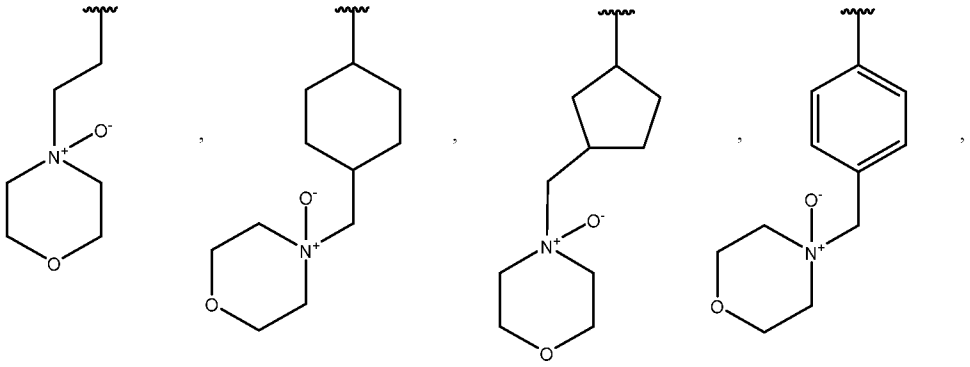
[00188] In other embodiments, the ionic monomers or moieties can have a side chain with a cationic group that is directly connected to the polymeric backbone or solid support. Side chains with a nitrogen-containing cationic group directly connected to the polymeric backbone or solid support can include, for example,



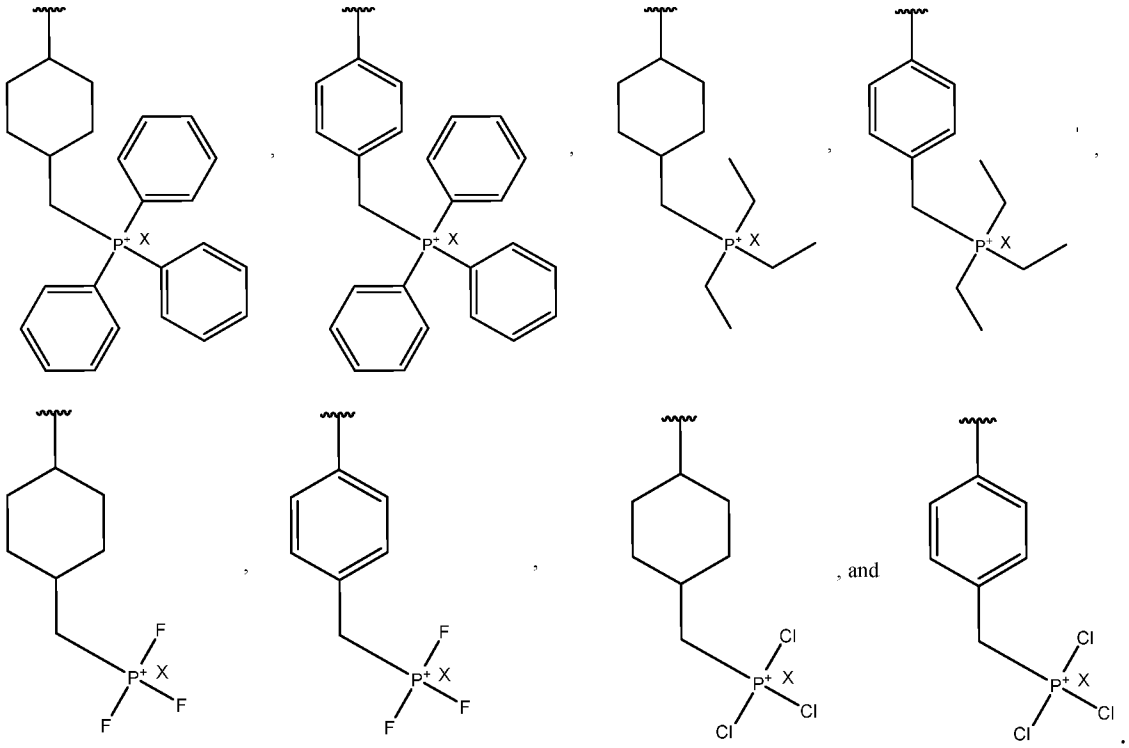
. In another embodiment, such nitrogen-containing side chains can include



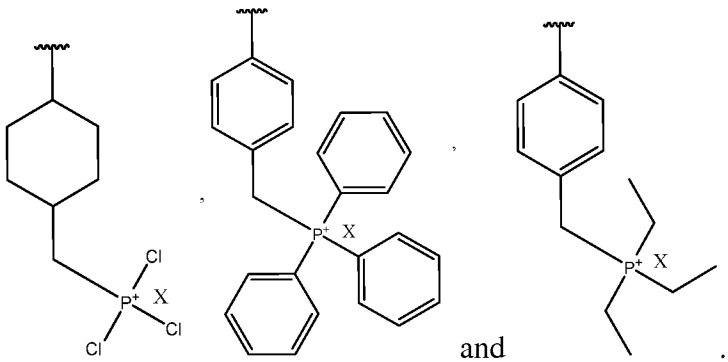
[00189] In some embodiments, the nitrogen-containing cationic group can be an N-oxide, where the negatively charged oxide (O-) is not readily dissociable from the nitrogen cation. Non- limiting examples of such groups include, for example,



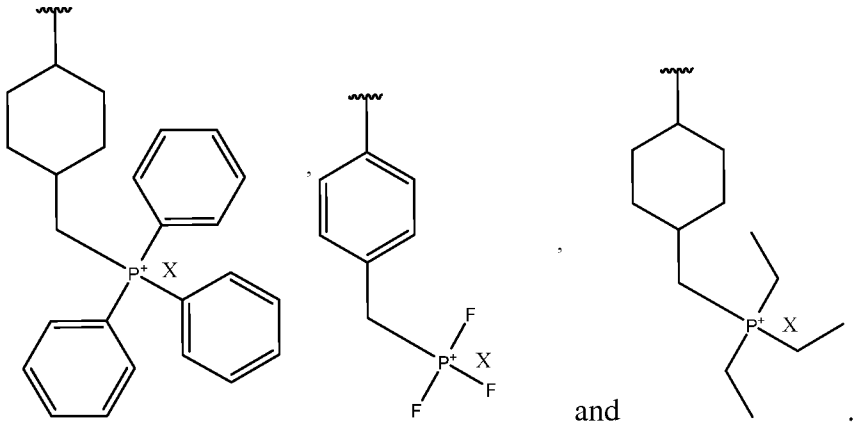
[00190] Side chains with a phosphorous-containing cationic group directly connected to the polymeric backbone can include, for example,



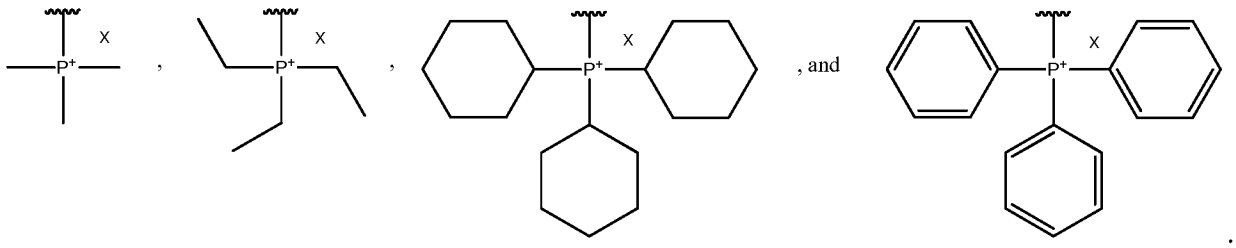
[00191] In some embodiments, the phosphorous-containing side chain is independently selected from



[00192] In some embodiments, the phosphorous-containing side chain is independently selected from



[00193] In other embodiments, the ionic monomers can have a side chain with a cationic group that is directly connected to the polymeric backbone. Side chains with a nitrogen-containing cationic group directly connected to the polymeric backbone can include, for example,



[00194] The ionic monomers can either all have the same cationic group, or can have different cationic groups. In some embodiments, each cationic group in the polymer is a nitrogen-containing cationic group. In other embodiments, each cationic group in the polymer is a phosphorous-containing cationic group. In yet other embodiments, the cationic group in some monomers of the polymer is a nitrogen-containing cationic group, whereas the cationic group in other monomers of the polymer is a phosphorous-containing cationic group. In an exemplary embodiment, each cationic group in the polymer is imidazolium. In another exemplary embodiment, the cationic group in some monomers of the polymer is imidazolium, while the cationic group in other monomers of the polymer is pyridinium. In yet another exemplary embodiment, each cationic group in the polymer is a substituted phosphonium. In yet another

exemplary embodiment, the cationic group in some monomers of the polymer is triphenyl phosphonium, while the cationic group in other monomers of the polymer is imidazolium.

[00195] In other embodiments, the monomers can have a side chain containing both a Bronsted-Lowry acid and a cationic group, where either the Bronsted-Lowry acid is connected to the polymeric backbone by a linker or the cationic group is connected to the polymeric backbone by a linker. In certain embodiments, the Bronsted-Lowry acid at each occurrence in the acidic-ionic monomer is independently selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid. In certain embodiments, the Bronsted-Lowry acid at each occurrence is independently sulfonic acid or phosphonic acid. In one embodiment, the Bronsted-Lowry acid at each occurrence is sulfonic acid. In exemplary embodiments, a side chain of an acidic-ionic monomer can contain imidazolium and acetic acid, or pyridinium and boronic acid.

[00196] In some embodiments, the nitrogen-containing cationic group at each occurrence in the acidic-ionic monomer is independently selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium, thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium. In one embodiment, the nitrogen-containing cationic group is imidazolium.

[00197] In some embodiments, the phosphorous-containing cationic group at each occurrence in the acidic-ionic monomer is independently selected from triphenyl phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, and trifluoro phosphonium. In one embodiment, the phosphorous-containing cationic group is triphenyl phosphonium.

[00198] The ionic monomers can either all have the same cationic group, or can have different cationic groups. In some embodiments, each cationic group in the polymer is a nitrogen-containing cationic group. In other embodiments, each cationic group in the polymer is a phosphorous-containing cationic group. In yet other embodiments, the cationic group in some monomers of the polymer is a nitrogen-containing cationic group, whereas the cationic group in other monomers of the polymer is a phosphorous-containing cationic group. In an exemplary embodiment, each cationic group in the polymer is imidazolium. In another exemplary embodiment, the cationic group in some monomers of the polymer is imidazolium, while the cationic group in other monomers of the polymer is pyridinium. In yet another exemplary embodiment, each cationic group in the polymer is a substituted phosphonium. In yet another

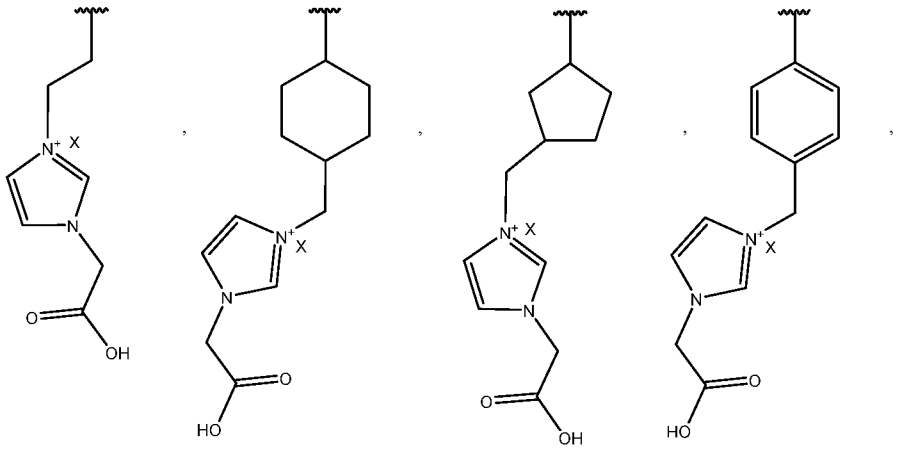
exemplary embodiment, the cationic group in some monomers of the polymer is triphenyl phosphonium, while the cationic group in other monomers of the polymer is imidazolium.

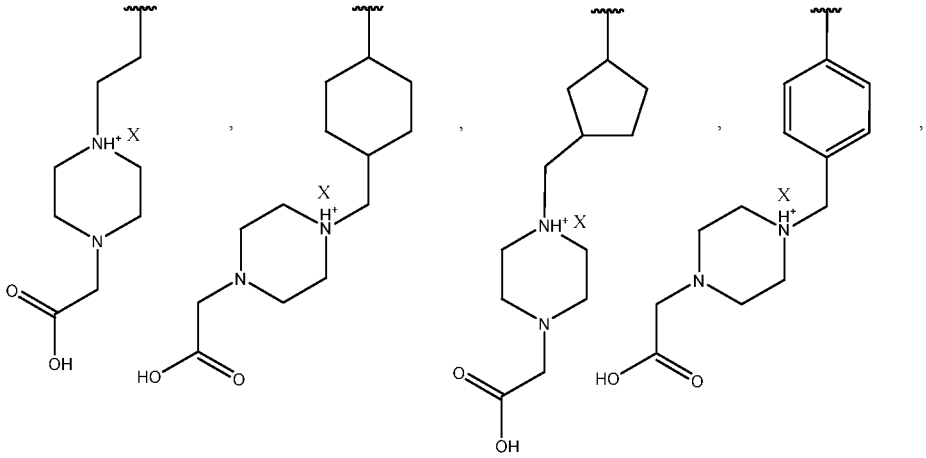
[00199] In some embodiments, the polymer can include at least one acidic-ionic monomer connected to the polymeric backbone, wherein at least one acidic-ionic monomer comprises at least one Bronsted-Lowry acid, and at least one cationic group, and wherein at least one of the acidic-ionic monomers comprises a linker connecting the acidic-ionic monomer to the polymeric backbone. The cationic group can be a nitrogen-containing cationic group or a phosphorous-containing cationic group as described herein. The linker can be selected from unsubstituted or substituted alkylene, unsubstituted or substituted cycloalkylene, unsubstituted or substituted alkenylene, unsubstituted or substituted arylene, and unsubstituted or substituted heteroarylene, where the terms unsubstituted and substituted have the meanings as disclosed herein.

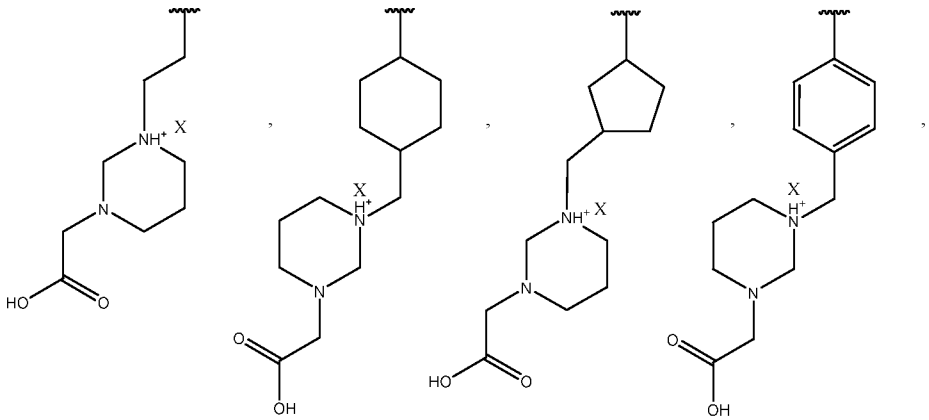
[00200] In other embodiments, the monomers can have a side chain containing both a Bronsted-Lowry acid and a cationic group, where the Bronsted-Lowry acid is directly connected to the polymeric backbone, the cationic group is directly connected to the polymeric backbone, or both the Bronsted-Lowry acid and the cationic group are directly connected to the polymeric backbone.

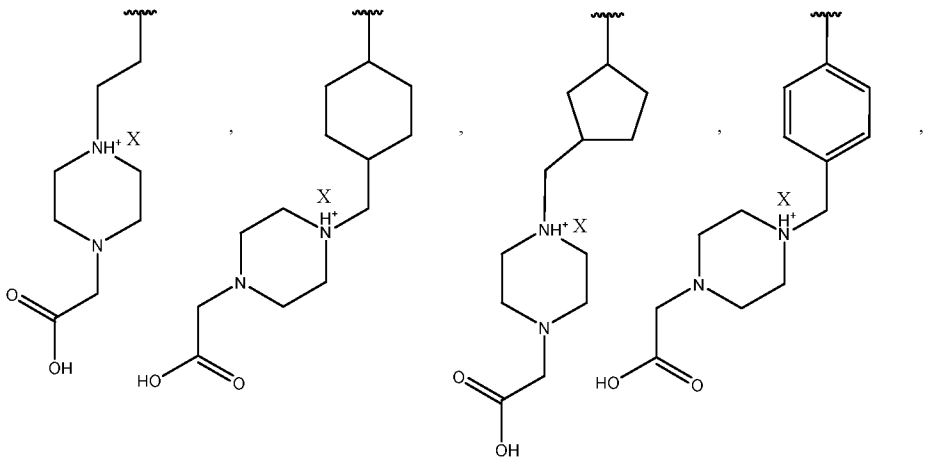
[00201] In certain embodiments, the linker is unsubstituted or substituted arylene, unsubstituted or substituted heteroarylene. In certain embodiments, the linker is unsubstituted or substituted arylene. In one embodiment, the linker is phenylene. In another embodiment, the linker is hydroxyl-substituted phenylene.

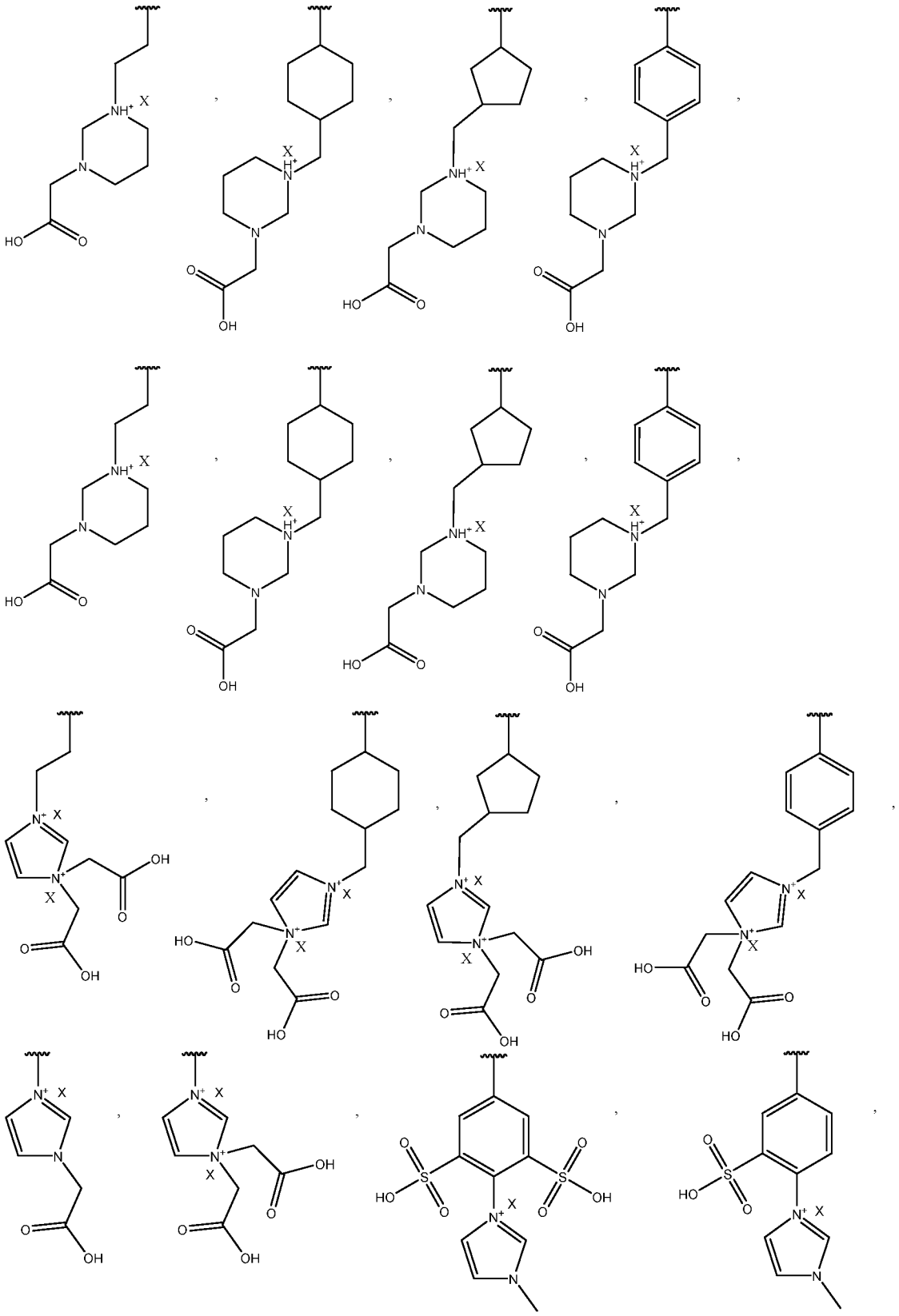
[00202] In other embodiments, the monomers can have a side chain containing both a Bronsted-Lowry acid and a cationic group, where either the Bronsted-Lowry acid is connected to the polymeric backbone by a linker or the cationic group is connected to the polymeric backbone by a linker. Monomers that have side chains containing both a Bronsted-Lowry acid and a cationic group can also be called “acidic ionomers”. Such side chains in acidic-ionic monomers that are connected by a linker can include, for example,

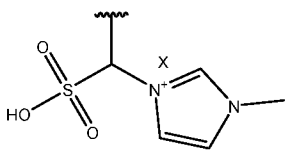




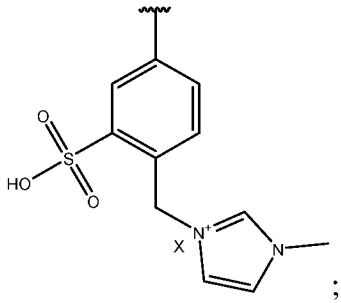








, and



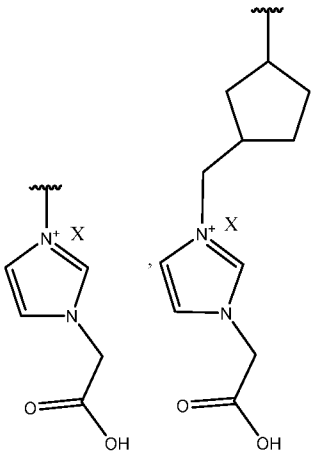
;

wherein each X is independently selected from F^-, Cl^-, Br^-, I^-, NO_2^-,NO_3^-, SO_4^{2-}, $R^7SO_4^-$, $R^7CO_2^-$, PO_4^{2-}, $R^7PO_3^-$, and $R^7PO_2^-$, where SO_4^{2-} and PO_4^{2-} are each independently associated with at least two Bronsted-Lowry acids at any X position on any side chain, and

each R^7 is independently selected from hydrogen, C_{1-4}alkyl, and C_{1-4}heteroalkyl.

[00203] In some embodiments, R^1 can be selected from hydrogen, alkyl, and heteroalkyl. In some embodiments, R^1 can be selected from hydrogen, methyl, or ethyl. In some embodiments, each X can be selected from Cl^-, NO_3^-, SO_4^{2-}, $R^7SO_4^-$, and $R^7CO_2^-$, where R^7 can be selected from hydrogen and C_{1-4}alkyl. In another embodiment, each X can be selected from Cl^-, Br^-, I^-, HSO_4^-, HCO_2^-, $CH_3CO_2^-$, and NO_3^-. In other embodiments, X is acetate. In other embodiments, X is bisulfate. In other embodiments, X is chloride. In other embodiments, X is nitrate.

[00204] In some embodiments, the acidic-ionic side chain is independently selected from



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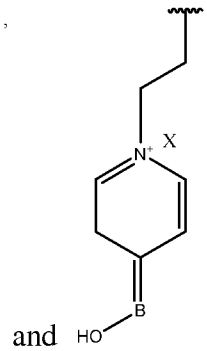
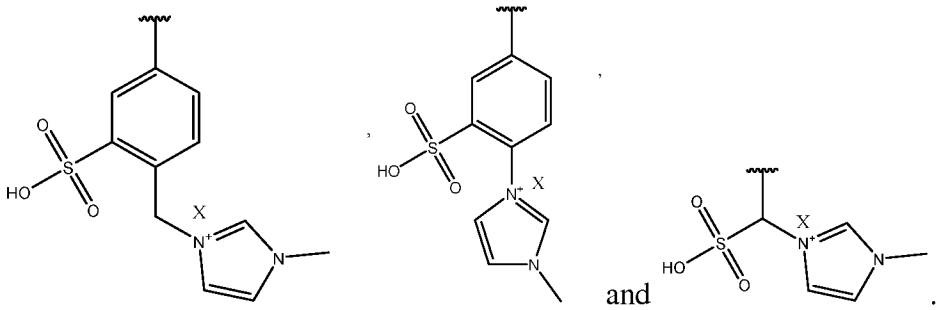
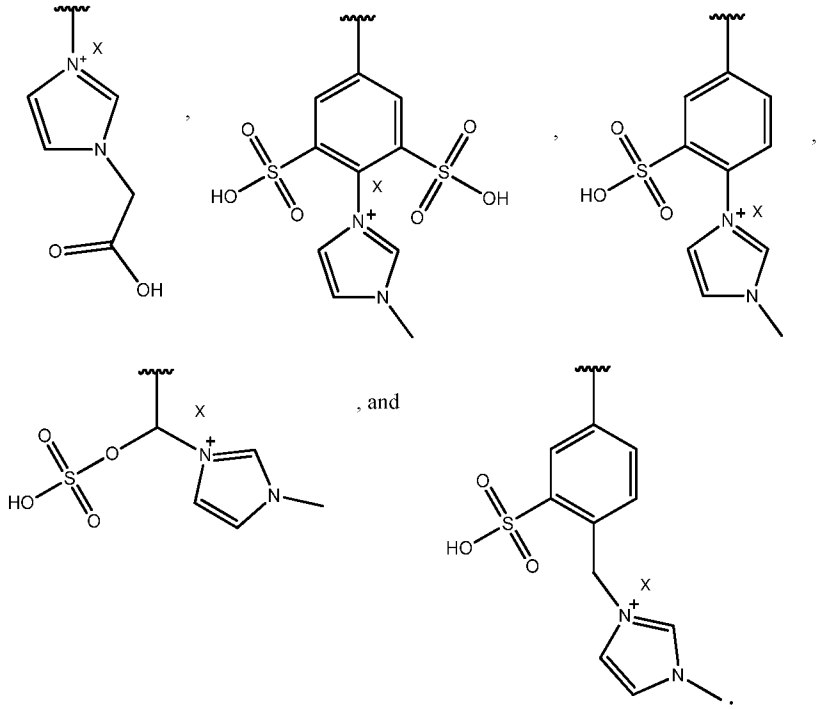


and .

[00205] In some embodiments, the acidic-ionic side chain is independently selected from



[00206] In other embodiments, the monomers can have a side chain containing both a Bronsted-Lowry acid and a cationic group, where the Bronsted-Lowry acid is directly connected to the polymeric backbone, the cationic group is directly connected to the polymeric backbone, or both the Bronsted-Lowry acid and the cationic group are directly connected to the polymeric backbone. Such side chains in acidic-ionic monomers can include, for example,



[00207] In some embodiments, the counterion is derived from acids selected from hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroioidic acid, nitric acid, nitrous acid, sulfuric acid, carbonic acid, phosphoric acid, phosphorous acid, acetic acid, formic acid, citric acid, methanesulfonic acid, ethanesulfonic acid, benzenesulfonic acid, dodecylsulfonic acid, and benzene phosphonic acid.

[00208] In some embodiments, the acidic and ionic monomers make up a substantial portion of the catalyst. In certain embodiments, the acidic and ionic monomers make up at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 90%, at least about 95%, or at least about 99% of the monomers of the polymer, based on the ratio of the number of acidic and ionic monomers to the total number of monomers present in the catalyst.

[00209] The ratio of the total number of acidic monomers to the total number of ionic monomers can be varied to tune the strength of the acid catalyst. In some embodiments, the total number of acidic monomers exceeds the total number of ionic monomers in the catalyst. In other embodiments, the total number of acidic monomers is at least about 2, at least about 3, at least about 4, at least about 5, at least about 6, at least about 7, at least about 8, at least about 9 or at least about 10 times the total number of ionic monomers in the catalyst. In certain embodiments, the ratio of the total number of acidic monomers to the total number of ionic monomers is about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1 about, 8:1, about 9:1 or about 10:1.

[00210] In some embodiments, the total number of ionic monomers exceeds the total number of acidic monomers in the catalyst. In other embodiments, the total number of ionic monomers is at least about 2, at least about 3, at least about 4, at least about 5, at least about 6, at least about 7, at least about 8, at least about 9 or at least about 10 times the total number of acidic monomers in the catalyst. In certain embodiments, the ratio of the total number of ionic monomers to the total number of acidic monomers is about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1 about, 8:1, about 9:1 or about 10:1.

[00211] The catalysts described herein can be characterized by the chemical functionalization of the catalyst. In some embodiments, the catalyst can have between about 0.1 and about 20 mmol, between about 0.1 and about 15 mmol, between about 0.01 and about 12 mmol, between about 0.01 and about 10 mmol, between about 1 and about 8 mmol, between about 2 and about 7 mmol, between about 3 and about 6 mmol, between about 1 and about 5, or between about 3 and about 5 mmol of the Bronsted-Lowry acid per gram of the catalyst. In some embodiments where the catalyst has at least some monomers with side chains having sulfonic acid as the Bronsted-Lowry acid, the catalyst can have between about 0.05 to about 10 mmol of the sulfonic acid per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having phosphonic acid as the Bronsted-Lowry acid, the catalyst can have between

about 0.01 and about 12 mmol of the phosphonic acid per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having acetic acid as the Bronsted-Lowry acid, the catalyst can have between about 0.01 and about 12 mmol of the acetic acid per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having isophthalic acid as the Bronsted-Lowry acid, the catalyst can have between about 0.01 and about 5 mmol of the isophthalic acid per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having boronic acid as the Bronsted-Lowry acid, the catalyst can have between about 0.01 and about 20 mmol of the boronic acid per gram of the catalyst.

[00212] In some embodiments of the polymer catalyst or solid-supported catalyst, each ionic monomer further includes a counterion for each nitrogen-containing cationic group or phosphorous-containing cationic group. In certain embodiments of the polymer catalyst or solid-supported catalyst, each counterion is independently selected from halide, nitrate, sulfate, formate, acetate, or organosulfonate. In some embodiments of the polymer catalyst or solid-supported catalyst, the counterion is fluoride, chloride, bromide, or iodide. In one embodiment of the polymer catalyst or solid-supported catalyst, the counterion is chloride. In another embodiment of the polymer catalyst or solid-supported catalyst, the counterion is sulfate. In yet another embodiment of the polymer catalyst or solid-supported catalyst, the counterion is acetate.

[00213] In some embodiments, the catalyst can have between about 0.01 and about 10 mmol, between about 0.01 and about 8.0 mmol, between about 0.01 and about 4 mmol, between about 1 and about 10 mmol, between about 2 and about 8 mmol, or between about 3 and about 6 mmol of the ionic group. In such embodiments, the ionic group includes the cationic group listed, as well as any suitable counterion described herein (*e.g.*, halide, nitrate, sulfate, formate, acetate, or organosulfonate). In some embodiments where the catalyst has at least some monomers with side chains having imidazolium as part of the ionic group, the catalyst can have between about 0.01 and about 8 mmol, between about 0.05 and about 8 mmol, between about 1 and about 6 mmol, or between about 2 and about 5 mmol per gram of the ionic group per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having pyridinium as part of the ionic group, the catalyst can have between between about 0.01 and about 8 mmol, between about 0.05 and about 8 mmol, between about 1 and about 6 mmol, or between about 2 and about 5 mmol per gramof the ionic group per gram of the catalyst. In other embodiments where the catalyst has at least some monomers with side chains having triphenyl

phosphonium as part of the ionic group, the catalyst can have between about 0.01 and about 5 mmol, between about 0.05 and about 5 mmol, between about 1 and about 4 mmol, or between about 2 and about 3 mmol per gram of the ionic group per gram of the catalyst.

[00214] The catalyst described herein can further include monomers having a side chain containing a non-functional group, such as a hydrophobic group. In some embodiments, the hydrophobic group is connected directly to the polymeric backbone. Suitable hydrophobic groups can include, for example, unsubstituted or substituted alkyl, unsubstituted or substituted cycloalkyl, unsubstituted or substituted aryl, or unsubstituted or substituted heteroaryl. In some embodiments, the hydrophobic group is unsubstituted or substituted C5 or C6 aryl. In certain embodiments, the hydrophobic group is unsubstituted or substituted phenyl. In one exemplary embodiment, the hydrophobic group is unsubstituted phenyl. Further, it should be understood that the hydrophobic monomers can either all have the same hydrophobic group, or can have different hydrophobic groups.

[00215] In some embodiments, the acidic monomers, the ionic monomers, the acidic-ionic monomers and the hydrophobic monomers, where present, can be arranged in alternating sequence or in a random order as blocks of monomers. In some embodiments, each block has not more than twenty, fifteen, ten, six, or three monomers.

[00216] In some embodiments, the catalyst is randomly arranged in an alternating sequence. With reference to the portion of the exemplary catalyst depicted in FIG. **3A**, the monomers are randomly arranged in an alternating sequence.

[00217] In other embodiments, the catalyst is randomly arranged as blocks of monomers. With reference to the portion of the exemplary catalyst depicted in FIG. **3B**, the monomers are arranged in blocks of monomers.

[00218] The catalysts described herein can also be cross-linked. Such cross-linked polymers can be prepared by introducing cross-linking groups. In some embodiments, cross-linking can occur within a given polymeric chain, with reference to the portion of the exemplary catalysts depicted in FIGS. **4A** and **4B**. In other embodiments, cross-linking can occur between two or more polymeric chains, with reference to the portion of the exemplary catalysts in FIGS. **5A**, **5B**, **5C** and **5D**.

[00219] In some embodiments, the polymer is cross-linked. In certain embodiments, at least about 1%, at least about 2%, at least about 3%, at least about 4%, at least about 5%, at least about 6%, at least about 7%, at least about 8%, at least about 9%, at least about 10%, at least about 15%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 90% or at least about 99% of the polymer is cross-linked.

[00220] In some embodiments, the polymers described herein are not substantially cross-linked, such as less than about 0.9% cross-linked, less than about 0.5% cross-linked, less than about 0.1% cross-linked, less than about 0.01% cross-linked, or less than 0.001% cross-linked.

[00221] With reference to FIGS. **4A**, **4B** and **5A**, it should be understood that R^1, R^2 and R^3, respectively, are exemplary cross linking groups. Suitable cross-linking groups that can be used to form a cross-linked polymer with the polymers described herein include, for example, substituted or unsubstituted divinyl alkanes, substituted or unsubstituted divinyl cycloalkanes, substituted or unsubstituted divinyl aryls, substituted or unsubstituted heteroaryls, dihaloalkanes, dihaloalkenes, dihaloalkynes. For example, cross-linking groups can include divinylbenzene, diallylbenzene, dichlorobenzene, divinylmethane, dichloromethane, divinylethane, dichloroethane, divinylpropane, dichloropropane, divinylbutane, dichlorobutane, ethylene glycol, and resorcinol.

[00222] The polymeric backbone described herein can include, for example, polyalkylenes, polyalkenyl alcohols, polycarbonate, polyarylenes, polyaryletherketones, and polyamide-imides. In certain embodiments, the polymeric backbone can be selected from polyethylene, polypropylene, polyvinyl alcohol, polystyrene, polyurethane, polyvinyl chloride, polyphenol-aldehyde, polytetrafluoroethylene, polybutylene terephthalate, polycaprolactam, and poly(acrylonitrile butadiene styrene). In certain embodiments of the polymer catalyst, the polymeric backbone is polyethyelene or polypropylene. In one embodiment of the polymer catalyst, the polymeric backbone is polyethylene. In another embodiment of the polymer catalyst, the polymeric backbone is polyvinyl alcohol. In yet another embodiment of the polymer catalyst, the polymeric backbone is polystyrene.

[00223] With reference to FIG. **6A**, in one exemplary embodiment, the polymeric backbone is polyethylene. With reference to FIG. **6B**, in another exemplary embodiment, the polymeric backbone is polyvinyl alcohol.

[00224] The polymeric backbone described herein can also include an ionic group integrated as part of the polymeric backbone. Such polymeric backbones can also be called "ionomeric backbones". In certain embodiments, the polymeric backbone can be selected frompolyalkyleneammonium, polyalkylenediammonium, polyalkylenepyrrolium, polyalkyleneimidazolium, polyalkylenepyrazolium, polyalkyleneoxazolium, polyalkylenethiazolium, polyalkylenepyridinium, polyalkylenepyrimidinium, polyalkylenepyrazinium, polyalkylenepyradizimium, polyalkylenethiazinium, polyalkylenemorpholinium, polyalkylenepiperidinium, polyalkylenepiperizinium, polyalkylenepyrollizinium, polyalkylenetriphenylphosphonium, polyalkylenetrimethylphosphonium, polyalkylenetriethylphosphonium, polyalkylenetripropylphosphonium, polyalkylenetributylphosphonium, polyalkylenetrichlorophosphonium, polyalkylenetrifluorophosphonium, and polyalkylenediazolium, polyarylalkyleneammonium, polyarylalkylenediammonium, polyarylalkylenepyrrolium, polyarylalkyleneimidazolium, polyarylalkylenepyrazolium, polyarylalkyleneoxazolium, polyarylalkylenethiazolium, polyarylalkylenepyridinium, polyarylalkylenepyrimidinium, polyarylalkylenepyrazinium, polyarylalkylenepyradizimium, polyarylalkylenethiazinium, polyarylalkylenemorpholinium, polyarylalkylenepiperidinium, polyarylalkylenepiperizinium, polyarylalkylenepyrollizinium, polyarylalkylenetriphenylphosphonium, polyarylalkylenetrimethylphosphonium, polyarylalkylenetriethylphosphonium, polyarylalkylenetripropylphosphonium, polyarylalkylenetributylphosphonium, polyarylalkylenetrichlorophosphonium, polyarylalkylenetrifluorophosphonium, and polyarylalkylenediazolium.

[00225] Cationic polymeric backbones can be associated with one or more anions, including but not limited to, F^-, Cl^-, Br^-, I^-, NO_2^-,NO_3^-, SO_4^{2-}, $R^7SO_4^-$, $R^7CO_2^-$, PO_4^{2-}, $R^7PO_3^-$, and $R^7PO_2^-$, where R^7 is selected from hydrogen, C_{1-4}alkyl, and C_{1-4}heteroalkyl. In one embodiment, each X can be selected from Cl^-, Br^-, I^-, HSO_4^-, HCO_2^-, $CH_3CO_2^-$, and NO_3^-. In other embodiments, X is acetate. In other embodiments, X is bisulfate. In other embodiments, X is chloride. In other embodiments, X is nitrate.

[00226] In other embodiments, the polymeric backbone is alkyleneimidazolium, which refers to an alkylene moiety, in which one or more of the methylene units of the alkylene moiety has been replaced with imidazolium. In one embodiment, the polymeric backbone is selected from polyethyleneimidazolium, polyprolyeneimidazolium, and polybutyleneimidazolium. It should

further be understood that, in other embodiments of the polymeric backbone, when a nitrogen-containing cationic group or a phosphorous-containing cationic group follows the term "alkylene", one or more of the methylene units of the alkylene moiety is substituted with that particular nitrogen-containing cationic group or phosphorous-containing cationic group.

[00227] Further, the number of atoms between side chains in the polymeric backbone can vary. In some embodiments, there are between zero and twenty atoms, zero and ten atoms, zero and six atoms, or zero and three atoms between side chains attached to the polymeric backbone.

[00228] In some embodiments, the polymer can be a homopolymer having at least two monomer units, and where all the units contained within the polymer are derived from the same monomer in the same manner. In other embodiments, the polymer can be a heteropolymer having at least two monomer units, and where at least one monomeric unit contained within the polymer that differs from the other monomeric units in the polymer. The different monomer units in the polymer can be in a random order, in an alternating sequence of any length of a given monomer, or in blocks of monomers.

[00229] Other exemplary polymers include, but are not limited to, polyalkylene backbones that are substituted with one or more groups selected from hydroxyl, carboxylic acid, unsubstituted and substituted phenyl, halides, unsubstituted and substituted amines, unsubstituted and substituted ammonias, unsubstituted and substituted pyrroles, unsubstituted and substituted imidazoles, unsubstituted and substituted pyrazoles, unsubstituted and substituted oxazoles, unsubstituted and substituted thiazoles, unsubstituted and substituted pyridines, unsubstituted and substituted pyrimidines, unsubstituted and substituted pyrazines, unsubstituted and substituted pyradizines, unsubstituted and substituted thiazines, unsubstituted and substituted morpholines, unsubstituted and substituted piperidines, unsubstituted and substituted piperizines, unsubstituted and substituted pyrollizines, unsubstituted and substituted triphenylphosphonates, unsubstituted and substituted trimethylphosphonates, unsubstituted and substituted triethylphosphonates, unsubstituted and substituted tripropylphosphonates, unsubstituted and substituted tributylphosphonates, unsubstituted and substituted trichlorophosphonates, unsubstituted and substituted trifluorophosphonates, and unsubstituted and substituted diazoles, where the terms unsubstituted and substituted have the meanings as disclosed herein.

[00230] For the polymers as described herein, multiple naming conventions are well recognized in the art. For instance, a polyethylene backbone with a direct bond to an

unsubstituted phenyl group (-CH_2-CH(phenyl)-CH_2-CH(phenyl)-) is also known as polystyrene. Should that phenyl group be substituted with an ethenyl group, the polymer can be named a polydivinylbenzene (-CH_2-CH(4-vinylphenyl)-CH_2-CH(4-vinylphenyl)-). Further non-limiting examples of heteropolymers include those that are functionalized after polymerization.

[00231] A non-limiting example would be polystyrene-co-divinylbenzene: (-CH_2-CH(phenyl)-CH_2-CH(4-ethylenephenyl)-CH_2-CH(phenyl)-CH_2-CH(4-ethylenephenyl)-). Here, the ethenyl functionality could be at the 2, 3, or 4 position on the phenyl ring.

[00232] With reference to FIG. **6C**, in yet another exemplary embodiment, the polymeric backbone is a polyalkyleneimidazolium.

[00233] Further, the number of atoms between side chains in the polymeric backbone can vary. In some embodiments, there are between zero and twenty atoms, zero and ten atoms, or zero and six atoms, or zero and three atoms between side chains attached to the polymeric backbone. With reference to FIG. **7A**, in one exemplary embodiment, there are three carbon atoms between the side chain with the Bronsted-Lowry acid and the side chain with the cationic group. In another example, with reference to FIG. **7B**, there are zero atoms between the side chain with the acidic moiety and the side chain with the ionic moiety.

[00234] It should be understood that the catalyst can include any of the Bronsted-Lowry acids, cationic groups, counterions, linkers, hydrophobic groups, cross-linking groups, and polymeric backbones described herein, as if each and every combination were listed separately. For example, in one embodiment, the catalyst can include benzenesulfonic acid (*i.e.*, a sulfonic acid with a phenyl linker) connected to a polystyrene backbone, and an imidazolium chloride connected directly to the polystyrene backbone. In another embodiment, the catalyst can include boronyl-benzyl-pyridinium chloride (*i.e.*, a boronic acid and pyridinium chloride in the same monomer unit with a phenyl linker) connected to a polystyrene backbone. In yet another embodiment, the catalyst can include benzenesulfonic acid and an imidazolium sulfate moiety each individually connected to a polyvinyl alcohol backbone.

[00235] Exemplary polymeric acid catalysts described herein include:

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium nitrate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium nitrate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium iodide-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bromide-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium acetate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium formate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-acetate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-nitrate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-chloride-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-bromide-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-iodide-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-bisulfate-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-acetate-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium chloride-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium acetate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium formate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triphenyl-(4-vinylbenzyl)-phosphonium chloride-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triphenyl-(4-vinylbenzyl)-phosphonium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triphenyl-(4-vinylbenzyl)-phosphonium acetate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-methyl-1-(4-vinylbenzyl)-piperdin-1-ium chloride-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-methyl-1-(4-vinylbenzyl)-piperdin-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-methyl-1-(4-vinylbenzyl)-piperdin-1-ium acetate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-4-oxide-*co*-divinyl benzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triethyl-(4-vinylbenzyl)-ammonium chloride-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triethyl-(4-vinylbenzyl)-ammonium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triethyl-(4-vinylbenzyl)-ammonium acetate-*co*-divinylbenzene];

poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-4-boronyl-1-(4-vinylbenzyl)-pyridinium chloride-*co*-divinylbenzene];

poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium chloride-*co*-1-(4-vinylphenyl)methylphosphonic acid-*co*-divinylbenzene];

poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-*co*-1-(4-vinylphenyl)methylphosphonic acid-*co*-divinylbenzene];

poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium acetate-*co*-1-(4-vinylphenyl)methylphosphonic acid-*co*-divinylbenzene];

poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium nitrate-*co*-1-(4-vinylphenyl)methylphosphonic acid-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-1-methyl-2-vinyl-pyridinium chloride-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-1-methyl-2-vinyl-pyridinium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-1-methyl-2-vinyl-pyridinium acetate-*co*-divinylbenzene];

poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-4-oxide-*co*-divinyl benzene];

poly [styrene-*co*-4-vinylphenylphosphonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylphenylphosphonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly [styrene-*co*-4-vinylphenylphosphonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly[styrene-*co*-3-carboxymethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly[styrene-*co*-3-carboxymethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-3-carboxymethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly[styrene-*co*-5-(4-vinylbenzylamino)-isophthalic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly[styrene-*co*-5-(4-vinylbenzylamino)-isophthalic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-5-(4-vinylbenzylamino)-isophthalic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly[styrene-*co*-(4-vinylbenzylamino)-acetic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene];

poly[styrene-*co*-(4-vinylbenzylamino)-acetic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene];

poly[styrene-*co*-(4-vinylbenzylamino)-acetic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene];

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenyl phosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenyl phosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium acetate-*co*-vinylbenzylmethylmorpholinium acetate-*co*-vinylbenzyltriphenyl phosphonium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium acetate-*co*-vinylbenzylmethylmorpholinium acetate-*co*-vinylbenzyltriphenyl phosphonium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylmorpholinium acetate-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylmorpholinium acetate-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene)

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylmethylimidazolium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylmethylimidazolium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylmethylimidazolium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylmethylimidazolium nitrate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylmethylimidazolium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylmethylimidazolium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylmethylimidazolium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylmethylimidazolium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzylmethylimidazolium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzyltriphenylphosphonium acetate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene);

poly(styrene-*co*-4-vinylbenzenephosphonic acid-*co*-vinylbenzyltriphenylphosphonium acetate-*co*-divinylbenzene);

poly(butyl-vinylimidazolium chloride–*co*–butylimidazolium bisulfate–*co*–4-vinylbenzenesulfonic acid);

poly(butyl-vinylimidazolium bisulfate–*co*–butylimidazolium bisulfate–*co*–4-vinylbenzenesulfonic acid);

poly(benzyl alcohol-*co*-4-vinylbenzylalcohol sulfonic acid-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzyl alcohol); and

poly(benzyl alcohol-*co*-4-vinylbenzylalcohol sulfonic acid-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzyl alcohol).

[00236] In some embodiments, exemplary polymers can include

poly [styrene-co-4-vinylbenzene sulfonic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium nitrate-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-3H-imidazol-1-ium iodide-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-benzoimidazol-1-ium chloride-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-pyridinium-bisulfate-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-pyridinium-chloride-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium chloride-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-4-(4-vinylbenzyl)-morpholine-4-oxide-co-divinyl benzene];

poly[styrene-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-1-(4-vinylphenyl)methyl phosphoninc acid-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzylchloride-co-1-methyl-2-vinyl-pyridinium bisulfate-co-divinylbenzene];

poly[styrene-co-4--vinylbenzene sulfonic acid-co-4-(4-vinylbenzyl)-morpholine-4-oxide-co-divinyl benzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-triphenyl-(4-vinylbenzyl)-phosphonium bisulfate-co-divinylbenzene];

poly[styrene-co-5-(4-vinylbenzylamino)- isophthalic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium chloride-co-divinylbenzene];

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzylmethylimidazolium chloride-co-vinylbenzylmethylmorpholinium chloride-co-vinylbenzyltriphenyl phosphonium chloride-co-divinylbenzene);

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylmethylimidazolium acetate-co-divinylbenzene);

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene);

poly(styrene-co-4-vinylbenzene phosphonic acid-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene);

poly(styrene-co-4-vinylbenzene phosphonic acid-co-vinylbenzyltriphenylphosphonium bisulfate-co-divinylbenzene); and

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene).

[00237] In some embodiments, exemplary polymers can include

poly[styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-pyridinium-chloride-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzylchloride-co-1-methyl-2-vinyl-pyridinium bisulfate-co-divinylbenzene];

poly(styrene-co-4-vinylbenzene phosphonic acid-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene);

poly [styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene]; and

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylmethylimidazolium acetate-co-divinylbenzene).

[00238] In some embodiments, exemplary polymers can include

poly [styrene-co-4-vinylbenzene sulfonic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-benzoimidazol-1-ium chloride-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-divinylbenzene];

poly [styrene-co-4-vinylbenzene sulfonic acid-co-1-(4-vinylbenzyl)-pyridinium-bisulfate-co-divinylbenzene];

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzylmethylimidazolium chloride-co-vinylbenzylmethylmorpholinium chloride-co-vinylbenzyltriphenyl phosphonium chloride-co-divinylbenzene); and

poly[styrene-co-4-vinylbenzene sulfonic acid-co-4-(4-vinylbenzyl)-morpholine-4-oxide-co-divinyl benzene].

[00239] In some embodiments, exemplary polymers can include

poly[styrene-co-4-vinylbenzene sulfonic acid-co-4-(4-vinylbenzyl)-morpholine-4-oxide-co-divinyl benzene];

poly(styrene-co-4-vinylbenzene sulfonic acid-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene);

poly [styrene-co-4-vinylbenzene sulfonic acid-1-(4-vinylbenzyl)-3H-imidazol-1-ium iodide-co-divinylbenzene];

poly[styrene-co-4-vinylbenzene sulfonic acid-co-triphenyl-(4-vinylbenzyl)-phosphonium bisulfate-co-divinylbenzene]; and

poly[styrene-co-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium bisulfate-co-1-(4-vinylphenyl)methyl phosphonic acid-co-divinylbenzene].

[00240] In some embodiments, the polymeric backbone is formed from one or more substituted or unsubstituted monomers. Polymerization processes using a wide variety of monomers are well known in the art (*see*, e.g., International Union of Pure and Applied Chemistry, et al., IUPAC Gold Book, *Polymerization*. (2000)). One such process involves monomer(s) with unsaturated substitution, such as vinyl, propenyl, butenyl, or other such substitutent(s). These types of monomers can undergo radical initiation and chain polymerization.

[00241] In other embodiments, monomers having heteroatoms can be combined with one or more difunctionalized compounds, such as, but not limited to, dihaloalkanes, di(alkylsulfonyloxy)alkanes, and di(arylsulfonyloxy)alkanes to form polymers. The monomers have at least two heteroatoms to link with the difunctionalized alkane to create the polymeric chain. These difunctionalized compounds can be further substituted as described herein. In some embodiments, the difunctionalized compound(s) can be selected from 1,2-dichloroethane, 1,2-dichloropropane, 1,3-dichloropropane, 1,2-dichlorobutane, 1,3-dichlorobutane,1,4-dichlorobutane, 1,2-dichloropentane, 1,3-dichloropentane,1,4-dichloropentane, 1,5-dichloropentane, 1,2-dibromoethane, 1,2-dibromopropane, 1,3-dibromopropane, 1,2-dibromobutane, 1,3-dibromobutane,1,4-dibromobutane, 1,2-dibromopentane, 1,3-dibromopentane,1,4-dibromopentane, 1,5-dibromopentane, 1,2-diiodoethane, 1,2-diiodopropane, 1,3-diiodopropane, 1,2-diiodobutane, 1,3-diiodobutane,1,4-diiodobutane, 1,2-diiodopentane, 1,3-diiodopentane,1,4-diiodopentane,1,5-diiodopentane, 1,2-dimethanesulfoxyethane, 1,2-dimethanesulfoxypropane, 1,3-dimethanesulfoxypropane, 1,2-dimethanesulfoxybutane, 1,3-dimethanesulfoxybutane,1,4-dimethanesulfoxybutane, 1,2-dimethanesulfoxypentane, 1,3-dimethanesulfoxypentane,1,4-dimethanesulfoxypentane,1,5-dimethanesulfoxypentane, 1,2-diethanesulfoxyethane, 1,2-diethanesulfoxypropane, 1,3-diethanesulfoxypropane, 1,2-diethanesulfoxybutane, 1,3-diethanesulfoxybutane,1,4-diethanesulfoxybutane, 1,2-diethanesulfoxypentane, 1,3-diethanesulfoxypentane,1,4-diethanesulfoxypentane,1,5-diethanesulfoxypentane, 1,2-dibenzenesulfoxyethane, 1,2-dibenzenesulfoxypropane, 1,3-dibenzenesulfoxypropane, 1,2-dibenzenesulfoxybutane, 1,3-dibenzenesulfoxybutane,1,4-dibenzenesulfoxybutane, 1,2-dibenzenesulfoxypentane, 1,3-dibenzenesulfoxypentane,1,4-dibenzenesulfoxypentane,1,5-dibenzenesulfoxypentane, 1,2-di-p-toluenesulfoxyethane, 1,2-di-p-toluenesulfoxypropane, 1,3-di-p-toluenesulfoxypropane, 1,2-di-p-toluenesulfoxybutane, 1,3-di-p-toluenesulfoxybutane,1,4-di-p-toluenesulfoxybutane, 1,2-di-p-toluenesulfoxypentane, 1,3-di-p-toluene sulfoxypentane,1,4-di-p-toluene sulfoxypentane, and1,5-di-p-toluene sulfoxypentane.

[00242] In some embodiments, the polymeric backbone is formed from one or more substituted or unsubstituted monomers selected from ethylene, propylene, hydroxyethylene, acetaldehyde, styrene, divinyl benzene, isocyanates, vinyl chloride, vinyl phenols, tetrafluoroethylene, butylene, terephthalic acid, caprolactam, acrylonitrile, butadiene, ammonias, diammonias, pyrrole, imidazole, pyrazole, oxazole, thiazole, pyridine, pyrimidine, pyrazine, pyradizimine, thiazine, morpholine, piperidine, piperizines, pyrollizine, triphenylphosphonate, trimethylphosphonate, triethylphosphonate, tripropylphosphonate, tributylphosphonate,

trichlorophosphonate, trifluorophosphonate, and diazole, where the terms unsubstituted and substituted have the meanings as disclosed herein.

[00243] The polymer catalysts described herein can form solid particles. One of skill in the art would recognize the various known techniques and methods to make solid particles from the polymers described herein. For example, a solid particle can be formed through the procedures of emulsion or dispersion polymerization, which are known to one of skill in the art. In other embodiments, the solid particles can be formed by grinding or breaking the polymer into particles, which are also techniques and methods that are known to one of skill in the art. Methods known in the art to prepare solid particles include coating the polymers described herein on the surface of a solid core. Suitable materials for the solid core can include an inert material (e.g., aluminum oxide, corn cob, crushed glass, chipped plastic, pumice, silicon carbide, or walnut shell) or a magnetic material. Polymeric coated core particles can be made by dispersion polymerization to grow a cross-linked polymer shell around the core material, or by spray coating or melting.

[00244] Other methods known in the art to prepare solid particles include coating the polymers described herein on the surface of a solid core. The solid core can be a non-catalytic support. Suitable materials for the solid core can include an inert material (*e.g.*, aluminum oxide, corn cob, crushed glass, chipped plastic, pumice, silicon carbide, or walnut shell) or a magnetic material. In one embodiment of the polymer catalyst, the solid core is made up of iron. Polymeric coated core particles can be made by techniques and methods that are known to one of skill in the art, for example, by dispersion polymerization to grow a cross-linked polymer shell around the core material, or by spray coating or melting.

[00245] The solid supported polymer catalyst particle can have a solid core where the polymer is coated on the surface of the solid core. In some embodiments, at least about 5%, at least about 10%, at least about 20%, at least about 30%, at least about 40%, or at least about 50% of the catalytic activity of the solid particle can be present on or near the exterior surface of the solid particle. In some embodiments, the solid core can have an inert material or a magnetic material. In one embodiment, the solid core is made up of iron.

[00246] The solid particles coated with the polymer described herein have one or more catalytic properties. In some embodiments, at least about 50%, at least about 60%, at least about

70%, at least about 80% or at least about 90% of the catalytic activity of the solid particle is present on or near the exterior surface of the solid particle.

[00247] In some embodiments, the solid particle is substantially free of pores, for example, having no more than about 50%, no more than about 40%, no more than about 30%, no more than about 20%, no more than about 15%, no more than about 10%, no more than about 5%, or no more than about 1% of pores. Porosity can be measured by methods well known in the art, such as determining the Brunauer-Emmett-Teller (BET) surface area using the absorption of nitrogen gas on the internal and external surfaces of a material (Brunauer, S. et al., J. Am. Chem. Soc. 1938, 60:309). Other methods include measuring solvent retention by exposing the material to a suitable solvent (such as water), then removing it thermally to measure the volume of interior pores. Other solvents suitable for porosity measurement of the polymer catalysts include, but are not limited to, polar solvents such as DMF, DMSO, acetone, and alcohols.

[00248] In other embodiments, the solid particles include a microporous gel resin. In yet other embodiments, the solid particles include a macroporous gel resin.

[00249] In other embodiments, the solid particle having the polymer coating has at least one catalytic property selected from:

a) disruption of at least one hydrogen bond in cellulosic materials;

b) intercalation of the polymer into crystalline domains of cellulosic materials; and

c) cleavage of at least one glycosidic bond in cellulosic materials.

[00250] In some embodiments, the polymer can include a support and a plurality of acidic moieties and cationic moieties attached to the support. In certain embodiments, the support is selected from biochar, carbon, amorphous carbon, activated carbon, silica, silica gel, alumina, magnesia, titania, zirconia, clays (e.g., kaolinite), magnesium silicate, silicon carbide, zeolites (e.g., mordenite), ceramics, and any combinations thereof. In one embodiment, the material is carbon. The material for carbon support can be biochar, amorphous carbon, or activated carbon. In one embodiment, the material is activated carbon.

[00251] In certain embodiments, the acidic groups on the acidic moiety are selected from sulfonic acid, phosphonic acid, acetic acid, isophthalic acid, and boronic acid. In certain embodiments, the ionic groups on the ionic moiety are selected from pyrrolium, imidazolium, pyrazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, pyrazinium, pyradizimium,

thiazinium, morpholinium, piperidinium, piperizinium, and pyrollizinium, phosphonium, trimethyl phosphonium, triethyl phosphonium, tripropyl phosphonium, tributyl phosphonium, trichloro phosphonium, triphenyl phosphonium and trifluoro phosphonium.

[00252] In some embodiments of the solid-supported catalyst where the Bronsted-Lowry acid is attached to the solid support by a linker, each linker is independently selected from unsubstituted or substituted alkylene, unsubstituted or substituted cycloalkylene, unsubstituted or substituted alkenylene, unsubstituted or substituted arylene, or unsubstituted or substituted heteroarylene, where the substituents are those as defined herein. In certain embodiments of the solid-supported catalyst, the linker is unsubstituted or substituted arylene, unsubstituted or substituted heteroarylene. In certain embodiments of the solid-supported catalyst, the linker is unsubstituted or substituted arylene. In one embodiment of the solid-supported catalyst, the linker is phenylene. In another embodiment of the solid-supported catalyst, the linker is hydroxyl-substituted phenylene.

[00253] In some embodiments of the solid-supported catalyst, each Bronsted-Lowry acid is directly attached to the solid support. In other embodiments of the solid-supported catalyst, the acidic moieties each further include a linker attaching the Bronsted-Lowry acid to the solid support. In certain embodiments of the solid-supported catalyst, some of the Bronsted-Lowry acids are directly connected to the solid support, while other Bronsted-Lowry acids are attached to the solid support by a linker.

[00254] The carbon support can have a surface area from 0.01 to 50 m^2/g of dry material. The carbon support can have a density from 0.5 to 2.5 kg/L. The support can be characterized using any suitable instrumental analysis methods or techniques known in the art, including for example scanning electron microscopy (SEM), powder X-ray diffraction (XRD), Raman spectroscopy, and Fourier Transform infrared spectroscopy (FTIR). The carbon support can be prepared from carbonaceous materials, including for example, shrimp shell, chitin, coconut shell, wood pulp, paper pulp, cotton, cellulose, hard wood, soft wood, wheat straw, sugarcane bagasse, cassava stem, corn stover, oil palm residue, bitumen, asphaltum, tar, coal, pitch, and any combinations thereof. One of skill in the art would recognize suitable methods to prepare the carbon supports used herein. *See, e.g.*, M. Inagaki, L.R. Radovic, *Carbon,* vol. 40, p. 2263 (2002), or A.G. Pandolfo and A.F. Hollenkamp, "Review: Carbon Properties and their role in supercapacitors," *Journal of Power Sources*, vol. 157, pp. 11-27 (2006).

[00255] In other embodiments, the material is silica, silica gel, alumina, or silica-alumina. One of skill in the art would recognize suitable methods to prepare these silica- or alumina-based solid supports used herein. *See, e.g.*, Catalyst supports and supported catalysts, by A.B. Stiles, Butterworth Publishers, Stoneham MA, 1987.

[00256] In yet other embodiments, the material is a combination of a carbon support, with one or more other supports selected from silica, silica gel, alumina, magnesia, titania, zirconia, clays (*e.g.*, kaolinite), magnesium silicate, silicon carbide, zeolites (*e.g.*, mordenite), and ceramics.

[00257] Polymer catalysts can be advantageous over other catalysts known in the art used for hydrolysis due to, for example, ease of handling. The solid nature of the catalysts can provide for ease of recycling (*e.g.*, by filtering the catalyst), without requiring distillation or extraction methods. For example, the density and size of the particle can be selected such that the catalyst particles can be separated from the materials used in a process for the break-down of biomaterials. Particles can be selected based on sedimentation rate, *e.g.*, relative to materials used or produced in a reaction mixture, particle density, or particle size. Alternatively, in some embodiments, solid particles coated with the catalysts that have a magnetically active core can be recovered by electromagnetic methods known to one of skill in the art.

[00258] The catalysts described herein have one or more catalytic properties. As used herein, a "catalytic property" of a material is a physical and/or chemical property that increases the rate and/or extent of a reaction involving the material. The catalytic properties can include at least one of the following properties: a) disruption of a hydrogen bond in cellulosic materials; b) intercalation of the catalyst into crystalline domains of cellulosic materials; and c) cleavage of a glycosidic bond in cellulosic materials. In other embodiments, the catalysts that have two or more of the catalytic properties described above, or all three of the catalytic properties described above.

[00259] In certain embodiments, the catalysts described herein have the ability to catalyze a chemical reaction by donation of a proton, and can be regenerated during the reaction process. In other embodiments, the catalysts described herein have a greater specificity for cleavage of a glycosidic bond than dehydration of a monosaccharide.

[00260] Provided herein are also compositions involving the catalysts that can be used in a variety of methods described herein, including the break-down of cellulosic material.

[00261] In one aspect, provided are compositions that include biomass and the catalysts described herein. In some embodiments, the composition can include biomass and an effective amount of a catalyst as described herein. In some embodiments, the composition further includes a solvent (*e.g.*, water). In some embodiments, the biomass includes cellulose, hemicellulose, or a combination thereof.

[00262] In yet another aspect, provided are compositions that include the catalysts described herein, one or more sugars, and residual biomass. In some embodiments, the one or more sugars are one or more monosaccharides, one or more oligosaccharides, or a mixture thereof. In certain embodiments, the one or more sugars are two or more sugars including at least one C4-C6 monosaccharide and at least one oligosaccharide. In one embodiment, the one or more sugars are selected from glucose, galactose, fructose, xylose, and arabinose.

[00263] Provided is also a chemically-hydrolyzed biomass composition that includes any of the catalysts described herein, one or more sugars, and residual biomass. In some embodiments, the one or more sugars are one or more monosaccharides, one or more oligosaccharides, or a mixture thereof. In other embodiments, the one or more sugars are two or more sugars that include at least one C4-C6 monosaccharide and at least one oligosaccharide. In yet other embodiments, the one or more sugars are selected from glucose, galactose, fructose, xylose, and arabinose.

[00264] Provided is also a saccharification intermediate that includes any of the catalysts described herein hydrogen-bonded to the biomass. In certain embodimemts of the saccharification intermediate, the ionic monomer or moiety of the catalyst is hydrogen-bonded to the carbohydrate alcohol groups present in cellulose, hemicellulose, and other oxygen-containing components of feedstock. In certain embodiments of the saccharification intermediate, the acidic monomer or moiety of the catalyst is hydrogen-bonded to the carbohydrate alcohol groups present in cellulose, hemicellulose, and other oxygen-containing components of lignocellulose present in the biomass, including the glycosidic linkages between sugar monomers. In some embodiments, the biomass has cellulose, hemicellulose or a combination thereof.

c) Saccharification conditions

[00265] The methods provided herein involve contacting the cellulosic material with a polymer catalyst under conditions sufficient to hydrolyze at least a portion of the cellulosic

material into sugars. In some embodiments, the cellulosic material can be contacted with the polymer catalyst in the presence of a solvent.

[00266] Further, it should be understood that any method known in the art that includes pretreatment, enzymatic hydrolysis (saccharification), fermentation, or a combination thereof, can be used with the catalysts in the methods described herein. The catalysts can be used before or after pretreatment methods to make the cellulose (and hemicellulose, where present) in the biomass more accessible to hydrolysis

[00267] The methods described can be performed in stirred-tank reactors or vessels under controlled pH, temperature, and mixing conditions. One skilled in the art would recognize that suitable processing time, temperature and pH conditions can vary depending on the amount and the nature of the cellulosic material. These factors are described in further detail below.

Solvent

[00268] In certain embodiments, the cellulosic material is contacted with the polymer catalyst in an aqueous environment. One suitable aqueous solvent is water, which can be obtained from various sources. Generally, water sources with lower concentrations of ionic species are preferable, as such ionic species can reduce effectiveness of the polymer catalyst. In some embodiments where the aqueous solvent is water, the water has less than 10% of ionic species (*e.g.*, salts of sodium, phosphorous, ammonium, magnesium, or other species found naturally in lignocellulosic biomass).

[00269] Moreover, in embodiments where the cellulosic material is hydrolyzed into sugars, water is consumed on a mole-for-mole basis with the sugars produced. In certain embodiments, the methods described herein can further include monitoring the amount of water present in the reaction and/or the ratio of water to cellulosic material over a period of time. In other embodiments, the methods described herein can further include supplying water directly to the reaction, for example, in the form of steam or steam condensate. For example, in some embodiments, the hydration conditions in the reactor is such that the water-to-cellulosic material ratio is is about 5:1, about 4:1, about 3:1, about 2:1, about 1:1, about 1:2, about 1:3, about 1:4, about 1:5, or less than about 1:5. It should be understood, however, that the ratio of water to cellulosic material can be adjusted based on the specific polymer catalyst used.

Processing time, temperature and pH conditions

[00270] In some embodiments, the cellulosic material can be in contact with the polymer catalyst for up to about 200 hours. In other embodiments, the feedstock can be in contact with the catalyst from about 1 to about 96 hours, from about 12 to about 72 hours, or from about 12 to about 48 hours.

[00271] In some embodiments, the feedstock can be in contact with the polymer at temperature in the range of about 25°C to about 150°C. In other embodiments, the feedstock can be in contact with the polymer in the range of about 30°C to about 125°C, about 30°C to about 140°C, about 80°C to about 120°C, about 80°C to about 130°C, about 100°C to 110°C, or about 100°C to about 130°C.

[00272] The pH is generally affected by the intrinsic properties of the polymer catalyst used. In some embodiments, the acidic moiety of the polymer catalyst can affect the pH of the reaction to degrade the cellulosic material. For example, the use of sulfuric acid moiety in a polymer catalyst results in a reaction pH of about 3. In other embodiments, a pH between about 0 and about 6 is used to degrade the cellulosic material. The reacted effluent typically has a pH of at least about 4, or a pH that is compatible with other processes such as enzymatic treatment. It should be understood, however, that the pH can be modified and controlled by the addition of acids, bases or buffers.

[00273] Moreover, the pH can vary within the reactor. For example, high acidity at or near the surface of the catalyst can be observed, whereas regions distal to the catalyst surface can have a substantially neutral pH. Thus, one of skill would recognize that determination of the solution pH should account for such spatial variation.

[00274] It should also be understood that, in certain embodiments, the methods described herein to degrade the cellulosic material can further include monitoring the reaction pH, and optionally adjusting the pH within the reactor. In some instances, as a low pH in solution can indicate an unstable polymer catalyst, in which the catalyst can be losing at least a portion of its acidic groups to the surrounding environment through leaching. In some embodiments, the pH near the surface of the polymer catalyst is below about 7, below about 6, or below about 5.

Amount and nature of the cellulosic material used

[00275] The amount of the cellulosic material used in the methods described herein relative to the amount solvent used can affect the rate of reaction and yield. The amount of the cellulosic material used can be characterized by the dry solids content. In certain embodiments, dry solids content refers to the total solids of a slurry as a percentage on a dry weight basis. In some embodiments, the dry solids content of the cellulosic materials is between about 5 wt% to about 95 wt %, between about 10 wt% to about 80 wt %, between about 15 wt % to about 75 wt %, or between about 15 wt % to about 50 wt %.

Amount of polymer catalyst used

[00276] The amount of the polymer catalysts used in the methods described herein can depend on several factors including, for example, type and composition of the cellulosic material used and the reaction conditions (*e.g.*, temperature, time, and pH). In one embodiment, the weight ratio of the polymer catalyst to the cellulosic material is about 0.1g/g to about 50 g/g, about 0.1g/g to about 25 g/g, about 0.1 g/g to about 10 g/g, about 0.1 g/g to about 5 g/g, about 0.1 g/g to about 2 g/g, about 0.1 g/g to about 1 g/g, or about 0.1 to about 0.75 g/g.

Batch versus continuous processing

[00277] Generally, the polymer catalyst and the cellulosic material are introduced into an interior chamber of a reactor, either concurrently or sequentially. The reaction can be performed in a batch process or a continuous process. For example, in one embodiment, the reaction is performed in a batch process, where the contents of the reactor are continuously mixed or blended, and all or a substantial amount of the products of the reaction are removed. In one variation, the reaction is performed in a batch process, where the contents of the reactor are initially intermingled or mixed but no further physical mixing is performed. In another variation, the reaction is performed in a batch process, wherein once further mixing of the contents, or periodic mixing of the contents of the reactor, is performed (*e.g.*, at one or more times per hour), all or a substantial amount of the products of the reaction are removed after a certain period of time.

[00278] In other embodiments, the reaction is performed in a continuous process, where the contents flow through the reactor with an average continuous flow rate but with no explicit mixing. After introduction of the polymer catalyst and the cellulosic material into the reactor,

the contents of the reactor are continuously or periodically mixed or blended, and after a period of time, less than all of the products of the reaction are removed. In one variation, the reaction is performed in a continuous process, where the mixture containing the catalyst and cellulosic material is not actively mixed. Additionally, mixing of catalyst and the cellulosic material can occur as a result of the redistribution of polymer catalysts settling by gravity, or the non-active mixing that occurs as the material flows through a continuous reactor.

Reactors

[00279] The reactors used for the methods described herein can be open or closed reactors suitable for use in containing the chemical reactions described herein. Suitable reactors can include, for example, a fed-batch stirred reactor, a batch stirred reactor, a continuous flow stirred reactor with ultrafiltration, a continuous plug-flow column reactor, an attrition reactor, or a reactor with intensive stirring induced by an electromagnetic field. *See e.g.*, Fernanda de Castilhos Corazza, Flavio Faria de Moraes, Gisella Maria Zanin and Ivo Neitzel, Optimal control in fed-batch reactor for the cellobiose hydrolysis, *Acta Scientiarum. Technology*, 25: 33-38 (2003); Gusakov, A. V., and Sinitsyn, A. P., Kinetics of the enzymatic hydrolysis of cellulose: 1. A mathematical model for a batch reactor process, *Enz. Microb. Technol.*, 7: 346-352 (1985); Ryu, S. K., and Lee, J. M., Bioconversion of waste cellulose by using an attrition bioreactor, Biotechnol. Bioeng. 25: 53-65(1983); Gusakov, A. V., Sinitsyn, A. P., Davydkin, I. Y., Davydkin, V. Y., Protas, O. V., Enhancement of enzymatic cellulose hydrolysis using a novel type of bioreactor with intensive stirring induced by electromagnetic field, *Appl. Biochem. Biotechnol.*, 56: 141-153(1996). Other suitable reactor types can include, for example, fluidized bed, upflow blanket, immobilized, and extruder type reactors for hydrolysis and/or fermentation.

[00280] In certain embodiments where the reaction is performed as a continuous process, the reactor can include a continuous mixer, such as a screw mixer. The reactors can be generally fabricated from materials that are capable of withstanding the physical and chemical forces exerted during the processes described herein. In some embodiments, such materials used for the reactor are capable of tolerating high concentrations of strong liquid acids; however, in other embodiments, such materials can not be resistant to strong acids.

[00281] At the start of the hydrolysis on larger scale, the reactor can be filled with cellulosic material by a top-load feeder containing a hopper capable of holding cellulosic material. Further, the reactor typically contains an outlet means for removal of contents (e.g., a sugar-containing

solution) from the reactor. Optionally, such outlet means is connected to a device capable of processing the contents removed from the reactor. Alternatively, the removed contents are stored. In some embodiments, the outlet means of the reactor is linked to a continuous incubator into which the reacted contents are introduced. Further, the outlet means provides for removal of residual cellulosic material by, e.g., a screw feeder, by gravity, or a low shear screw.

[00282] It should also be understood that additional cellulosic material and/or catalyst can be added to the reactor, either at the same time or one after the other.

Recovery of sugars

[00283] In some embodiments, the methods described herein further include recovering the sugars that are produced from the hydrolysis of the cellulosic material. In another embodiment, the method for degrading cellulosic material using the polymer catalyst described herein further includes recovering the degraded or converted cellulosic material.

[00284] The sugars, which are typically soluble, can be separated from the insoluble residual cellulosic material using technology well known in the art such as, for example, centrifugation, filtration, and gravity settling.

[00285] Separation of the sugars can be performed in the hydrolysis reactor or in a separator vessel. In an exemplary embodiment, the method for degrading cellulosic material is performed in a system with a hydrolysis reactor and a separator vessel. Reactor effluent containing the monosaccharides and/or oligosaccharides is transferred into a separator vessel and is washed with a solvent (*e.g.*, water), by adding the solvent into the separator vessel and then separating the solvent in a continuous centrifuge. Alternatively, in another exemplary embodiment, a reactor effluent containing residual solids (*e.g.*, residual cellulosic materials) is removed from the reactor vessel and washed, for example, by conveying the solids on a porous base (*e.g.*, a mesh belt) through a solvent (*e.g.*, water) wash stream. Following contact of the stream with the reacted solids, a liquid phase containing the monosaccharides and/or oligosaccharides is generated. Optionally, residual solids can be separated by a cyclone. Suitable types of cyclones used for the separation can include, for example, tangential cyclones, spark and rotary separators, and axial and multi-cyclone units.

[00286] In another embodiment, separation of the sugars is performed by batch or continuous differential sedimentation. Reactor effluent is transferred to a separation vessel, optionally

combined with water and/or enzymes for further treatment of the effluent. Over a period of time, solid biomaterials (*e.g.*, residual treated biomass), the solid catalyst, and the sugar-containing aqueous material can be separated by differential sedimentation into a plurality of phases (or layers). Generally, the catalyst layer can sediment to the bottom, and depending on the density of the residual biomass, the biomass phase can be on top of, or below, the aqueous phase. When the phase separation is performed in a batch mode, the phases are sequentially removed, either from the top of the vessel or an outlet at the bottom of the vessel. When the phase separation is performed in a continuous mode, the separation vessel contains one or more than one outlet means (*e.g.*, two, three, four, or more than four), generally located at different vertical planes on a lateral wall of the separation vessel, such that one, two, or three phases are removed from the vessel. The removed phases are transferred to subsequent vessels or other storage means. By these processes, one of skill in the art would be able to capture (1) the catalyst layer and the aqueous layer or biomass layer separately, or (2) the catalyst, aqueous, and biomass layers separately, allowing efficient catalyst recycling, retreatment of biomass, and separation of sugars. Moreover, controlling rate of phase removal and other parameters allows for increased efficiency of catalyst recovery. Subsequent to removal of each of the separated phases, the catalyst and/or biomass can be separately washed by the aqueous layer to remove adhered sugar molecules.

[00287] The sugars isolated from the vessel can be subjected to further processing steps (*e.g.*, as drying, fermentation) to produce biofuels and other bio-products. In some embodiments, the monosaccharides that are isolated can be at least about 1% pure, at least about 5% pure, at least about 10% pure, at least about 20% pure, at least about 40% pure, at least about 60% pure, at least about 80% pure, at least about 90% pure, at least about 95% pure, at least about 99% pure, or greater than 99% pure, as determined by analytical procedures known in the art, such as determination by high performance liquid chromatography (HPLC), functionalization and analysis by gas chromatography, mass spectrometry, spectrophotometric procedures based on chromophore complexation and/or carbohydrate oxidation-reduction chemistry.

[00288] The residual biomass isolated from the vessels can be useful as a combustion fuel or as a feed source of non-human animals such as livestock.

Rate and Yield

[00289] The use of the polymer catalysts described herein can increase the rate and/or yield of saccharification. The ability of the polymer catalyst to hydrolyze the cellulose and hemicellulose components of the cellulosic material to soluble sugars can be measured by determining the effective first-order rate constant,

$$\boldsymbol{k_1(\text{species } i) = -\frac{\ln(1 - X_i)}{\Delta t}},$$

where Δt is the duration of the reaction and X_i is the extent of reaction for species i (*e.g.*, glucan, xylan, arabinan). In some embodiments, the polymer catalysts described herein are capable of degrading the cellulosic material into one or more sugars at a first-order rate constant of at least about 0.001 per hour, at least about 0.01 per hour, at least about 0.1 per hour, at least about 0.2 per hour, at least about 0.3 per hour, at least about 0.4 per hour, at least about 0.5 per hour, or at least about 0.6 per hour.

[00290] The hydrolysis yield of the cellulose and hemicellulose components of the cellulosic material to soluble sugars by the polymer catalyst can be measured by determining the degree of polymerization of the residual cellulosic material. The lower the degree of polymerization of the residual cellulosic material, the greater the hydrolysis yield. In some embodiments, the polymer catalysts described herein are capable of converting cellulosic material into one or more sugars and residual cellulosic material, wherein the residual cellulosic material has a degree of polymerization of less than about 300, less than about 250, less than about 200, less than about 150, less than about 100, less than about 90, less than about 80, less than about 70, less than about 60, or less than about 50.

Recovery of the polymer catalysts

[00291] The catalysts used for saccharification of biomass can be recovered and reused. Sedimentation of the catalyst is used to recover the catalyst following use. In some embodiments, the catalyst can sink, while other residuals solids can remain suspended in the saccharification reaction mixture.

[00292] The sedimentation rate can be measured by the sedimentation coefficient,

$$s = \frac{mv}{F}$$

where m is the mass of the particle, v is its sinking velocity (terminal velocity of the sinking particle in the selected solvent), and F is the force applied to cause the sinking. For gravity sedimentation, F = mg, and

$$s = \frac{v}{g}$$

where g is the acceleration due to gravity.

[00293] For simple gravimetric sedimentation in water, the sedimentation rate of the catalyst can, in some embodiments, be about 10^{-6}-10^{-2}, about 10^{-5}-10^{-3}, or about 10^{-4}-10^{-3}.

[00294] The density of the catalyst can also have an impact on its ease of recovery from saccharification. In some embodiments, the gravimetric density of the catalyst is about 0.5-3.0 kg/L, about 1.0-3.0 kg/L, or about 1.1-3.0 kg/L. One of skill in the art would recognize that various methods and techniques suitable for measuring the density of a catalyst as described herein.

d) Saccharide composition

[00295] The polymer catalysts described above can be used to degrade cellulosic materials into a saccharide composition, or a mixture of two or more saccharide compositions.. The saccharide composition can be in the form of a hydrolysate, produced from the hydrolysis of the cellulosic materials. In some embodiments, the saccharide compositions can be separated by techniques well known in the art, such as chromatographic methods. Any method of degrading cellulosic material or biomass as disclosed herein should be understood by the skilled artisan to represent a method that can also produce two or more saccharide compositions.

[00296] Saccharification refers to the hydrolysis of cellulosic materials (*e.g.*, biomass) into one or more saccharides (or sugars), by breaking down the complex carbohydrates of cellulose (and hemicellulose, where present) in the biomass. The one or more sugars can be monosaccharides and/or oligosaccharides. As used herein, "oligosaccharide" refers to a compound containing two or more monosaccharide units linked by glycosidic bonds. In certain embodiments, the one or more sugars are selected from glucose, cellobiose, xylose, xylulose, arabinose, mannose and galactose.

[00297] It should be understood that the cellulosic material can be subjected to a one-step or a multi-step hydrolysis process. For example, in some embodiments, the cellulosic material is first contacted with the polymer catalyst, and then the resulting product is contacted with one or more enzymes in a second hydrolysis reaction (*e.g.*, using enzymes).

[00298] In some embodiments, the saccharide composition includes at least one C5 saccharide and at least one C6 saccharide. A "C5 saccharide" refers to a five-carbon sugar (or pentose), where as a "C6 saccharide" refers to a six-carbon sugar (or hexose). Examples of C5 saccharides include arabinose, lyxose, ribose, xylose, ribulose, and xylulose. Examples of C6 saccharides include allose, altrose, glucose, mannose, gulose, idose, galactose, talose, psicose, fructose, sorbose and tagatose. These saccharides can have chiral centers, and in some embodiments, the saccharide composition can include C5 saccharides and/or C6 saccharides that can be present as either the D- or L-isomer. In other embodiments, the saccharide composition can include a racemic mixture of the C5 saccharides and/or C6 saccharides.

[00299] In certain embodiments, the saccharide composition includes at least one C5 saccharide and the at least one C6 saccharide are present in the saccharide composition in a ratio suitable for fermentation to produce the ethylene glycol compound. In another embodiment, the saccharide composition includes at least one C5 saccharide and the at least one C6 saccharide are present in the saccharide composition in a ratio suitable for fermentation to produce one or more precursor compounds of propylene, such as, but not limited to, ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. Also, glucose or fructose liberated from biomass can be used to produce these compounds, all of which can serve as precursors for polypropylene. In one embodiment, the saccharide composition includes two C5 saccharides and one C6 saccharide present in a ratio suitable for fermentation to produce one or more components suitable for use in a bio-based polymer. The ratio of the C5 and C6 saccharides can be further suitable to feed the fermentation host producing the ethylene glycol compound or one or more compounds that can be transformed into propylene.

[00300] For example, in one embodiment where the saccharide composition includes xylose, glucose and arabinose. In such an embodiment, the xylose, glucose and arabinose can be present in a ratio of at least about 5 to about 1 to about 1, at least about 10 to about 1 to about 1, at least about 15 to about 1 to about 1, at least about 20 to about 1 to about 1. In one embodiment, the xylose, glucose and arabinose is present in a ratio of about 20 to about 1 to about 1. The ratio of the sugars present can be optimized for conversion into the component of the bio-based polymer

(*e.g.*, ethylene glycol), while the glucose and arabinose present can be consumed by the fermentation host producing the component of the bio-based polymer (*e.g.*, ethylene glycol). Thus, in certain embodiments, an exogenous source of sugar can not be needed to feed the fermentation host.

[00301] It should be understood that the ratio of the C5 and C6 saccharides present in saccharide composition can be varied based on the reaction conditions described above in degrading cellulosic materials. Further, it should be understood that the optimal ratio of the saccharides can vary depending the types of saccharides, the component of the bio-based polymer produced by fermentation, and the type of fermentation host used.

[00302] In other embodiments, the saccharide composition has a concentration suitable for fermentation without prior concentration (*e.g.*, by evaporation). It should also be understood that the saccharide composition can vary based on the type of cellulosic material used, as well as the reaction conditions described above in degrading cellulosic material.

[00303] The one or more sugars obtained from hydrolysis of cellulosic material can be used in a subsequent fermentation process to produce biofuels (*e.g.*, ethanol) and other bio-based chemicals (*e.g.*, bio-based polymers). For example, in some embodiments, the one or more sugars obtained by the methods described herein can undergo subsequent bacterial or yeast fermentation to produce biofuels and other bio-based chemicals. In certain embodiments, a given ratio and concentration of sugars present in the saccharide composition can be varied depending on the fermentation host.

Fermentation of the Saccharide Composition

[00304] The saccharide composition obtained from hydrolysis of cellulosic material can be used in downstream processes to produce biofuels and other bio-based chemicals. In one embodiment, the saccharide composition obtained from hydrolysis of cellulosic material can be used to produce bio-based polymers, or component(s) thereof. In other embodiments, the saccharide composition obtained from hydrolysis of cellulosic material using the polymer catalyst described herein can be fermented to produce one or more downstream products (*e.g.*, ethanol and other biofuels, vitamins, lipids, proteins).

a) Fermentation product mixture

[00305] The saccharide composition can undergo fermentation to produce one or more difunctional compounds. Such difunctional compounds can have an N-carbon chain, with a first functional group and a second functional group. In some embodiments, the first and second functional groups can be independent selected from –OH, -NH_2, -COH, and –COOH.

[00306] The difunctional compounds can be alcohols, carboxylic acids, hydroxyacids, or amines. Exemplary difunctional alcohols can include ethylene glycol, 1,3-propanediol, and 1,4-butanediol. Exemplary difunctional carboxylic acids can include succinic acid, adipic acid, and pimelic acid. Exemplary difunctional hydroxyacids can include glycolic acid, and 3-hydroxypropanoic acid. Exemplary difunctional amines can include 1,4-diaminobutane, 1,5-diaminopentane, and 1,6-diaminohexane.

[00307] In some embodiments, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that can have ethylene glycol, succinic acid, adipic acid, or butanediol, or a combination thereof. In one embodiment, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that has ethylene glycol. In certain embodiments, the ethylene glycol compound can be monoethylene glycol, diethylene glycol, and polyethylene glycol. In one embodiment, the ethylene glycol compound is monoethylene glycol. The ethylene glycol compound can be suitable for use in a polymer that is recyclable, at least partially bio-degradable, or a combination thereof.

[00308] In some embodiments, the difunctional compounds can be isolated from the fermentation product mixture, and/or further purified. Any suitable isolation and purification techniques known in the art can be used.

[00309] In some embodiments, the methods described herein include converting saccharide compositions chemically, by fermentation or a combination thereof, into intermediate compounds (e.g., D-xylulose, D-xylulose-5-phosphate, D-ribulose-5-phosphate, D-ribulose, D-ribulose-1-phosphate, glycolaldehyde, and DHAP) and subsequently converting such intermediate compounds into ethylene glycol, directly or through additional intermediate compounds.

[00310] In some embodiments, the methods described herein include converting saccharide compositions chemically, by fermentation or a combination thereof, into intermediate compounds (e.g., glyceraldehyde, 2-phosphoglycerate, 3-phosphoglycerate, glycerate, serine, hydroxypyruvate, ethanolamine, or glycolaldehyde), and subsequently converting such intermediate compounds into ethylene glycol, directly or through additional intermediate compounds. *See, e.g.,* US2011/0312049. Glucose directly forms 3-phosphoglycerate, which is coverted by oxidation to 3-phosphohydroxypyruvate. 3-phosphohydroxypyruvate is transaminated with glutamate to form 3-phosphoserine, which is in turn hydrolyzed (*e.g.,* by a serine phosphatase) to serine.

[00311] In other embodiments, the saccharide composition can undergo fermentation to produce one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. All of these compounds can be transformed to propylene via chemical or further fermentation.

[00312] In some embodiments, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that can include ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a combination thereof. In one embodiment, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that has lactic acid or 1,2-propanediol. In one embodiment, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that has either or both of 1-propanol and 2-propanol. In one embodiment, the methods described herein include combining the saccharide composition with a fermentation host to produce a fermentation product mixture that has either or both of 1-butanol and 2-butanol. The one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol can be suitable for use in a polymer that is recyclable, at least partially bio-degradable, or a combination thereof.

[00313] In some embodiments, the methods described herein include converting saccharide compositions chemically, by fermentation or a combination thereof, into intermediate compounds, including, but not limited to, β-D-glucose-6-phosphate, 2-dihydroxyacetone (DHAP), glycoaldehyde, D-xylose-5-phosphate, D-ribulose-5-phosphate, L-ribulose-5-phosphate, D-ribulose-1-phosphate, methylglyoxal, acetol, 1,2-propanediol, propanal, 1-propanol, propanoyl-CoA, propanoyl phosphate, propanoate, L-lactaldehyde, L-lactic acid,

glycerol-1-phosphate, glycerol, dihydroxyacetone, 3-hydroxypropionaldehyde, 3-hydroxypropianate, and 1,3 propanediol. These intermediates can be converted directly to propylene or through other intermediate compounds.

[00314] In one embodiment, β-D-glucose-6-phosphate is formed from either β-D-glucose or β-D-galactose, then undergoes glycolysis to produce DHAP. D-Xylose can also be be transformed to to DHAP through a pathway that includes D-xylose-5-phosphate and D-ribulose-1-phosphate. D- and L-arabinose can lead to DHAP via a route that includes transformation to the corresponding ribulose followed by phosphorylation.

[00315] In turn, DHAP can be converted through a pathway including methylglyoxal, acetol to provide 1,2-propane diol. This diol can be fermented to produce propanal and then 1-propanol. 1-Propanol can be convered into propylene via dehydration techniques well know in the art. 1,2-Propanediol can also be transformed to propanoate using a pathway that includes propanal and propanal-CoA. 1,2-Propane diol can be converted to L-lactaldehyde leading to L-lactic acid. In another embodiment, DHAP can be converted to either glycerol-1-phosphate or dihydroxyacetone, then to glycerol. Glycerol can be fermented to 3-hydroxypropionaldehyde, which can lead to 3-hydroxypropionate and 1,3-propane diol.

b) Fermentation Host

[00316] The fermentation hosts can include wild type microorganisms or recombinant microorganisms, *e.g.,* biocatalyts. Biocatalysts can be microorganisms selected from bacteria, filamentous fungi and yeast. Biocatalysts can be wild type microorganisms or recombinant microorganisms, and include *Escherichia, Zymomonas, Saccharomyces, Candida, Pichia, Streptomyces, Bacillus, Lactobacillus, and Clostridium.* In another embodiment, biocatalysts can be selected from recombinant *Escherichia coli, Zymomonas mobilis, Bacillus stearothermophilus, Saccharomyces cerevisiae, Clostridia thermocellum, Thermoanaerobacterium saccharolyticum, and Pichia stipites.* In some embodiments, the recombinant biocatalysts can be selected from *Escherichia, Homo, Salmonella, Saccharomyces, Clostridium, Citrobacter, Pseudomonas, Bacillus, Caulobacter, Synechocystis, Arabidopsis, Azopirillum, Sulfolobus, Sphingomonas, Corynebacterium, Methanothermobacter, Schizosaccharomyces, and Klebsiella.* In some embodiments, the wild type microorganisms or recombinant microorganisms can be selected from *Escherichia coli, Homo sapiens, Salmonella enterica, Saccharomyces cerevisiae, Clostridium butyricum, Citrobacter freundii Clostridium*

pasteurianum, Pseudomonas putida, Bacillus coagulans, Caulobacter cescentus, Synechocystis sp. PCC 6803, Mycoplasma pneumoniae, Arabidopsis thaliana col, Azopirillum brasilense, Sulfolobus solfataricus, Sphingomonas sp. XLDN2-5, Corynebacterium sp. SHS0007, Pseudomonas sp. ML2, Salmonella typhimurium LT2, Salmonella entericagene, Methanothermobacter thermautotrophicus Delta H, Schizosaccharomyces pombe, and Klebsiella pnuemoniae.

[00317] In one embodiment, the fermentation host is bacteria. In some embodiments, the bacteria are classified in the family of *Enterobacteriaceae*. Examples of genera in the family include *Aranicola, Arsenophonus, Averyella, Biostraticola, Brenneria, Buchnera, Budvicia, Buttiauxella, Candidatus, Curculioniphilus, Cuticobacterium, Candidatus Ishikawaella, Macropleicola, Phlomobacter, Candidatus Riesia, Candidatus Stammerula, Cedecea, Citrobacter, Cronobacter, Dickeya, Edwardsiella, Enterobacter, Erwinia, Escherichia, Ewingella, Grimontella, Hafnia, Klebsiella, Kluyvera, Leclercia, Leminorella, Margalefia, Moellerella, Morganella, Obesumbacterium, Pantoea, Pectobacterium, Photorhabdus, Phytobacter, Plesiomonas, Pragia, Proteus, Providencia, Rahnella, Raoultella, Salmonella, Samsonia, Serratia, Shigella, Sodalis, Tatumella, Thorasellia, Tiedjeia, Trabulsiella, Wigglesworthia, Xenorhabdus, Yersinia*, and *Yokenella*. In one embodiment, the bacteria are *Escherichia coli* (*E. coli*).

[00318] In some embodiments, the fermentation host is genetically modified. In one embodiment, the fermentation host is genetically modified *E. coli*. For example, the fermentation host can be genetically modified to enhance the efficiency of specific pathways encoded by certain genes. In one embodiment, the fermentation host can be modified to enhance expression of endogenous genes that can positively regulate specific pathways. In another embodiment, the fermentation can be further modified to suppress expression of certain endogenous genes.

[00319] Many biocatalysts used in fermentation to produce target chemicals have been described and others can be discovered, produced through mutation, or engineered through recombinant means. Any biocatalyst that uses fermentable sugars produced from saccharification of biomass using the present system can be used to make the target chemical(s) that it is known to produce by fermentation.

[00320] Of interest are biocatalysts that produce alcohols or biofuels, including ethanol and butanol. Alcohols include, but are not limited to methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, propanediol, butanediol, glycerol, erythritol, xylitol, and sorbitol. For example, fermentation of carbohydrates to acetone, butanol, and ethanol (ABE fermentation) by solventogenic *Clostridia* is well known (Jones and Woods (1986) Microbiol. Rev. 50:484-524). A fermentation process for producing high levels of butanol, also producing acetone and ethanol, using a mutant strain of *Clostridium* acetobutylicum is described in U.S. Pat. No. 5,192,673. The use of a mutant strain of *Clostridium beijerinckii* to produce high levels of butanol, also producing acetone and ethanol, is described in U.S. Pat. No. 6,358,717. Co-owned and co-pending patent applications WO 2007/041269 and WO 2007/050671, which are herein incorporated by reference, disclose the production of 1-butanol and isobutanol, respectively, in genetically engineered microbial hosts. U.S. patent applications No. 11/741,892 and No. 11/741,916, which are herein incorporated by reference, disclose the production of 2-butanol in genetically engineered microbial hosts. Isobutanol, 1-butanol or 2-butanol can be produced from fermentation of hydrolysate produced using the present system by a microbial host following the disclosed methods. Genetically modified strains of *E. coli* have also been used as biocatalysts for ethanol production (Underwood et al., (2002) Appl. Environ. Microbio. 68:6263-6272). US20120122169 discloses the use of two *E. coli* ethylene glycol producing strains having differential overexpression of the gene coding for yqhD.

[00321] A genetically modified strain of *Zymomonas mobilis* that has improved production of ethanol is described in US 2003/0162271 A1. A further engineered ethanol-producing strain of *Zymomonas mobilis* and its use for ethanol production are described in co-owned and co-pending U.S. patent applications 60/847,813 and 60/847,856, respectively, which are herein incorporated by reference. Ethanol can be produced from fermentation of hydrolysate produced using the present system by *Zymomonas mobilis* following the disclosed methods. Saccharification of pretreated biomass which had pretreatment liquor containing inhibitors removed, to fermentable sugars followed by fermentation of the sugars to a target chemical is exemplified in Example 4 herein for the production of ethanol from pretreated corn cobs using *Z. mobilis* as the biocatalyst for the fermentation of sugars to ethanol.

[00322] Lactic acid has been produced in fermentations by recombinant strains of *E. coli* (Zhou et al., (2003) Appl. Environ. Microbiol. 69:399-407), natural strains of *Bacillus* (US20050250192), and *Rhizopus oryzae* (Tay and Yang (2002) Biotechnol. Bioeng. 80:1-12).

Recombinant strains of *E. coli* have been used as biocatalysts in fermentation to produce 1,3 propanediol (U.S. Pat. No. 6,013,494, U.S. Pat. No. 6,514,733), and adipic acid (Niu et al., (2002) Biotechnol. Prog. 18:201-211). Acetic acid has been made by fermentation using recombinant *Clostridia* (Cheryan et al., (1997) Adv. Appl. Microbiol. 43:1-33), and newly identified yeast strains (Freer (2002) World J. Microbiol. Biotechnol. 18:271-275). Production of succinic acid by recombinant *E. coli* and other bacteria is disclosed in U.S. Pat. No. 6,159,738, and by mutant recombinant *E. coli* in Lin et al., (2005) Metab. Eng. 7:116-127). Pyruvic acid has been produced by mutant *Torulopsis glabrata* yeast (Li et al., (2001) Appl. Microbiol. Technol. 55:680-685) and by mutant *E. coli* (Yokota et al., (1994) Biosci. Biotech. Biochem. 58:2164-2167). Recombinant strains of *E. coli* have been used as biocatalysts for production of para-hydroxycinnamic acid (US20030170834) and quinic acid (US20060003429). A mutant of *Propionibacterium acidipropionici* has been used in fermentation to produce propionic acid (Suwannakham and Yang (2005) Biotechnol. Bioeng. 91:325-337), and butyric acid has been made by *Clostridium tyrobutyricum* (Wu and Yang (2003) Biotechnol. Bioeng. 82:93-102). Propionate and propanol have been made by fermentation from threonine by *Clostridium sp.* strain 17cr1 (Janssen (2004) Arch. Microbiol. 182:482-486). A yeast-like *Aureobasidium pullulans* has been used to make gluconic acid (Anantassiadis et al., (2005) Biotechnol. Bioeng. 91:494-501), by a mutant of *Aspergillis niger* (Singh et al., (2001) Indian J. Exp. Biol. 39:1136-43). 5-keto-D-gluconic acid was made by a mutant of *Gluconobacter oxydans* (Elfari et al., (2005) Appl Microbiol. Biotech. 66:668-674), itaconic acid was produced by mutants of *Aspergillus terreus* (Reddy and Singh (2002) Bioresour. Technol. 85:69-71), citric acid was produced by a mutant *Aspergillus niger* strain (Ikram-Ul-Haq et al., (2005) Bioresour. Technol. 96:645-648), and xylitol was produced by *Candida guilliermondii* FTI 20037 (Mussatto and Roberto (2003) J. Appl. Microbiol. 95:331-337). 4-hydroxyvalerate-containing biopolyesters, also containing significant amounts of 3-hydroxybutyric acid 3-hydroxyvaleric acid, were produced by recombinant *Pseudomonas putid*a and *Ralstonia eutropha* (Gorenflo et al., (2001) Biomacromolecules 2:45-57). L-2,3-butanediol was made by recombinant *E. coli* (Ui et al., (2004) Lett. Appl. Microbiol. 39:533-537).

[00323] In some embodiments where the saccharide composition undergoes fermentation to produce an ethylene glycol compound, a stable strain of *E. coli* can be transformed to contain a pathway for converting xylose to D-ribulose by metabolically engineering one or more of the following pathways:

a) D-xylose to D-xylulose using an engineered xylose isomerase from, for example, the *Escherichia coli* gene xylA from *Pseudomonas putida* or the gene xylA from *Bacillus coagulans*.

b) D-xylulose to D-xylulose-5-phosphate using an engineered xylulokinase from, for example, the gene xylB from *Escherichia coli*, *Caulobacter cescentus*, or *Pseudmonas putida*.

c) D-xylulose-5-phosphate to D-ribulose-5-phosphate using an engineered ribulose phosphate 3-epimerase from, for example, the gene rpe from *Escherichia coli, Synechocystis sp. PCC 6803,* or *Mycoplasma pneumoniae.*); and

d) D-ribulose-5-phosphate to D-ribulose using an engineered phosphoribulokinase or D-ribulose-5-phosphate kinase from, for example, the gene PRK from *Arabidopsis thaliana col* or gene prk from *Synechocystis sp. PCC 6803*.

[00324] In other embodiments, the stable strain of *E. coli* can further be transformed to contain a pathway from D-ribulose to ethylene glycol by metabolically engineering one or more of the following pathways:

a) D-ribulose + ATP to D-ribulose-1-phosphate + ADP using an engineered D-ribulokinase from, for example, the fuculokinase gene fucK from *Escherichia coli*;

b) D-ribulose-1-phosphate to glycolaldehyde + DHAP using an engineered D-ribulose-phosphate aldolase from, for example, the gene fucA from *Escherichia coli*; and

c) Glycolaldehyde + NADH + H^+ to ethylene glycol + NAD^+ using an engineered 1,2-propanediol oxidoreductase from, for example, the gene fucO from *Escherichia coli*.

[00325] In some embodiments, the saccharide composition comprises xylose and the chemical intermediate is selected from one or more of xylulose, D-xylulose-5-phosphate, D-ribulose-5-phosphate, D-ribulose, D-ribulose-1-phosphate, glycolaldehyde, and 2-dihydroxyacetone phosphate. In other embodiments, the saccharide composition comprises xylose and the chemical intermediate is selected from one or more of D-xylulose-5-phosphate, D-ribulose-1-phosphate, and 2-dihydroxyacetone phosphate. In some embodiments, the saccharide composition comprises xylose and the chemical intermediate is selected from xylonate, 2-dehydro-3-deoxy-D-pentonate, and glycoaldehyde.

[00326] In some embodiments, the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme selected from xylose isomerase, xylulokinase, ribulose phosphate 3-epimerase, phosphoribulokinase, D-ribulose-5-phosphate kinase, D-ribulokinase, D-ribulose-phosphate aldolase, and 1,2-propanediol oxidoreductase. In some embodiments, the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme selected from xylose dehydrogenase, xylonate dehydratase, 2-dehydro-3-deoxy-D-pentonate aldolase and glycoaldehyde reductase. In other embodiments, the chemical intermediate is selected from glyceraldehyde, 2-phosphoglycerate, 3-phosphoglycerate, glycerate, serine, hydroxypyruvate, ethanolamine, and glycolaldehyde.

[00327] In some embodiments, the fermentation host is genetically modified to convert xylose to ribulose, and ribulose to the ethylene glycol compound or the chemical intermediate. In some embodiments, the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least two ethylene glycol pathway enzymes.

[00328] In some embodiments, the chemical intermediate between the sugar in the saccharide composition and the final product can be selected from D-xylulose, D-xylulose-5-phosphate, D-ribulose-5-phosphate, D-ribulose, D-ribulose-1-phosphate, glycolaldehyde and DHAP. In some embodiments, the chemical intermediate between the sugar in the saccharide composition and the final product can be selected from D-xylulose, D-xylulose-5-phosphate, D-ribulose-5-phosphate. In other embodiments, the chemical intermediate between the sugar in the saccharide composition and the final product can be selected from D-ribulose-1-phosphate, glycolaldehyde and DHAP.

[00329] DHAP is a gateway intermediate in that multiple pathways can be genetically engineered to create DHAP, such as the path from D-ribulose above, and multiple pathways are already known in the art to convert DHAP to other intermediates or final products. For example, FIGS. **10** and **11** depict pathways from DHAP to 1,2-propane diol, lactic acid, and 1-propanol. Further discussion of these pathways is detailed below. These known pathways beginning with DHAP intersect with routes to compounds that can be chemically converted to propylene. Also contemplated is the development of genetically engineered routes from DHAP, or other key intermediates, to compounds known as precursors of propylene.

[00330] In some embodiments, the fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme selected from xylose dehydrogenase, xylonate dehydratase, 2-dehydro-3-deoxy-D-pentonate aldolase and glycoaldehyde reductase. The chemical intermediate can be, for example, selected from glyceraldehyde, 2-phosphoglycerate, 3-phosphoglycerate, glycerate, serine, hydroxypyruvate, ethanolamine, and glycolaldehyde. In other embodiments, the fermentation host can be genetically modified to convert xylose to ribulose, and ribulose to the ethylene glycol compound or the chemical intermediate. *See, e.g.,* Liu et al. (2013) Appl. Microbiol. Biotechnol. 97:3409-3417.

[00331] In some embodiments, the fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least two ethylene glycol pathway enzymes. The ethylene glycol pathway enzyme can be selected from a serine aminotransferase, a serine decarboxylase, a serine oxidoreductase, a hydroxypyruvate decarboxylase, a glycoaldehyde reductase, an ethanolamine aminotransferase, an ethanolamine oxidoreductase, a hydroxypyruvate reductase, a glycerate decarboxylase, a 3-phosphoglycerate phosphatase, a glycerate kinase, a 2-phosphoglycerate phosphatase, a glycerate-2-kinase, and a glyceraldehyde dehydrogenase. In another embodiment, the ethylene glycol pathway enzyme can be selected from a glycerate dehydrogenase, a glycolaldehyde reductase, a hydroxypyruvate decarboxylase, a hydroxypyruvate isomerase, and a glyoxylate carboligase. In other embodiments, the ethylene glycol pathway enzyme can be selected from a glycolyl-CoA transferase, a glyoxylate reductase, a glycolyl-CoA synthetase, a glycolyl-CoA reductase, a glycolaldehyde reductase, a glycolate reductase, a glycolate kinase, a phosphotransglycolylase, a glycolylphosphate reductase, and a glycolyl-CoA reductase.

[00332] In some embodiments where the saccharide composition undergoes fermentation to produce a propylene precursor, a stable strain of *E. coli* can be transformed to contain a pathway for converting C5 and C6 sugars to DHAP and glycoaldehyde by metabolically engineering one or more of the pathways shown in FIG. **9**. For example, β-D-Glucose and β-D-galactose can be metabolized using ATP to give β-D-glucose-6-phosphate via the Leloir pathway. *See, e.g.,* Frey (1946)_ FASEB J. 10:461-470). The β-D-glucose-6-phosphate can be transformed into DHAP by glycolysis using ATP.

[00333] Other routes to propylene pathway intermediates include, but are not limited to:

a) converting D-xylose to D-xylulose-5-phosphate as described above, then convert to D-ribulose-1-phosphate using an engineered L-ribulose 5-phosphate 4-epimerase from, for example, the gene araD from *Azopirillum brasilense*, *Eschericia coli* or *Sulfolobus solfataricus*, or the gene araDh from *Sulfolobus solfataricus*. D-ribulose-1-phosphate can be transformed to DHAP as described above.

b) converting L-arabinose to L-ribulose via an engineered L-arabinose isomerase or L-arabinose 1-dehydrogenase from, for example, the gene araA in *Azospirillum brasilense* or *Escherichia coli,* or the gene carA from *Sphingomonas sp. XLDN2-5.* Phosphorylation of L-ribulose using ATP and an engineered L-ribulokinase from, for example, the gene araB, from *Azospirillum brasilense* or *Escherichia coli*, followed by transformation to D-xyulose-5-phospate via an engineered L-ribulose 5-phosphate 4-epimerase from, for example, the genes araD, sgbE, or ulaF, from *Escherichia coli* leads to the a) pathway above to DHAP. *See, e.g.,* Patrick et al. (1968) J. Biol. Chem. 243: 4312-4318; Patrick et al. (1969) J. Biol. Chem. 244: 4277-4283.

c) converting D-arabinose to D-ribulose using an engineered L-fucose isomerase from, for example, the gene fucI from *Escherichia coli* (*see, e.g.,* Boulter, (1973) J. Bacteriol. 113:687-696), followed by phosphorylation using ATP to give D-ribulose-1-phosphate using an engineered L-fuculokinase from, for example, the gene fucK from *Escherichia coli* (*see, e.g.,* LeBlanc (1971) J. Bacteriol. 106:90-96). D-ribulose-1-phosphate is transformed to DHAP as described in step a) above. In some embodiments, the saccharide composition comprises glucose or galactose and the chemical intermediate is selected from glucose-6-phosphate, 2-dihydroxyacetone phosphate, and glycoaldehyde.

[00334] In some embodiments, the saccharide composition comprises one or more sugars selected from glucose, galactose, arabinose, and xylose, and the chemical intermediate is selected from glucose-6-phosphate, D-ribulose-1-phosphate, and 2-dihydroxyacetone phosphate.

[00335] FIGS. **10** and **11** illustrate metabolic pathways from key C3 intermediates, such as DHAP, to propylene precursor compounds:

a) converting DHAP to methylglyoxal and phosphate using an engineered methylglyoxal synthase from, for example, the *Escherichia coli* gene mgsA in *Escherichia coli. See, e.g.,* Cooper (1984) Ann. Rev. Microbiol. 38:49-68. Methylglyoxal can be converted to acetol using NADPH via an engineered L-glyceraldehyde 3-phosphate reductase or methylglyoxal reductase from, for example, the gene yeaE from *Escherichia coli* or the gene dkgA from *Corynebacterium*

sp. SHS0007 or *Escherichia coli*. *See, e.g.,* Misra et al. (1996) Mol. Cell Biochem. 156:117-124. Then, transformation of acetol and NADH to 1,2-propanediol can be achieved with an engineered L-1,2-propanediol dehydrogenase or glycerol dehydrogenase from, for example, the gene gldA from *Escherichia coli*, the gene bedD from *Pseudomonas sp. ML2*, the gene dhaB1 from *Klebsiella pneumoniae* or the gene AKR1B1 from *Homo sapien*. *See, e.g.,* Gonzalez et al. (2008) Metab. Eng. 105:234-235. 1,2-Propanediol can be converted to propanal with an engineered propanediol dehydratase from, for example, the genes pduC, pduD, and pduE from *Salmonella enterica* or *Salmonella typhimurium LT2*, then with NADH producing 1-propanol using an engineered propanol dehydrogenase from, for example, the gene pduQ in *Salmonella entericagene*. *See, e.g.,* Cheng et al. (2008) Bioessays 30:1084-1095.

b) converting 1,2-propanediol to propanal using an engineered propanediol dehydratase from, for example, the genes pduC, pduD, and pduE from *Salmonella enterica* or *Salmonella typhimurium LT2* which is then transformed with NAD^+ and CoA to propanoyl-CoA using an engineered CoA-dependent propionaldehyde dehydrogenase from, for example, the gene pduP from *Salmonella enterica* or *Salmonella typhimurium LT2*. *See, e.g.,* Cheng et al. Phosphorylation results in forming propanoyl phosphate using an engineered phosphate propanoyltransferase from, for example, the pduL from *Salmonella enterica* or *Salmonella typhimurium LT2* (*see, e.g.,* Babik (1997) J. Bacteriol. 179:6633-6639), which can be converted into propanoate with an engineered propionate kinase from, for example, the gene pduW from *Salmonella enterica* or *Salmonella typhimurium LT2* (*see, e.g.,* Cheng et al.).

c) converting 1,2-propane diol and NAD^+ to L-lactaldehyde with an engineered L-1,2-propanediol oxidoreductase_from, for example, the gene fucO from *Escherichia coli*. *See, e.g.,* Ting et al. (1964) Biochim. Biophys. Acta 89:217-225. Another route to L-lactaldehyde involves transforming methylglyoxal with NADPH using an engineered methylglyoxal reductase from, for example, the gene GRE2 from *Saccharomyces. cerevisiae*. *See, e.g.,* Chen (2003) Yeast 20:545-559. L-Lactaldehyde and NAD^+ can be transformed to L-lactic acid using an engineered aldehyde dehydrogenase from, for example, either the gene ALD2 or the gene ALD3 from *Saccharomyces cerevisiae*. *See, e.g.,* Navarro-Avino et al. (1999) Yeast 15:829-842.

d) converting DHAP to glycerol-1-phosphate using an engineered glycerol-1-phosphate dehydrogenase from, for example, the gene EgsA from *Methanothermobacter thermautotrophicus Delta H* or an engineered glycerol-3-phosphate dehydrogenase from, for example, the gene GpsA from *Escherichia coli*. *See, e.g.,* Koga et al. (2003) Biosci. Biotech.

Biochem. 67:1605-1608; Clark et al. (1980) J. Biol. Chem. 255:714-717. Dephosphorylation provides glycerol using an engineered sugar phosphatase from, for example, the gene yfbT from *Escherichia coli. See, e.g.,* Sussman (1981) Biochim. Biophys. Acta 661:199-204. DHAP can also be converted to dihydroxyacetone using an engineered dihydroxyacetone kinase from, for example, the gene DAK2 from *Saccharomyces cerevisiase* (*see, e.g.,* Molin (2003) J. Biol. Chem. 278:1415-1423), or the gene dak2 from *Schizosaccharomyces pombe. See, e.g.,* Kimura et al. (1998) Biochim. Biophys. Acta 1442:361-368. Dihydroxyacetone can in turn be converted to glycerol with an engineered glycerol dehydrogenase from, for example, the gene gldA from *Escherichia coli*, the gene bedD from *Pseudomonas sp. ML2,* or the gene dhaB1 from *Klebsiella pneumoniae.* Transformation of glycerol to 3-hydroxypropionaldehyde can be achieved with an engineered glycerol dehydratase from, for example, the gene dhaB1 from *Clostribium butyricum* or *Klebsiella pneumonia*e, or the genes DhaB, DhaC, and DhE from *Citrobacter freundii. See, e.g.,* Seyfried et al. (1996) J. Bacteriol. 178:5793-5796; Zheng et al. (2006) Process Biol. 41:2160-2169). Conversion to 3-hydroxypropionate can be performed using an engineered γ-glutamyl-γ-aminobutyraldehyde dehydrogenase from, for example, the gene puuC from *Escherichia coli. See, e.g.,* Joje, et al. (2008) Appl. Microbiol. Biotechnol. 81:51-60. 3-Hydroxypropionaldehyde can also be converted to 1,3-propanediol using an engineered 1,3-propanediol dehydrogenase from, for example, the gene dhaT from *Clostribium butyricum, Clostridium pasteurium, Citrobacter freundii* or *Klebsiella pneumoniae. See, e.g.,* Raynaud, et al., (2003) PNAS 100:5010-5015.

[00336] In some embodiments, the fermentation host is genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-ribulose 5-phosphate 4-epimerase, L-arabinose isomerase, L-arabinose 1-dehydrogenase, L-ribulokinase, L-ribulose 5-phosphate 4-epimerase, L-fucose, L-fuculokinase, methylglyoxal synthase, L-glyceraldehyde 3-phosphate, methylglyoxal reductase, L-1,2-propanediol dehydrogenase, glycerol dehydrogenase, propanediol dehydratase, propanol dehydrogenase, propanediol dehydratase, CoA-dependent propionaldehyde dehydrogenase, phosphate propanoyltransferase, propionate kinase, L-1,2-propanediol oxidoreductase, aldehyde dehydrogenase, glycerol-1-phosphate dehydrogenase, glycerol-3-phosphate dehydrogenase, sugar phosphatase, dihydroxyacetone kinase, glycerol dehydrogenase, glycerol dehydratase, γ-glutamyl-γ-aminobutyraldehyde dehydrogenase, and 1,3-propanediol dehydrogenase. In other embodiments, the fermentation host is genetically modified to include at least one exogenous

nucleic acid encoding at least one propylene pathway enzyme selected from D-ribulose-phosphate aldolase and L-ribulose 5-phosphate 4-epimerase.

[00337] In some embodiments, the fermentation host is genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from D-ribulose-phosphate aldolase and L-ribulose 5-phosphate 4-epimerase. In other embodiments, the saccharide composition includes xylose, and the chemical intermediate is selected from D-xylulose-5-phosphate, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-arabinose isomerase, L-arabinose 1-dehydrogenase, L-ribulokinase, L-ribulose 5-phosphate 4-epimerase, and D-ribulose-phosphate aldolase.

[00338] In some embodiments, the saccharide composition includes L-arabinose, and the chemical intermediate is selected from L-ribulose-5 phosphate, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-fucose, L-fuculokinase, and D-ribulose-phosphate aldolase.

[00339] In some embodiments, the saccharide composition includes D-arabinose and the chemical intermediate is selected from L-ribulose, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from methylglyoxal reductase, L-1,2-propanediol dehydrogenase, glycerol dehydrogenase, propanediol dehydratase, and propanol dehydrogenase.

[00340] In some embodiments, the saccharide composition includes glucose or galactose and the chemical intermediate is selected from glucose-6-phosphate, 2-dihydroxyacetone phosphate, and glycoaldehyde. The fermentation host is genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from D-ribulose-phosphate aldolase and L-ribulose 5-phosphate 4-epimerase.

[00341] In some embodiments, the saccharide composition includes xylose, and the chemical intermediate is selected from D-xylulose-5-phosphate, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host is genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-

arabinose isomerase, L-arabinose 1-dehydrogenase, L-ribulokinase, L-ribulose 5-phosphate 4-epimerase, and D-ribulose-phosphate aldolase.

[00342] In some embodiments, the saccharide composition includes L-arabinose, and the chemical intermediate is selected from L-ribulose-5 phosphate, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-fucose, L-fuculokinase, and D-ribulose-phosphate aldolase.

[00343] In some embodiments, the saccharide composition includes D-arabinose and the chemical intermediate is selected from L-ribulose, D-ribulose-1-phosphate and 2-dihydroxyacetone phosphate. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from methylglyoxal reductase, L-1,2-propanediol dehydrogenase, glycerol dehydrogenase, propanediol dehydratase, and propanol dehydrogenase.

[00344] In some embodiments, the chemical intermediate is selected from 1,2-propanediol, methyl glyoxal, L-lactaldehyde, and lactic acid. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from L-1,2-propanediol oxidoreductase and aldehyde dehydrogenase. In other embodiments, the chemical intermediate is selected from 2-dihydroxyacetone phosphate, glycerol, 3-proprionaldehyde, and 1,3-propane diol. The fermentation host can be genetically modified to include at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from glycerol-1-phosphate dehydrogenase, glycerol-3-phosphate dehydrogenase, sugar phosphatase, dihydroxyacetone kinase, glycerol dehydrogenase, glycerol dehydratase, γ-glutamyl-γ-aminobutyraldehyde dehydrogenase, and 1,3-propanediol dehydrogenase.

[00345] One skilled in the art will understand that all of the pathway steps disclosed herein are merely exemplary and that any of the substrate-product pairs disclosed herein suitable to produce a desired product and for which an appropriate activity is available for the conversion of the substrate to the product can be readily determined by one skilled in the art based on the knowledge in the field. It is understood that any of the pathways disclosed herein can be utilized to generate a non-naturally occurring microbial organism that produces any pathway intermediate or product, as desired. As disclosed herein, such a microbial organism that produces

an intermediate can be used in combination with another microbial organism expressing downstream pathway enzymes to produce a desired product. However, it is understood that a non-naturally occurring microbial organism that produces a pathway intermediate can be utilized to produce the intermediate as a desired product.

[00346] Those skilled in the art will understand that reference to a reaction also constitutes reference to the reactants and products of the reaction. Similarly, unless otherwise expressly stated herein, reference to a reactant or product also references the reaction, and reference to any of these metabolic constituents also references the gene or genes encoding the enzymes that catalyze or proteins involved in the referenced reaction, reactant or product. Likewise, given the well known fields of metabolic biochemistry, enzymology and genomics, reference herein to a gene or encoding nucleic acid also constitutes a reference to the corresponding encoded enzyme and the reaction it catalyzes or a protein associated with the reaction as well as the reactants and products of the reaction.

[00347] Any suitable methods known in the art can be employed to metabolically engineer the one or more pathways described above. One of skill in the art would recognize that the genetic alterations of microbial organisms include, for example, modifications introducing expressible nucleic acids encoding metabolic polypeptides, other nucleic acid additions, nucleic acid deletions and/or other functional disruption of the microbial organism's genetic material. Such modifications include, for example, coding regions and functional fragments thereof, for heterologous, homologous or both heterologous and homologous polypeptides for the referenced species. These modifications can be introduced for example, by introduction of an encoding nucleic acid into the host genetic material such as by integration into a host chromosome or as non-chromosomal genetic material such as a plasmid. The term "heterologous" refers to a molecule or activity derived from a source other than the referenced species whereas "homologous" refers to a molecule or activity derived from the host microbial organism.

[00348] It is further understood, as disclosed herein, that more than one exogenous nucleic acid can be introduced into the host microbial organism on separate nucleic acid molecules, on polycistronic nucleic acid molecules, or a combination thereof, and still be considered as more than one exogenous nucleic acid. In the case where two exogenous nucleic acids encoding a desired activity are introduced into a host microbial organism, it is understood that the two exogenous nucleic acids can be introduced as a single nucleic acid, for example, on a single

plasmid, on separate plasmids, can be integrated into the host chromosome at a single site or multiple sites, and still be considered as two exogenous nucleic acids.

[00349] Those skilled in the art will understand that the genetic alterations, including metabolic modifications exemplified herein, are described with reference to a suitable host organism such as *E. coli* and their corresponding metabolic reactions or a suitable source organism for desired genetic material such as genes for a desired metabolic pathway. However, given the complete genome sequencing of a wide variety of organisms and the high level of skill in the area of genomics, those skilled in the art will readily be able to apply the teachings and guidance provided herein to essentially all other organisms. For example, the *E. coli* metabolic alterations exemplified herein can readily be applied to other species by incorporating the same or analogous encoding nucleic acid from species other than the referenced species. Such genetic alterations include, for example, genetic alterations of species homologs, in general, and in particular, orthologs, paralogs or nonorthologous gene displacements.

[00350] An ortholog is a gene or genes that are related by vertical descent and are responsible for substantially the same or identical functions in different organisms. In contrast, paralogs are homologs related by, for example, duplication followed by evolutionary divergence and have similar or common, but not identical functions. A nonorthologous gene displacement is a nonorthologous gene from one species that can substitute for a referenced gene function in a different species. Orthologs, paralogs and nonorthologous gene displacements can be determined by methods well known to those skilled in the art. Those skilled in the art will understand that the identification of metabolic modifications can include identification and inclusion or inactivation of orthologs. To the extent that paralogs and/or nonorthologous gene displacements are present in the referenced microorganism that encode an enzyme catalyzing a similar or substantially similar metabolic reaction, those skilled in the art also can utilize these evolutionally related genes.

[00351] It is understood that any of the one or more exogenous nucleic acids can be introduced into a microbial organism to produce a non-naturally occurring microbial organism. Depending on the biosynthetic pathway constituents of a selected host microbial organism, the non-naturally occurring microbial organisms will include at least one exogenously expressed pathway-encoding nucleic acid and up to all encoding nucleic acids for one or more disclosed biosynthetic pathways. For example, ethylene glycol biosynthesis can be established in a host deficient in a pathway enzyme or protein through exogenous expression of the corresponding

encoding nucleic acid. In a host deficient in all enzymes or proteins of an ethylene glycol pathway, exogenous expression of all enzyme or proteins in the pathway can be included, although it is understood that all enzymes or proteins of a pathway can be expressed even if the host contains at least one of the pathway enzymes or proteins.

[00352] Methods for constructing and testing the expression levels of a non-naturally occurring host can be performed, for example, by recombinant and detection methods well known in the art. Such methods can be found described in, for example, Sambrook et al., Molecular Cloning: A Laboratory Manual, Third Ed., Cold Spring Harbor Laboratory, New York (2001); and Ausubel et al., Current Protocols in Molecular Biology, John Wiley and Sons, Baltimore, Md. (1999). Exogenous nucleic acid sequences involved in a disclosed pathway can be introduced stably or transiently into a host cell using techniques well known in the art including, but not limited to, conjugation, electroporation, chemical transformation, transduction, transfection, and ultrasound transformation.

[00353] An expression vector or vectors can be constructed to include one or more biosynthetic pathway elements encoding nucleic acids as exemplified herein operably linked to expression control sequences functional in the host organism. Expression vectors applicable for use in the microbial host organisms of the invention include, for example, plasmids, phage vectors, viral vectors, episomes and artificial chromosomes, including vectors and selection sequences or markers operable for stable integration into a host chromosome. Additionally, the expression vectors can include one or more selectable marker genes and appropriate expression control sequences. Selectable marker genes also can be included that, for example, provide resistance to antibiotics or toxins, complement auxotrophic deficiencies, or supply critical nutrients not in the culture media. Expression control sequences can include constitutive and inducible promoters, transcription enhancers, transcription terminators, and the like which are well known in the art. When two or more exogenous encoding nucleic acids are to be co-expressed, both nucleic acids can be inserted, for example, into a single expression vector or in separate expression vectors.

[00354] The transformation of exogenous nucleic acid sequences involved in a metabolic or synthetic pathway can be confirmed using methods well known in the art. Such methods include, for example, nucleic acid analysis such as Northern blots or polymerase chain reaction (PCR) amplification of mRNA, or immunoblotting for expression of gene products, or other suitable analytical methods to test the expression of an introduced nucleic acid sequence or its

corresponding gene product. It is understood by those skilled in the art that the exogenous nucleic acid is expressed in a sufficient amount to produce the desired product, and it is further understood that expression levels can be optimized to obtain sufficient expression using methods well known in the art and as disclosed herein.

c) Fermentation conditions

[00355] Any suitable fermentation conditions in the art can be employed to ferment the saccharide composition described herein to produce bio-based products, and components thereof. In one embodiment, provided herein is a composition including a saccharide composition and a fermentation host under conditions such that ethylene glycol is capable of being produced. In one embodiment, provided herein is a composition comprising a saccharide composition and a fermentation host under conditions such that one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol are capable of being produced.

[00356] In some embodiments, saccharification described above can be combined with fermentation in a separate or a simultaneous process. The fermentation can use the aqueous sugar phase or, if the sugars are not substantially purified from the reacted biomass, the fermentation can be performed on an impure mixture of sugars and reacted biomass. Such methods include, for example, separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and cofermentation (SSCF), hybrid hydrolysis and fermentation (HHF), separate hydrolysis and co-fermentation (SHCF), hybrid hydrolysis and co-fermentation (HHCF), and direct microbial conversion (DMC).

[00357] For example, SHF uses separate process steps to first enzymatically hydrolyze cellulosic material to fermentable sugars (*e.g.*, glucose, cellobiose, cellotriose, and pentose sugars), and then ferment the sugars to ethanol.

[00358] In SSF, the enzymatic hydrolysis of cellulosic material and the fermentation of sugars to ethanol are combined in one step. *See* Philippidis, G. P., Cellulose bioconversion technology, in Handbook on Bioethanol: Production and Utilization, Wyman, C. E., ed., Taylor & Francis, Washington, D.C., 179-212 (1996).

[00359] SSCF involves the cofermentation of multiple sugars. *See* Sheehan, J., and Himmel, M., Enzymes, energy and the environment: A strategic perspective on the U.S. Department of Energy's research and development activities for bioethanol, *Biotechnol. Prog.*, 15: 817-827 (1999).

[00360] HHF involves a separate hydrolysis step, and in addition a simultaneous saccharification and hydrolysis step, which can be carried out in the same reactor. The steps in an HHF process can be carried out at different temperatures; for example, high temperature enzymatic saccharification followed by SSF at a lower temperature that the fermentation strain can tolerate.

[00361] DMC combines all three processes (enzyme production, hydrolysis, and fermentation) in one or more steps where the same organism is used to produce the enzymes for conversion of the cellulosic material to fermentable sugars and to convert the fermentable sugars into a final product. *See* Lynd, L. R., Weimer, P. J., van Zyl, W. H., and Pretorius, I. S., Microbial cellulose utilization: Fundamentals and biotechnology, *Microbiol. Mol. Biol. Reviews*, 66: 506-577 (2002).

Bio-Based Polymers

[00362] Among the downstream products described herein produced by fermentation of sugars liberated from cellulosic materials are bio-based polymers. The bio-based polymers can be recyclable and/or at least partially bio-degradable. Many bio-based polymers can be incorporated into plastics as described above. In one embodiment, the bio-based polymer is polyethylene glycol. In another embodiment, the bio-based polymer is polypropylene.

[00363] In one embodiment, the bio-based polymer is polyethylene terephthalate, or copolyesters thereof. Such a bio-based polymer can be produced by reacting a terephthalate component and a diol component, as described in U.S. Patent Application Nos. 2009/0246430 and 2010/0028512.

[00364] In some embodiments, the bio-based polymer can include between about 25-75 wt%, between about 30-70 wt%, or between about 40-65 wt% of the terephthalate component. The terephthalate component can include, for example, terephthalic acid, dimethylterephthalate, or isophthalic acid, or a combination thereof. In other embodiments, of the terephthalate component is bio-derived, such that at least a portion of the terephthalate component is produced

from cellulosic materials. In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the terephthalate component is derived from cellulosic material. Any suitable methods currently known in the art can be employed to produce a bio-derived terephthalate component. For example, carene can be derived from cellulosic materials, and converted to cymene and oxidized to form terephthalic acid. In another example, limonene can be derived from cellulosic materials, and converted to terpene and then cymene, which can be oxidized to form terephthalic acid. *See e.g.*, U.S. Patent No. 2009/0246430.

[00365] In some embodiments, the bio-based polymer can include between about 25-50 wt%, between about 25-45%, between about 25-40%, or between about 25-35 wt% of the diol component. The diol component can include an ethylene glycol compound, such as monoethylene glycol, wherein at least a portion of the ethylene glycol compound is bio-derived and produced according to the methods described herein. In certain embodiments, at least about 1 wt%, at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 40 wt%, at least about 50 wt%, at least about 60 wt%, at least about 70 wt%, at least about 80 wt%, at least about 90 wt%, or about 100 wt% of the diol component is derived from cellulosic material. In other embodiments, the diol component can further include cyclohexane dimethanol.

[00366] It should be understood that any descriptions of the terephthalate component can be combined with any descriptions of the diol component the same as if each and every combination were specifically and individually listed. For example, in some embodiments, the bio-based polymer can include between about 30-70 wt% of the terephthalate component and between about 25-45% of the diol component.

[00367] Provided herein is a product containing an ethylene glycol-containing compound produced by the step of combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising the ethylene glycol-containing compound, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic

monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose.

[00368] Provided herein is a product containing a propylene-containing compound produced by the step of combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more second compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more second compounds, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose. In some embodiments, the the propylene-containing compound is converted into a polypropylene-containing compound.

[00369] One of skill in the art would recognize that the bio-based polymer can include additional ingredients (*e.g.*, coloring agent or other additives as described above) to make the polymer suitable for use in various plastics applications. Plastics are used to produce a diverse array of products, including, but not limited to,

a) household and kitchenware (*e.g.,* bottles, dishes, utensils, packaging, such as food wrapping and easy seal or reusable bags, non-stick cookware, coffee pots, refridgerator components, microwave casing and components, household implement handles and other components, surface

laminates such as countertops, toothbrushes, and hair dryers), toilets, sinks and other bathroom fixtures, plumbing piping and systems, lighting fixtures, flooring (*e.g.*, carpeting, rugs, and laminates), furniture, windows and frames, insulation, textiles (*e.g.*, clothing, shoes and soles, fabrics, upholstery, curtains and window treatments, coverings, rope/string,and high performance fibers), cosmetics, and handbags/tote bags/luggage;

b) surgical and medical implements (*e.g.*, syringes, tubing, liquid and solid packaging, prescription bottles, handles for surgical/medical instruments, sterile clothing and masks), medical implants and devices, eyeglass lenses and frames, and contact eye lenses;

c) electronics, including heat resistant components; circuit boards; electrical wire coverings; electrical switches; casings, screens, and components for, *e.g.*, applicances, computers, printers, cellular phones and other mobile devices, CDs, cassette tapes, radios, clocks and watches, TVs, VCRs, video games and consoles; vehicle components such as body parts, upholstery, engine components, and cabin parts; and

d) laboratory equipment, chemical bottles, drums and carboys, tubing, gaskets, bearings, valves, seals, pumps, knobs, piping, sealants, adhesives, resins, foams, coatings, tapes, packaging such as for commercial products or shipping, pipettes and tips, brushes, and paints, dyes, and pigments.

[00370] In some embodiments, polyethylene terephthalate can be used to produce one or more products selected from vehicle components, electronics, plastic bottles, such as those used for carbonated and non-carbonated beverages, and food packaging, such as egg cartons and plastic films.. For example, in one embodiment, polyethylene terephthalate can be used to produce a beverage container (*e.g.*, a bottle). Polypropylene, for example, can be used to produce one or more products selected from plastic bottles, food containers, packaging, household and kitchenware, bags, furniture, insulation, toys, vehicle components, chemical drums and totes, and piping.

[00371] In some embodiments, the product is selected from household and kitchenware (*e.g.*, bottles, dishes, utensils, packaging, such as food wrapping and easy seal or reusable bags, non-stick cookware, coffee pots, refridgerator components, microwave casing and components, household implement handles and other components, surface laminates such as countertops, toothbrushes, and hair dryers). In some embodiments, the product is selected from bottles, dishes, utensils, and packaging. In some embodiments, the product is selected from toilets, sinks

and other bathroom fixtures, plumbing piping and systems, lighting fixtures, flooring (*e.g.*, carpeting, rugs, and laminates), furniture, windows and frames, insulation cosmetics, and handbags/tote bags/luggage. In other embodiments, the product is a textile, such as clothing, shoes and soles, fabrics, upholstery, curtains and window treatments, coverings, rope/string, and high performance fibers.

[00372] In some embodiments, the product is selected from surgical and medical implements (*e.g.*, syringes, tubing, liquid and solid packaging, prescription bottles, handles for surgical/medical instruments, sterile clothing and masks), medical implants and devices, eyeglass lenses and frames, and contact eye lenses. In other embodiments, the product is selected from surgical and medical implements, and medical implants and devices.

[00373] In some embodiments, the product is selected from electronics, including heat resistant components; circuit boards; electrical wire coverings; electrical switches; casings, screens, and components for, *e.g.*, applicances, computers, printers, cellular phones and other mobile devices, CDs, cassette tapes, radios, alarm and other clocks and watches, TVs, VCRs, video games and consoles; and vehicle components such as body parts, upholstery, engine components, and cabin parts. In other embodiments, the product is selected from casings, screens and components for applicances, computers, printers, cellular phones and other mobile devices, and TVs. In other embodiments, the product is selected from vehicle components such as body parts, upholstery, engine components, and cabin parts.

[00374] In some embodiments, the product is selected from laboratory equipment, chemical bottles, drums and carboys, tubing, gaskets, bearings, valves, seals, pumps, knobs, piping, sealants, adhesives, resins, foams, coatings, tapes, packaging such as for commercial products or shipping, pipettes and tips, brushes, and paints, dyes, and pigments. In other embodiments, the product is selected from laboratory equipment, chemical bottles, drums and carboys, and packaging such as for commercial products or shipping. In some embodiments, the product is selected from gaskets, bearings, valves, seals, pumps, knobs, piping, sealants, adhesives, resins, foams, coatings, tapes, brushes, and paints, dyes, and pigments.

General Methods of Preparing the Catalysts

[00375] The polymers described herein can be made using polymerization techniques known in the art, including for example techniques to initiate polymerization of a plurality of monomer units.

[00376] In some embodiments, the catalysts described herein can be formed by first forming an intermediate polymer functionalized with the ionic group, but is free or substantially free of the acidic group. The intermediate polymer can then be functionalized with the acidic group. In other embodiments, the catalysts described herein can be formed by first forming an intermediate polymer functionalized with the acidic group, but is free or substantially free of the ionic group. The intermediate polymer can then be functionalized with the ionic group. In yet other embodiments, the catalysts described herein can be formed by polymerizing monomers with both acidic and ionic groups.

[00377] Provided is also a method of preparing any of the polymers described herein, by:

a) providing a starting polymer;

b) combining the starting polymer with a nitrogen-containing compound or phosphorous-containing compound to produce an ionic polymer having at least one cationic group; and

c) combining the ionic polymer with an effective acidifying reagent to produce the polymer;

wherein the steps a), b), and c) are performed in the order a), b), and c); or in the order a), c), and b); where the polymer is produced in step b) instead of step c).

[00378] In some embodiments, the starting polymer is selected from polyethylene, polypropylene, polyvinyl alcohol, polycarbonate, polystyrene, polyurethane, or a combination thereof. In certain embodiments, the starting polymer is a polystyrene. In certain embodiments, the starting polymer is poly(styrene-co-vinylbenzylhalide-co-divinylbenzene). In another embodiment, the starting polymer is poly(styrene-co-vinylbenzylchloride-co-divinylbenzene).

[00379] In some embodiments of the method to prepare any of the polymers described herein, the nitrogen-containing compound is selected from a pyrrolium compound, an imidazolium compound, a pyrazolium compound, an oxazolium compound, a thiazolium compound, a pyridinium compound, a pyrimidinium compound, a pyrazinium compound, a

pyradizimium compound, a thiazinium compound, a morpholinium compound, a piperidinium compound, a piperizinium compound, and a pyrollizinium compound. In certain embodiments, the nitrogen-containing compound is an imidazolium compound.

[00380] In some embodiments of the method to prepare any of the polymers described herein, the phosporus-containing compound is selected from a triphenyl phosphonium compound, a trimethyl phosphonium compound, a triethyl phosphonium compound, a tripropyl phosphonium compound, a tributyl phosphonium compound, a trichloro phosphonium compound, and a trifluoro phosphonium compound.

[00381] In some embodiments of the method to prepare any of the polymers described herein, the acid is selected from sulfuric acid, phosphoric acid, hydrochloric acid, acetic acid and boronic acid. In one embomdiment, the acid is sulfuric acid.

[00382] Also provided is a method of preparing any of the polymers described herein having a polystyrene backbone, by: a) providing a polystyrene; b) reacting the polystyrene with a nitrogen-containing compound to produce an ionic polymer; and c) reacting the ionic polymer with an acid to produce a third polymer. In certain embodiments, the polystyrene is poly(styrene-co-vinylbenzylhalide-co-divinylbenzene). In one embodiment, the polystyrene is poly(styrene-co-vinylbenzylchloride-co-divinylbenzene).

[00383] In some embodiments, the polymer has one or more catalytic properties selected from:

a) disruption of at least one hydrogen bond in cellulosic materials;

b) intercalation of the polymer into crystalline domains of cellulosic materials; and

c) cleavage of at least one glycosidic bond in cellulosic materials.

[00384] Provided herein are also such intermediate polymers, including those obtained at different points within a synthetic pathway for producing the fully functionalized polymers described herein. In some embodiments, the polymers described herein can be made, for example, on a scale of at least about 100 g, at least about 1 kg, at least about 20 kg, at least about 100 kg, at least about 500 kg, or at least about 1 ton in a batch or continuous process.

[00385] The entire disclosure of each of the patent documents and non-patent literature referred to herein is incorporated by reference in its entirety for all purposes. This application

incorporates by reference in their entirety US Application No. 13/406,490, US Application No. 13/406,517, and US Application No. 13/657,724.

EXAMPLES

Preparation of Polymeric Materials

[00386] Except where otherwise indicated, commercial reagents were obtained from Sigma-Aldrich, St. Louis, MO, USA, and were purified prior to use following the guidelines of Perrin and Armarego. *See* Perrin, D. D. & Armarego, W. L. F., *Purification of Laboratory Chemicals, 3rd ed.*; Pergamon Press, Oxford, 1988. Nitrogen gas for use in chemical reactions was of ultra-pure grade, and was dried by passing it through a drying tube containing phosphorous pentoxide. Unless indicated otherwise, all non-aqueous reagents were transferred under an inert atmosphere via syringe or Schlenk flask. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Where necessary, chromatographic purification of reactants or products was accomplished using forced-flow chromatography on 60 mesh silica gel according to the method described of Still *et al.*, *See* Still *et al.*, *J. Org. Chem.*, 43: 2923 (1978). Thin-layer chromatography (TLC) was performed using silica-coated glass plates. Visualization of the developed chromatogram was performed using either Cerium Molybdate (*i.e.*, Hanessian) stain or $KMnO_4$ stain, with gentle heating, as required. Fourier-Transform Infrared (FTIR) spectroscopic analysis of solid samples was performed on a Perkin-Elmer 1600 instrument equipped with a horizontal attenuated total reflectance (ATR) attachment using a Zinc Selenide (ZnSe) crystal.

Example 1: Preparation of poly[styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene]

[00387] To a 500 mL round bottom flask (RBF) containing a stirred solution of 1.08 g of poly(vinylalcohol) in 250.0 mL of deionized H_2O at 0°C, was gradually added a solution containing 50.04 g (327.9 mmol) of vinylbenzyl chloride (mixture of 3- and 4- isomers), 10.13 g (97.3 mmol) of styrene, 1.08 g (8.306 mmol) of divinylbenzene (DVB, mixture of 3- and 4-isomers) and 1.507 g (9.2 mmol) of azobisisobutyronitrile (AIBN) in 150 mL of a 1:1 (by volume) mixture of benzene / tetrahydrofuran (THF) at 0°C. After 2 hours of stirring at 0 °C to homogenize the mixture, the reaction flask was transferred to an oil bath to increase the reaction temperature to 75°C, and the mixture was stirred vigorously for 28 hours. The resulting polymer beads were vacuum filtered using a fritted-glass funnel to collect the polymer product. The beads were washed repeatedly with 20% (by volume) methanol in water, THF, and MeOH, and

dried overnight at 50°C under reduced pressure to yield 59.84 g of polymer. The polymer beads were separated by size using sieves with mesh sizes 100, 200, and 400.

Example 2: Preparation of poly [styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00388] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 50 g, 200 mmol) was charged into a 500 mL three neck flask (TNF) equipped with a mechanical stirrer, a dry nitrogen line, and purge valve. Dry dimethylformamide (185 ml) was added into the flask (*via* cannula under N_2) and stirred to form a viscous slurry of polymer resin. 1-Methylimidazole (36.5 g, 445mmol) was then added and stirred at 95°C for 8 h. After cooling, the reaction mixture was filtered using a fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried.

[00389] The chemical functionalization of the polymer material, expressed in millimoles of functional groups per gram of dry polymer resin (mmol/g) was determined by ion exchange titrimetry. For the determination of cation-exchangeable acidic protons, a known dry mass of polymer resin was added to a saturated aqueous solution of sodium chloride and titrated against a standard sodium hydroxide solution to the phenolphthalein end point. For the determination of anion-exchangeable ionic chloride content, a known dry mass of polymer resin was added to an aqueous solution of sodium nitrate and neutralized with sodium carbonate. The resulting mixture was titrated against a standardized solution of silver nitrate to the potassium chromate endpoint. For polymeric materials in which the exchangeable anion was not chloride, the polymer was first treated by stirring the material in aqueous hydrochloric acid, followed by washing repeatedly with water until the effluent was neutral (as determined by pH paper). The chemical functionalization of the polymer resin with methylimidazolium chloride groups was determined to be 2.60 mmol/g *via* gravimetry and 2.61 mmol/g *via* titrimetry.

Example 3: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene]

[00390] Poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-iumchloride-*co*-divinylbenzene] (63 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 300 mL) was gradually added into the flask under stirring which resulted in formation of dark-red colored slurry of resin. The slurry was stirred at 85°C for 4 h. After cooling to room temperature, the reaction mixture was

filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 1.60 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 4: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00391] Poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene] (sample of Example 3), contained in fritted glass funnel, was washed repeatedly with 0.1 M HCl solution to ensure complete exchange of HSO_4^- with Cl^- . The resin was then washed with de-ionized water until the effluent was neutral, as determined by pH paper. The resin was finally air-dried.

Example 5: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium acetate-*co*-divinylbenzene]

[00392] The suspension of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene] (sample of Example 3) in 10 % aqueous acetic acid solution was stirred for 2 h at 60°C to ensure complete exchange of HSO_4^- with AcO^-. The resin was filtered using fritted glass funnel and then washed multiple times with de-ionized water until the effluent was neutral. The resin was finally air-dried.

Example 6: Preparation of poly [styrene-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00393] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 250 three neck flask (TNF) equipped with a mechanical stirrer, a dry nitrogen line, and purge valve. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) and stirred to give viscous resin slurry. 1-Ethylimidazole (4.3 g, 44.8 mmol) was then added to the resin slurry and stirred at 95°Cunder 8 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer resin with ethylimidazolium chloride groups was determined to be 1.80 mmol/g, as determined by titrimetry following the procedure of Example 1.

Example 7: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene]

[00394] Poly [styrene-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-co-divinylbenzene] (5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 45 mL) was gradually added into the flask under stirring which resulted in the formation of dark-red colored uniform slurry of resin. The slurry was stirred at 95-100°C for 6 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 1.97 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 8: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00395] Poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-ethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene] resin beads (sample of Example 7) contained in fritted glass funnel was washed multiple times with 0.1 M HCl solution to ensure complete exchange of HSO_4^- with Cl^- . The resin was then washed with de-ionized water until the effluent was neutral, as determined by pH paper. The resin was finally washed with ethanol and air dried.

Example 9: Preparation of poly [styrene-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00396] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Chloroform (50 ml) was added into the flask and stirred to form slurry of resin. Imidazole (2.8 g, 41.13mmol) was then added to the resin slurry and stirred at 40°C for 18 h. After completion of reaction, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer resin with imidazolium chloride groups was determined to be 2.7 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 10: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene]

[00397] Poly[styrene-*co*-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene](5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 80 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 95°C for 8 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 1.26 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 11: Preparation of poly [styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium chloride-*co*-divinylbenzene]

[00398] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 4 g, 16 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (50 ml) was added into the flask (*via* cannula under N_2) and stirred to form viscous slurry of polymer resin. 1-Methylbenzimidazole (3.2 g, 24.2mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 18h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with methylbenzimidazolium chloride groups was determined to be 1.63 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 12: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium bisulfate-*co*-divinylbenzene]

[00399] Poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-benzoimidazol-1-ium chloride-*co*-divinylbenzene] (5.5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 42 mL) and fuming sulfuric acid (20% free SO_3, 8 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 85°C for 4 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were

finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 1.53 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 13: Preparation of poly [styrene-*co*-1-(4-vinylbenzyl)-pyridinium chloride-*co*-divinylbenzene]

[00400] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 5 g, 20 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (45 ml) was added into the flask (*via* cannula under N_2) while stirring and consequently, the uniform viscous slurry of polymer resin was obtained. Pyridine(3 mL, 37.17 mmol) was then added to the resin slurry and stirred at 85-90°C for 18 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer resin with pyridinium chloride groups was determined to be 3.79 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 14: Preparation of poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridinium-bisulfate-*co*-divinylbenzene]

[00401] Poly[styrene-*co*-1-(4-vinylbenzyl)-pyridinium chloride-*co*-divinylbenzene] (4 g) resin beads were charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 45 mL) was gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored uniform slurry of resin. The slurry was heated at 95-100°C under continuous stirring for 5 h. After completion of reaction, the cooled reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 0.64 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 15: Preparation of poly [styrene-*co*-1-(4-vinylbenzyl)-pyridinium chloride-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00402] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and

condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) while stirring which resulted in the formation of viscous slurry of polymer resin. Pyridine(1.6 mL, 19.82 mmol) and 1-methylimidazole (1.7 mL, 21.62 mmol) were then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 18 h. After completion of reaction, the reaction mixture was cooled, filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with pyridinium chloride and 1-methylimidazolium chloride groups was determined to be 3.79 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 16: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-pyridiniumchloride-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium bisulfate-*co*-divinylbenzene]

[00403] Poly[styrene-*co*-1-(4-vinylbenzyl)-pyridinium chloride-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene](5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 75 mL) and fuming sulfuric acid (20% free SO_3, 2 mL)were then gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored uniform slurry of resin. The slurry was heated at 95-100°C under continuous stirring for 12 h. After completion of reaction, the cooled reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 1.16 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 17: Preparation of poly[styrene-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium chloride-*co*-divinylbenzene]

[00404] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (85 ml) was added into the flask (*via* cannula under N_2) while stirring which resulted in the formation of uniform viscous slurry of polymer resin. 1-Methylmorpholine (5.4 mL, 49.12mmol) were then added to the resin slurry and the resulting

reaction mixture was stirred at 95°C for 18 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with methylmorpholinium chloride groups was determined to be 3.33 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 18: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium bisulfate-*co*-divinylbenzene]

[00405] Poly [styrene-*co*-1-4-methyl-4-(4-vinylbenzyl)-morpholin-4-ium chloride-*co*-divinylbenzene](8 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 50 mL) was gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 90°C for 8 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 1.18 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 19: Preparation of [polystyrene-*co*-triphenyl-(4-vinylbenzyl)-phosphoniumchloride-*co*-divinylbenzene]

[00406] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) while stirring and the uniform viscous slurry of polymer resin was obtained. Triphenylphosphine (11.6 g, 44.23mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 18 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with triphenylphosphonium chloride groups was determined to be 2.07 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 20: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triphenyl-(4-vinylbenzyl)-phosphonium bisulfate-*co*-divinylbenzene]

[00407] Poly (styrene-*co*-triphenyl-(4-vinylbenzyl)-phosphonium chloride- *co*-divinylbenzene) (7 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 40 mL) and fuming sulfuric acid (20% free SO_3, 15 mL)were gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 95°C for 8 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 2.12 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 21: Preparation of poly[styrene-*co*-1-(4-vinylbenzyl)-piperidine-*co*-divinylbenzene]

[00408] Poly(styrene-*co*-vinylbenzyl chloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (50 ml) was added into the flask (*via* cannula under N_2) while stirring which resulted in the formation of uniform viscous slurry of polymer resin. Piperidine (4 g, 46.98 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 16 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried.

Example 22: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-(4-vinylbenzyl)-piperidine-*co*-divinyl benzene]

[00409] Poly[styrene-*co*-1-(4-vinylbenzyl)-piperidine-*co*-divinyl benzene] (7 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 45 mL) and fuming sulfuric acid (20% free SO_3, 12 mL) were gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 95°C for 8 h. After completion of reaction, the cooled reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer

with sulfonic acid groups was determined to be 0.72 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 23: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-1-methyl-1-(4-vinylbenzyl)-piperdin-1-ium chloride-*co*-divinyl benzene]

[00410] Poly (styrene-*co*-4-(1-piperidino)methylstyrene-*co*-divinylbenzene) (4 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (40 ml) was added into the flask (*via* cannula under N_2) under stirring to obtain uniform viscous slurry. Iodomethane (1.2 ml) and potassium iodide (10 mg) were then added into the flask. The reaction mixture was stirred at 95°C for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed multiple times with dilute HCl solution to ensure complete exchange of I^- with Cl^-. The resin was finally washed with de-ionized water until the effluent was neutral, as determined by pH paper. The resin was finally air-dried.

Example 24: Preparation of poly[styrene-*co*-4-(4-vinylbenzyl)-morpholine-*co*-divinyl benzene]

[00411] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (50 ml) was added into the flask (*via* cannula under N_2) while stirring and consequently, the uniform viscous slurry of polymer resin was obtained. Morpholine (4 g, 45.92 mmol) was then added to the resin slurry and the resulting reaction mixture was heated at 95°C under continuous stirring for 16 h. After completion of reaction, the reaction mixture was cooled, filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried.

Example 25: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-*co*-divinyl benzene]

[00412] Poly[styrene-*co*-4-(4-vinylbenzyl)-morpholine-*co*-divinyl benzene](10 g) was charged into a 200 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 90 mL) and fuming sulfuric acid (20% free SO_3, 10 mL)were gradually added into the flask while stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 95°C for 8 h. After cooling, the reaction

mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 0.34 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 26: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-4-oxide-*co*-divinyl benzene]

[00413] Poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-*co*-divinyl benzene](6 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Methanol (60 mL) was then charged into the flask, followed by addition of hydrogen peroxide (30 % solution in water, 8.5 mL). The reaction mixture was refluxed under continuous stirring for 8 h. After cooling, the reaction mixture was filtered, washed sequentially with de-ionized water and ethanol, and finally air dried.

Example 27: Preparation of poly[styrene-*co*-4-vinylbenzyl-triethylammonium chloride-*co*-divinylbenzene]

[00414] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) while stirring and consequently the uniform viscous slurry of polymer resin was obtained. Triethylamine(5 mL, 49.41 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 18 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer resin with triethylammonium chloride groups was determined to be 2.61 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 28: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-triethyl-(4-vinylbenzyl)-ammonium chloride-*co*-divinylbenzene]

[00415] Poly[styrene-*co*-triethyl-(4-vinylbenzyl)-ammonium chloride-*co*-divinylbenzene] (6 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 60 mL) was gradually added into the flask under

stirring which consequently resulted in the formation of dark-red colored uniform slurry of resin. The slurry was stirred at 95-100°C for 8 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 0.31 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 29:Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-divinylbenzene]

[00416] Poly(styrene-*co*-vinylbenzyl chloride-*co*-divinylbenzene) (6 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 25 mL) was gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 90°C for 5 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 0.34 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 30: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00417] Poly [styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride -*co*-divinylbenzene](5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (20 ml) was added into the flask (*via* cannula under N_2) while stirring and the uniform viscous slurry of polymer resin was obtained. 1-Methylimidazole (3 mL, 49.41 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 18 h. After cooling, reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water. The resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid group and methylimidiazolium chloride groups was determined to be 0.23 mmol/g and 2.63 mmol/g, respectively, as determined by titrimetry following the procedure of Example 2.

Example 31: Preparation of poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-4-boronyl-1-(4-vinylbenzyl)-pyridinium chloride-*co*-divinylbenzene]

[00418] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) while stirring and consequently the uniform viscous slurry of polymer resin was obtained. 4-Pyridyl-boronic acid(1.8 g, 14.6 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 2 days. 1-Methylimidazole(3 mL, 49.41 mmol) was then added to the reaction mixture and stirred further at 95°C for 1 day. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with boronic acid group was determined to be 0.28 mmol/g respectively, as determined by titrimetry following the procedure of Example 2.

Example 32: Preparation of poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-ium chloride-*co*-1-(4-vinylphenyl)methylphosphonic acid-*co*-divinylbenzene]

[00419] Poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene](Cl^- density= ~ 2.73 mmol/g, 5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Triethylphosphite (70 ml) was added into the flask and the resulting suspension was stirred at 120°C for 2 days. The reaction mixture was filtered using fritted glass funnel and the resin beads were washed repeatedly with de-ionized water and ethanol. These resin beads were then suspended in concentrated HCl (80 ml) and refluxed at 115°Cunder continuous stirring for 24 h. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water. The resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with phosphonic acid group and methylimidiazolium chloride groups was determined to be 0.11 mmol/g and 2.81 mmol/g, respectively, as determined by titrimetry following the procedure of Example 2.

Example 33: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-vinyl-2-pyridine-*co*-divinylbenzene]

[00420] Poly (styrene-*co*-vinylbenzylchloride-*co*-vinyl-2-pyridine-*co*-divinylbenzene) (5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 80 mL) was gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was

stirred at 95°C for 8 h. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum, washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with sulfonic acid groups was determined to be 3.49 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 34: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-vinylbenzylchloride-*co*-1-methyl-2-vinyl-pyridinium chloride-*co*-divinylbenzene]

[00421] Poly [styrene-*co*-4-vinylbenzenesulfonic acid -*co*-vinylbenzylchloride-*co*-vinyl-2-pyridine-*co*-divinylbenzene] (4 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) under stirring to obtain uniform viscous slurry. Iodomethane (1.9 ml) was then gradually added into the flask followed by addition of potassium iodide (10 mg). The reaction mixture was stirred at 95°C for 24 h. After cooling to room temperature, the cooled reaction mixture was filtered using fritted glass funnel under vacuum and then washed multiple times with dilute HCl solution to ensure complete exchange of I^- with Cl^- . The resin beads were finally washed with de-ionized water until the effluent was neutral, as determined by pH paper and then air-dried.

Example 35: Preparation of poly[styrene-*co*-4-vinylbenzenesulfonic acid-*co*-4-(4-vinylbenzyl)-morpholine-4-oxide-*co*-divinyl benzene]

[00422] Poly[styrene-*co*-4-(4-vinylbenzyl)-morpholine-4-oxide-*co*-divinyl benzene] (3 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Cold concentrated sulfuric acid (>98% w/w, H_2SO_4, 45 mL) was gradually added into the flask under stirring which consequently resulted in the formation of dark-red colored slurry. The slurry was stirred at 95°C for 8 h. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum, washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were finally washed with ethanol and air dried.

Example 36: Preparation of poly [styrene-*co*-4-vinylphenylphosphonic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00423] Poly[styrene-*co*-3-methyl-1-(4-vinylbenzyl)-3H-imidazol-1-iumchloride-*co*-divinylbenzene] (Cl^- density= ~ 2.73 mmol/g, 5 g) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Diethylphosphite (30 ml) and *t*-butylperoxide (3.2 ml) were added into the flask and the resulting suspension was stirred at 120°C for 2 days. The reaction mixture was filtered using fritted glass funnel and the resin beads were washed repeatedly with de-ionized water and ethanol. These resin beads were then suspended in concentrated HCl (80 ml) and refluxed at 115°C under continuous stirring for 2 days. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water. The resin beads were finally washed with ethanol and air dried. The chemical functionalization of the polymer with aromatic phosphonic acid group was determined to be 0.15 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 37: Preparation of poly[styrene-*co*-3-carboxymethyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00424] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dimethylformamide (50 ml) was added into the flask and stirred to form a slurry of resin. Imidazole(2.8 g, 41.13mmol) was then added to the resin slurry and stirred at 80°C for 8 h. The reaction mixture was then cooled to 40°C and *t*-butoxide(1.8 g) was added into the reaction mixture and stirred for 1 h. Bromoethylacetate (4 ml) was then added to and the reaction mixture was stirred at 80°C for 6 h. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water. The washed resin beads were suspended in the ethanolic sodium hydroxide solution and refluxed overnight. The resin beads were filtered and successively washed with deionized water multiple times and ethanol, and finally air dried. The chemical functionalization of the polymer with carboxylic acid group was determined to be 0.09 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 38: Preparation of poly[styrene-*co*-5-(4-vinylbenzylamino)-isophthalic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00425] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2) while stirring and consequently the uniform viscous slurry of polymer resin was obtained. Dimethyl aminoisophthalate(3.0 g, 14.3 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 16 h. 1-Methylimidazole(2.3 mL, 28.4 mmol) was then added to the reaction mixture and stirred further at 95°C for 1 day. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol. The washed resin beads were suspended in the ethanolic sodium hydroxide solution and refluxed overnight. The resin beads were filtered and successively washed with deionized water multiple times and ethanol, and finally air dried. The chemical functionalization of the polymer with carboxylic acid group was determined to be 0.16 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 39: Preparation of poly[styrene-*co*-(4-vinylbenzylamino)-acetic acid-*co*-3-methyl-1-(4-vinylbenzyl)-3*H*-imidazol-1-ium chloride-*co*-divinylbenzene]

[00426] Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (Cl^- density= ~ 4.0 mmol/g, 10 g, 40 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Dry dimethylformamide (80 ml) was added into the flask (*via* cannula under N_2)while stirring and consequently the uniform viscous slurry of polymer resin was obtained. Glycine (1.2 g, 15.9 mmol) was then added to the resin slurry and the resulting reaction mixture was stirred at 95°C for 2 days. 1-Methylimidazole(2.3 mL, 28.4 mmol) was then added to the reaction mixture and stirred further at 95°C for 12 hours. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with de-ionized water and ethanol, and finally air dried. The chemical functionalization of the polymer with carboxylic acid group was determined to be 0.05 mmol/g, as determined by titrimetry following the procedure of Example 2.

Example 40: Preparation of poly[styrene-co-(1-vinyl-1*H*-imidazole)-co-divinylbenzene]

[00427] To a 500 mL round bottom flask (RBF) containing a stirred solution of 1.00 g of poly(vinylalcohol) in 250.0 mL of deionized H_2O at 0°C is gradually added a solution containing 35 g (371mmol) of 1-vinylimidazole, 10 g (96 mmol) of styrene, 1 g (7.7mmol) of divinylbenzene (DVB) and 1.5 g (9.1mmol) of azobisisobutyronitrile (AIBN) in 150 mL of a 1:1

(by volume) mixture of benzene / tetrahydrofuran (THF) at 0°C. After 2 hours of stirring at 0 °C to homogenize the mixture, the reaction flask is transferred to an oil bath to increase the reaction temperature to 75°C, and the mixture is stirred vigorously for 24 hours. The resulting polymer is vacuum filtered using a fritted-glass funnel, washed repeatedly with 20% (by volume) methanol in water, THF, and MeOH, and then dried overnight at 50°C under reduced pressure.

Example 41: Preparation of poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00428] 1-methylimidazole (4.61 g, 56.2 mmol), 4-methylmorpholine (5.65 g, 56.2 mmol), and triphenylphosphine (14.65, 55.9 mmol) were charged into a 500 mL flask equipped with a magnetic stir bar and a condenser. Acetone (100 ml) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (1% DVB, Cl^- density= 4.18 mmol / g dry resin, 40.22g, 168 mmol) was charged into the flask while stirring until a uniform polymer suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using a fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried overnight at 70 °C. The chemical functionalization of the polymer resin with chloride groups was determined to be 2.61 mmol / g dry resin *via* titrimetry.

Example 42: Preparation of sulfonated poly(styrene-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00429] Poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (35.02 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 175 mL) was gradually added into the flask and stirred to form dark-red resin suspension. The mixture was stirred overnight at 90°C. After cooling to room temperature, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated polymer resin was air dried to a final moisture content of 56% g H_2O / g wet polymer. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 3.65 mmol / g dry resin.

Example 43: Preparation of poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00430] 1-methylimidazole (7.02 g, 85.5 mmol), 4-methylmorpholine (4.37 g, 43.2 mmol) and triphenylphosphine (11.09, 42.3 mmol) were charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Acetone (100 ml) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (1% DVB, Cl^- density= 4.18 mmol / g dry resin, 40.38g, 169 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 18 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight. The chemical functionalization of the polymer resin with chloride groups was determined to be 2.36 mmol / g dry resin dry resin *via* titrimetry.

Example 44: Preparation of sulfonated poly(styrene-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00431] Poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-co-vinylbenzyltriphenylphosphonium chloride-co-divinylbenzene) (35.12 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 175 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were finally air dried. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 4.38 mmol / g dry resin.

Example 45: Preparation of poly(styrene-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00432] 4-methylmorpholine (8.65 g, 85.5 mmol) and triphenylphosphine (22.41, 85.3 mmol) were charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Acetone (100 ml) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (1 % DVB, Cl^- density= 4.18 mmol / g dry resin,

40.12g, 167 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight. The chemical functionalization of the polymer resin with chloride groups was determined to be 2.22 mmol / g dry resin *via* titrimetry.

Example 46: Preparation of sulfonated poly(styrene-*co*-vinylbenzylmethylmorpholinium bisulfate-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene)

[00433] Poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-vinylbenzylmethylmorpholinium chloride-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (35.08 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 175 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 52% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 4.24 mmol / g dry resin.

Example 47: Preparation of phenol-formaldehyde resin

[00434] Phenol (12.87 g, 136.8 mmol) was dispensed into a 100 mL round bottom flask (RBF) equipped with a stir bar and condenser. De-ionized water (10g) was charged into the flask. 37% Formalin solution (9.24g, 110 mmol) and oxalic acid (75mg) were added. The resulting reaction mixture was refluxed for 30 min. Additional oxalic acid (75mg) was then added and refluxing was continued for another 1 hour. Chunk of solid resin was formed, which was ground to a coarse powder using a mortar and pestle. The resin was repeatedly washed with water and methanol and then dried at 70 °C overnight.

Example 48: Preparation of chloromethylated phenol-formaldehyde resin

[00435] Phenol-formaldehyde resin (5.23 g, 44 mmol) was dispensed into a 100 mL three neck round bottom flask (RBF) equipped with a stir bar, condenser and nitrogen line. Anhydrous dichloroethane (DCE, 20ml) was then charged into the flask. To ice-cooled suspension of resin in DCE, zinc chloride (6.83g, 50 mmol) was added. Chloromethyl methyl

ether (4.0 ml, 51 mmol) was then added dropwise into the reaction. The mixture was warmed to room temperature and stirred at 50°C for 6h. The product resin was recovered by vacuum filtration and washed sequentially with water, acetone and dichloromethane. The washed resin was dried at 40°C overnight.

Example 49: Preparation of triphenylphosphine functionalized phenol-formaldehyde resin

[00436] Triphenylphosphine (10.12, 38.61 mmol) were charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Acetone (30 ml) was added into the flask and mixture was stirred at 50°C for 10 min. Chloromethylated phenol-formaldehyde resin (4.61g, 38.03 mmol) was charged into flask while stirring. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70°C overnight.

Example 50: Preparation of sulfonated triphenylphosphine-functionalized phenol-formaldehyde resin

[00437] Triphenylphosphine-functionalized phenol-formaldeyde resin (5.12 g, 13.4 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 25 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated resin was dried under air to a final moisture content of 49% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 3.85 mmol / g dry resin.

Example 51: Preparation of poly(styrene-*co*-vinylimidazole-*co*-divinylbenzene)

[00438] De-ionized water (75mL) was charged into flask into a 500 mL three neck round bottom flask equipped with a mechanical stirrer, condenser and N_2 line. Sodium chloride (1.18g) and carboxymethylcellulose (0.61g) were charged into the flask and stirred for 5 min. The solution of vinylimidazole (3.9 mL, 42.62 mmol), styrene (4.9 mL, 42.33 mmol) and divinylbenzene (0.9 mL, 4.0 mmol) in iso-octanol (25mL) was charged into flask. The resulting emulsion was stirred at 500 rpm at room temperature for 1h. Benzoyl peroxide (75%, 1.205g) was added, and temperature was raised to 80 °C. The reaction mixture was heated for 8h at 80 °C

with stirring rate of 500 rpm. The polymer product was recovered by vacuum filtration and washed with water and acetone multiple times. The isolated polymer was purified by soxhlet extraction with water and acetone. The resin was dried at 40°C overnight.

Example 52: Preparation of poly(styrene-*co*-vinylmethylimidazolium iodide-*co*-divinylbenzene)

[00439] Poly(styrene-*co*-vinylimidazole-*co*-divinylbenzene) (3.49 g, 39 mmol) was dispensed into a 100 mL three neck round bottom flask (RBF) equipped with a stir bar, condenser and nitrogen line. Anhydrous tetrahydrofuran (20ml) was then charged into the flask. To ice-cooled suspension of resin in tetrahydrofuran, potassium *t*-butoxide (5.62 g, 50 mmol) was added and stirred for 30 min. Iodomethane (3.2 ml, 51 mmol) was then added dropwise into the reaction. The mixture was warmed to room temperature and stirred at 50°C for 6h. The product resin was recovered by vacuum filtration and washed sequentially with water, acetone and dichloromethane. The washed resin was dried at 40°C overnight.

Example 53: Preparation of sulfonated poly(styrene-*co*-vinylmethylimidazolium bisulfate-*co*-divinylbenzene)

[00440] Poly(styrene-*co*-vinylmethylimidazolium iodide-*co*-divinylbenzene) (3.89 g, 27.8 mmol) was charged into a 100 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 20 mL) was gradually added into the flask and stirred to form dark-red colored slurry. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated polymer was dried under air to a final moisture content of 51% g H_2O / g wet resin.

Example 54: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00441] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (38.44 g, 145.1mmol). Acetone (50 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (8% DVB, Cl^- density= 4.0 mmol / g dry resin, 30.12g, 115.6 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under

vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight. The chemical functionalization of the polymer resin with triphenylphosphonium chloride groups was determined to be 1.94 mmol / g dry resin *via* titrimetry.

Example 55: Preparation of sulfonated poly(styrene-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00442] Poly(styrene-*co*- vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (40.12 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 160 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 54% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 4.39 mmol / g dry resin.

Example 56: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene

[00443] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (50.22 g, 189.6 mmol). Acetone (50 mL) was added into the flask and mixture was stirred at 50 oC for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (4% DVB, Cl^- density= 5.2 mmol / g dry resin, 30.06g, 152.08 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight. The chemical functionalization of the polymer resin with triphenylphosphonium chloride groups was determined to be 2.00 mmol / g dry resin *via* titrimetry.

Example 57: Preparation of sulfonated poly(styrene-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00444] Poly(styrene-*co*- vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (40.04 g,) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 160 mL) was gradually added into the flask and stirred to

form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 47% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 4.36 mmol / g dry resin.

Example 58: Preparation of poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene)

[00445] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged 1-methylimidazole (18mL, 223.5 mmol). Acetone (75 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (8% DVB, Cl^- density= 4.0 mmol / g dry resin, 40.06, 153.7 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70°C overnight. The chemical functionalization of the polymer resin with methylimidazolium chloride groups was determined to be 3.54 mmol / g dry resin *via* titrimetry.

Example 59: Preparation of sulfonated poly(styrene-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-divinylbenzene)

[00446] Poly(styrene-*co*- vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene) (30.08 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 120 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 50% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 2.87 mmol / g dry resin.

Example 60: Preparation of poly(styrene-*co*-vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene)

[00447] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged 1-methylimidazole (20mL, 248.4 mmol). Acetone (75 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (4% DVB, Cl^- density= 5.2 mmol / g dry resin, 40.08, 203.8 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70°C overnight. The chemical functionalization of the polymer resin with methylimidazolium chloride groups was determined to be 3.39 mmol / g dry resin *via* titrimetry.

Example 61: Preparation of sulfonated poly(styrene-*co*-vinylbenzylmethylimidazolium bisulfate-*co*-divinylbenzene)

[00448] Poly(styrene-*co*- vinylbenzylmethylimidazolium chloride-*co*-divinylbenzene) (30.14 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 120 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 55% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 2.78 mmol / g dry resin.

Example 62: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00449] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (44.32 g, 163.9mmol). Acetone (50 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (13% DVB macroporous resin, Cl^- density= 4.14 mmol / g dry resin, 30.12g, 115.6 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight.

Example 63: Preparation of sulfonated poly(styrene-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00450] Poly(styrene-*co*- vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (30.22 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 90 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C for 1 hour. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 46% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 2.82 mmol / g dry resin.

Example 64: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00451] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (55.02 g, 207.7mmol). Acetone (50 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (6.5% DVB macroporous resin, Cl^- density= 5.30 mmol / g dry resin, 30.12g, 157.4 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70°C overnight.

Example 65: Preparation of sulfonated poly(styrene-co-vinylbenzyltriphenyl phosphonium bisulfate-co-divinylbenzene)

[00452] Poly(styrene-*co*- vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (30.12 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 90 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C for 1 hour. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 49% g H_2O / g wet resin. The chemical

functionalization of the polymer resin with sulfonic acid groups was determined to be 2.82 mmol / g dry resin.

Example 66: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00453] To a 250 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (38.42 g, 145.0 mmol). Acetone (50 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (4% DVB, Cl^- density= 4.10 mmol / g dry resin, 30.12g, 115.4 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70°C overnight.

Example 67: Preparation of sulfonated poly(styrene-*co*-vinylbenzyltriphenylphosphonium bisulfate-*co*-divinylbenzene)

[00454] Poly(styrene-*co*- vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (30.18 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 120 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 59% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 3.03 mmol / g dry resin.

Example 68: Preparation of poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene)

[00455] To a 500 mL flask equipped with a magnetic stir bar and condenser was charged triphenylphosphine (44.22 g, 166.9 mmol). Acetone (70 mL) was added into the flask and mixture was stirred at 50 °C for 10 min. Poly(styrene-*co*-vinylbenzylchloride-*co*-divinylbenzene) (4% DVB, Cl^- density= 3.9 mmol / g dry resin, 35.08 g, 130.4 mmol) was charged into flask while stirring until a uniform suspension was obtained. The resulting reaction mixture was

refluxed for 24 h. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum, washed sequentially with acetone and ethyl acetate, and dried at 70 °C overnight.

Example 69: Preparation of sulfonated poly(styrene-*co*-vinylbenzyltriphenyl phosphonium bisulfate-*co*-divinylbenzene)

[00456] Poly(styrene-*co*-vinylbenzyltriphenylphosphonium chloride-*co*-divinylbenzene) (30.42 g) was charged into a 500 mL flask equipped with a magnetic stir bar and condenser. Fuming sulfuric acid (20% free SO_3, 120 mL) was gradually added into the flask and stirred to form dark-red colored slurry of resin. The slurry was stirred at 90°C overnight. After cooling, the reaction mixture was filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent was neutral, as determined by pH paper. The sulfonated beads were dried under air to a final moisture content of 57% g H_2O / g wet resin. The chemical functionalization of the polymer resin with sulfonic acid groups was determined to be 3.04 mmol / g dry resin.

Example 70: Preparation of poly(butyl-vinylimidazolium chloride–*co*–butylimidazolium chloride–*co*–styrene)

[00457] To a 500 mL flask equipped with a mechanical stirrer and reflux condenser is added 250 mL of acetone, 10g of imidzole, 14g of vinylimidazole, 15g of styrene, 30g of dichlorobutane and 1g of azobisisobutyronitrile (AIBN). The solution is stirred under reflux conditions for 12 hours to produce a solid mass of polymer. The solid polymer is removed from the flask, washed repeatedly with acetone, and ground to a coarse powder using a mortar and pestle to yield the product.

Example 71: Preparation of sulfonated poly(butyl-vinylimidazolium bisulfate–*co*–butylimidazolium bisulfate–*co*–styrene)

[00458] Poly(butyl-vinylimidazolium chloride–*co*–butylimidazolium chloride–*co*–styrene) 30.42 g) is charged into a 500 mL flask equipped with a mechanical stirrer. Fuming sulfuric acid (20% free SO_3, 120 mL) is gradually added into the flask until the polymer is fully suspended. The resulting slurry is stirred at 90°C for 5 hours. After cooling, the reaction mixture is filtered using fritted glass funnel under vacuum and then washed repeatedly with de-ionized water until the effluent is neutral, as determined by pH paper.

Catalytic Digestion of Lignocellulosic Materials

Example B1: Digestion of Sugarcane Bagasse using Catalyst described in Example 3

[00459] Sugarcane bagasse (50% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. The composition of the lignocellulosic biomass was determined using a method based on the procedures known in the art. *See* R. Ruiz and T. Ehrman, "Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography," NREL Laboratory Analytical Procedure LAP-002 (1996); D. Tempelton and T. Ehrman, "Determination of Acid-Insoluble Lignin in Biomass," NREL Laboratory Analytical Procedure LAP-003 (1995); T. Erhman, "Determination of Acid-Soluble Lignin in Biomass," NREL Laboratory Analytical Procedure LAP-004 (1996); and T. Ehrman, "Standard Method for Ash in Biomass," NREL Laboratory Analytical Procedure LAP-005 (1994).

[00460] To a 15 mL cylindrical glass reaction vial was added: 0.50 g of the cane bagasse sample, 0.30 g of Catalyst as prepared in Example 3 (initial moisture content: 12% g H_2O / g dispensed catalyst), and 800μL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 120°C for four hours.

Example B2: Separation of Catalyst/Product Mixture from the Hydrolysis of Sugarcane Bagasse

[00461] The cylindrical glass reactor from Example B1 was cooled to room temperature and unsealed. 5.0 mL of distilled H_2O was added to the vial reactor and the resulting mixture of liquids and solids was agitated for 2 minutes by magnetic stirring. Following agitation, the solids were allowed to sediment for 30 seconds to produce the layered mixture. The solid catalyst formed a layer at the bottom of the vial reactor. Lignin and residual biomass formed a solid layer above the solid catalyst. The short-chained beta-glucans formed a layer of amorphous solids above the lignin and residual biomass. Finally, the soluble sugars formed a liquid layer above the short-chained beta-glucans.

Example B3: Recovery of Sugars and Soluble Carbohydrates from the Hydrolysis of Sugarcane Bagasse

[00462] The supernatant and residual insoluble materials from Example B2 were separated by decantation. The soluble-sugar content of hydrolysis products was determined by a combination of high performance liquid chromatography (HPLC) and spectrophotometric methods. HPLC determination of soluble sugars and oligosaccharides was performed on a Hewlett-Packard 1050 Series instrument equipped with a refractive index (RI) detector using a 30 cm x 7.8 mm Phenomenex HPB column with water as the mobile phase. The sugar column was protected by both a lead-exchanged sulfonated-polystyrene guard column and a tri-alkylammoniumhydroxide anionic-exchange guard column. All HPLC samples were microfiltered using a 0.2 μm syringe filter prior to injection. Sample concentrations were determined by reference to a calibration generated from known standards.

[00463] The ability of the catalyst to hydrolyze the cellulose and hemicellulose components of the biomass to soluble sugars was measured by determining the effective first-order rate constant. The extent of reaction for a chemical species (*e.g.*, glucan, xylan, arabinan) was determined by calculating the ratio of moles of the recovered species to the theoretical moles of the species that would be obtained as a result of complete conversion of the input reactant based on the known composition of the input biomass and the known molecular weights of the reactants and products and the known stoichiometries of the reactions under consideration.

[00464] For the digestion of sugarcane bagasse using catalyst as described in Example 3, the first-order rate constant for conversion of xylan to xylose was determined to be 0.3/hr. The first-order rate constant for conversion of glucan to soluble monosaccharides and oligosaccharides (including disaccharides) was determined to be 0.08/hr.

Example B4: Recovery of Insoluble Oligo-glucans from Hydrolyzed Sugarcane Bagasse

[00465] An additional 5.0 mL of water was added to the residual solids from Example B3 and the mixture was gently agitated to suspend only the lightest particles. The suspension was decanted to remove the light particles from the residual lignin and residual catalyst, which remained in the solid sediment at the bottom of the reactor. The solid particles were concentrated by centrifugation.

[00466] The number average degree of polymerization (DOP_N) of residual water-insoluble glucans (including short-chain oligosaccharides)was determined by extracting the glucans into ice-cold phosphoric acid, precipitating the extracted carbohydrates into water, and measuring the ratio of terminal reducing sugars to the number of total sugar monomers the method of Zhang and Lynd. *See* Y.-H. Percival Zhang and Lee R. Lynd, "Determination of the Number-Average Degree of Polymerization of Cellodextrins and Cellulose with Application to Enzymatic Hydrolysis," *Biomacromolecules*, 6, 1510-1515 (2005). UV-Visible spectrophotometric analysis was performed on a Beckman DU-640 instrument. In cases where the digestion of hemicellulose was complete (as determined by HPLC), DOP determination of the residual cellulose was performed without the need for phosphoric acid extraction. In some cases, the number average degree of polymerization was verified by Gel Permeation Chromatography (GPC) analysis of cellulose was performed using a procedure adapted from the method of Evans *et al.* *See* R. Evans, R. Wearne, A.F.A. Wallis, "Molecular Weight Distribution of Cellulose as Its Tricarbanilate by High Performance Size Exclusion Chromatography," *J. Appl. Pol. Sci.*, 37, 3291-3303 (1989).

[00467] In a 20 mL reaction vial containing 3 mL of dry DMSO, was suspended an approximately 50 mg sample of cellulose (dried overnight at 50°C under reduced pressure). The reaction vial was sealed with a PFTE septum, flushed with dry N_2, followed by addition of 1.0 mL phenylisocyanate via syringe. The reaction mixture was incubated at 60°C for 4 hours with periodic mixing, until the majority of cellulose was dissolved. Excess isocyanate was quenched by addition of 1.0 mL of dry MeOH. Residual solids were pelletized by centrifugation, and a 1 mL aliquot of the supernatant was added to 5 mL of 30% v/v MeOH / dH_2O to yield the carbanilated cellulose as an off-white precipitate. The product was recovered by centrifugation, and repeatedly washed with 30% v/v MeOH, followed by drying for 10 hours at 50°C under reduced pressure. GPC was performed on a Hewlett-Packard 1050 Series HPLC using a series of TSK-Gel (G3000Hhr, G4000Hhr, G5000Hhr) columns and tetrahydrofuran (THF) as the mobile phase with UV/Vis detection. The molecular weight distribution of the cellulose was determined using a calibration based on polystyrene standards of known molecular weight.

[00468] For the digestion of sugarcane bagasse using catalyst as shown in Example 3, the number average degree of polymerization of the oligo-glucans was determined to be 19 ± 4 anhydroglucose (AHG) units. The observed reduction of the degree of polymerization of the residual cellulose to a value significantly lower than the degree of polymerization for the

crystalline domains of the input cellulose (for which DOP_N> 200 AHG units) indicates that the catalyst successfully hydrolyzed crystalline cellulose. The first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.2/hr.

Example B5: Separation and Recovery of Lignin, Residual Unreacted Biomass and Catalyst from Hydrolyzed Sugarcane Bagasse

[00469] An additional 10mL of water was added to the residual solids in Example B4. The mixture was agitated to suspend the residual lignin (and residual unreacted biomass particles) without suspending the catalyst. The recovered catalyst was washed with water and then dried to constant mass at 110°C in a gravity oven to yield 99.6% g/g recovery. The functional density of sulfonic acid groups on the recovered catalyst was determined to be 1.59±0.02mmol/g by titration of the recovered catalyst indicating negligible loss of acid functionalization.

Example B6: Reuse of Recovered Catalyst

[00470] Some of the catalyst recovered from Example B5 (0.250 g dry basis) was returned to the 15 mL cylindrical vial reactor. 0.50 g of additional biomass (composition identical to that in Example 45) and 800 μL of deionized H_2O were added to the reactor, and the contents were mixed thoroughly, as described in Example 41. The reactor was sealed and incubated at 115°C for four hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2-B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.3/hr. The first-order rate constant for conversion of glucan to soluble monosaccharides and oligosaccharides (including disaccharides) was determined to be 0.1/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N = 20±4AHG units, and the first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.2/hr.

Example B7: Hydrolysis of Corn Stover using Catalyst as prepared in Example 34

[00471] Corn stover (7.2% g H_2O/g wet biomass, with a dry-matter composition of: 33.9% g glucan/g dry biomass, 24.1% g xylan / g dry biomass, 4.8% g arabinan / g dry biomass, 1.5% g galactan / g dry biomass, 4.0% g acetate / g dry biomass, 16.0% g soluble extractives / g dry biomass, 11.4% g lignin / g dry biomass, and 1.4% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.45 g of the cane bagasse sample, 0.22 g of Catalyst as prepared in Example 34 (initial

moisture content: 0.8% g H_2O / g dispensed catalyst), and 2.3 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 110°C for five hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.1/hr. The first-order rate constant for conversion of glucan to soluble monosaccharides and oligosaccharides (including disaccharides) was determined to be 0.04/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N= 20±4 AHG units, and the first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.06/hr.

Example B8: Hydrolysis of Oil Palm Empty Fruit Bunches using Catalyst as prepared in Example 20

[00472] Shredded oil palm empty fruit bunches (8.7% g H_2O/g wet biomass, with a dry-matter composition of: 35.0% g glucan/g dry biomass, 21.8% g xylan / g dry biomass, 1.8% g arabinan / g dry biomass, 4.8% g acetate / g dry biomass, 9.4% g soluble extractives / g dry biomass, 24.2% g lignin / g dry biomass, and 1.2% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.46 g of the cane bagasse sample, 0.43 g of Catalyst as prepared in Example 20 (initial moisture content: 18.3% g H_2O / g dispensed catalyst), and 1.3 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 110°C for five hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.4/hr. The first-order rate constant for conversion of glucan to soluble monosaccharides and oligosaccharides (including disaccharides) was determined to be 0.04/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N = 20±4AHG units, and the first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.06/hr.

Example B9: Hydrolysis of Sugarcane Bagasse using Catalyst as prepared in Example 32

[00473] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.53 g of the cane bagasse sample, 0.52 g of Catalyst as prepared in Example 32 (initial moisture content: 3.29% g H_2O / g dispensed catalyst), and 1.4 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for four hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.59/hr. The first-order rate constant for conversion of glucan to soluble monosaccharides and oligosaccharides (including disaccharides) was determined to be 0.05/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N = 23±4AHG units, and the first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.07/hr.

Example B10: Hydrolysis of Sugarcane Bagasse using Catalyst as prepared in Example 18

[00474] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.51 g of the cane bagasse sample, 0.51 g of Catalyst as prepared in Example 18 (initial moisture content: 7.9% g H_2O / g dispensed catalyst), and 1.4 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for four hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.06/hr. The first-order rate constant for conversion of glucan to soluble oligo-, di-, and mono-saccharides was determined to be 0.05/hr. The number average degree of

polymerization of residual cellulose was determined to be 20±4AHG units, and the first order rate constant for conversion of β-glucan to short-chain oligo-glucans was determined to be 0.07/hr.

Example B11: High-Selectivity to Sugars

[00475] Shredded oil palm empty fruit bunches (8.7% g H_2O/g wet biomass, with a dry-matter composition of: 35.0% g glucan/g dry biomass, 21.8% g xylan / g dry biomass, 1.8% g arabinan / g dry biomass, 4.8% g acetate / g dry biomass, 9.4% g soluble extractives / g dry biomass, 24.2% g lignin / g dry biomass, and 1.2% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.51 g of the cane bagasse sample, 0.51 g of Catalyst as prepared in Example 3 (initial moisture content: 8.9% g H_2O / g dispensed catalyst), and 2.6 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for four hours. Following the reaction, 10.0 mL of deionized H_2O was added to the product mixture to dissolve the soluble species and the solids were allowed to sediment. HPLC determination of sugar dehydration products and organic acids liberated from biomass samples was performed on an Agilent 1100 Series instrument using a 30cm x 7.8 mm Supelcogel™ H column (or a Phenomenex HOA column in some cases) with 0.005N sulfuric acid in water as the mobile phase. Quantitation of sugar degradation products: formic acid, levulinic acid, 5-hydroxymethylfurfural, and 2-furaldehyde, was performed by reference to a calibration curve generated from high-purity solutions of known concentration. The first order rate constant for the production of degradation products was found to be < 0.001/hr, representing >99% mol sugars / mol degradation products.

Example B12: Fermentation of Cellulosic Sugars from Sugarcane Bagasse

[00476] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 1.6 g of the cane bagasse sample, 1.8 g of Catalyst as prepared in Example 3 (initial

moisture content: 12.1% g H_2O / g dispensed catalyst), and 5.0 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 110°C for five hours. After five hours, an additional 1.0 mL of distilled H2O was added to the reaction mixture, which was then incubated at 105°C for an additional 2 hours. The wet reactant cake was loaded into a syringe equipped with a 0.2 micrometer filter and the hydrolysate was pressed out of the product mixture into a sterile container. To a culture tube was added 2.5mL of culture media (prepared by diluting 10 g of yeast extract and 20 g peptone to 500 mL in distilled water, followed by purification by sterile filtration), 2.5 mL of the hydrolysate, and 100 mL of yeast slurry (prepared by dissolving 500mg of Alcotec 24 hour Turbo Super yeast into 5mL of 30°C of sterile H_2O. The culture was grown at 30°C in shaking incubator, with 1 mL aliquots removed at 24, 48 and 72 hours. For each aliquot, the optical density of the culture was determined by spectrophotometer aliquot. The aliquot was purified by centrifugation and the supernatant was analyzed by HPLC to determine the concentrations of glucose, xylose, galactose, arabinose, ethanol, and glycerol. After 24 hours, ethanol and glycerol were found in the fermentation supernatant, indicating at least 65% fermentation yield on a molar basis relative to the initial glucose in the hydrolysate.

Example B13: Fermentation of Cellulosic Sugars from Cassava Stem

[00477] Cassava stem (2.0% g H_2O/g wet cassava stem, with a dry-matter composition of: 53.0% g glucan/g dry biomass, 6.0% g xylan / g dry biomass, 2.5% g arabinan / g dry biomass, 5.5% g acetate / g dry biomass, 5.9% g soluble extractives / g dry biomass, 24.2% g lignin / g dry biomass, and 2.1% g ash / g dry biomass) was shredded in a coffee-grinder such that the maximum particle size was no greater than 2 mm. To a 15 mL cylindrical glass reaction vial was added: 1.9 g of the shredded cassava stem, 2.0 g of Catalyst as prepared in Example 3 (initial moisture content: 12.0% g H_2O / g dispensed catalyst), and 8.0 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 110°C for five hours. After five hours, an additional 2.0 mL of distilled H2O was added to the reaction mixture, which was then incubated at 105°C for an additional 2 hours. The wet reactant cake was loaded into a syringe equipped with a 0.2 micrometer filter and the hydrolysate was pressed out of the product

mixture into a sterile container. To a culture tube was added 2.5mL of culture media (prepared by diluting 10 g of yeast extract and 20 g peptone to 500 mL in distilled water, followed by purification by sterile filtration), 2.5 mL of the hydrolysate, and 100 mL of yeast slurry (prepared by dissolving 500mg of Alcotec 24 hour Turbo Super yeast into 5mL of 30°C of sterile H_2O. The culture was grown at 30°C in shaking incubator, with 1 mL aliquots removed at 24, 48 and 72 hours. For each aliquot, the optical density of the culture was determined by spectrophotometer aliquot. The aliquot was purified by centrifugation and the supernatant was analyzed by HPLC to determine the concentrations of glucose, xylose, galactose, arabinose, ethanol, and glycerol. After 24 hours, ethanol and glycerol were found in the fermentation supernatant, indicating at least 70% fermentation yield on a molar basis relative to the initial glucose in the hydrolysate.

Example B14: Fermentation of Glucose obtained from Insoluble Starch

[00478] To 15 mL cylindrical glass reaction vial was added: 4.0 g of corn starch (3% g H_2O/g wet starch, with a dry-matter composition of: 98% g glucan/g dry biomass), 3.9 g of Catalyst as prepared in Example 3 (initial moisture content: 12.25% g H_2O / g dispensed catalyst), and 12.0 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 110°C for five hours. After five hours, an additional 2.0 mL of distilled H2O was added to the reaction mixture, which was then incubated at 105°C for an additional 2 hours. The wet reactant cake was loaded into a syringe equipped with a 0.2 micrometer filter and the hydrolysate was pressed out of the product mixture into a sterile container. To a culture tube was added 2.5mL of culture media (prepared by diluting 10 g of yeast extract and 20 g peptone to 500 mL in distilled water, followed by purification by sterile filtration), 2.5 mL of the hydrolysate, and 100 mL of yeast slurry (prepared by dissolving 500mg of Alcotec 24 hour Turbo Super yeast into 5mL of 30°C of sterile H_2O. The culture was grown at 30°C in shaking incubator, with 1 mL aliquots removed at 24, 48 and 72 hours. For each aliquot, the optical density of the culture was determined by spectrophotometer aliquot. The aliquot was purified by centrifugation and the supernatant was analyzed by HPLC to determine the concentrations of glucose, xylose, galactose, arabinose, ethanol, and glycerol. After 24 hours, ethanol and glycerol were found in the fermentation supernatant, indicating at least 88% fermentation yield on a molar basis relative to the initial glucose in the hydrolysate.

Example B15: Enzymatic Saccharification of Oligo-glucans Obtained from Digestion of Sugarcane Bagasse with Catalyst as prepared in Example 3

[00479] 50.0 mg of the oligo-gucans obtained in Example B4 was suspended in 0.4 mL of 0.05 molar acetate buffer solution at pH 4.8 in a culture tube. The suspension was pre-warmed to 40°C, after which, 0.5 FPU of Celluclast® cellulase enzyme from *Trichoderma reesei* and 2 IU of cellobiase enzyme from *Aspergillus niger* (diluted in 0.1 mL of citrate buffer at 40°C) was added. A 50.0 mL aliquot was sampled from the enzymatic reaction every hour for five hours. For each aliquot, the reaction was terminated by diluting the 50.0 mL sample to 0.7 mL in distilled water and adding 0.3 mL of DNS reagent (prepared by diluting 91 g of potassium sodium tartrate, 3.15g dinitrosalicylic acid, 131 mL of 2 molar sodium hydroxide 2.5 g phenol and 2.5g sodium sulfite to 500 mL with distilled H_2O). The 1 mL mixture was sealed in a microcentrifuge tube and boiled for exactly 5 minutes in water. The appearance of reducing sugars was measured by comparing the absorbance at 540 nm to a calibration curve generated from glucose samples of known concentration. The first order rate constant for reducing sugar liberation in the saccharification reaction was determined to be 0.15/hr.

Comparative Example B16: Attempted Hydrolysis of Sugarcane Bagasse with Cross-linked, Sulfonated-Polystyrene (Negative Control 1)

[00480] The cellulose digestion capability of the catalysts described herein was compared to that of conventional acidified polymer-resins used for catalysis in organic and industrial chemistry (T. Okuhara, "Water-Tolerant Polymer catalysts," *Chem. Rev.*, 102, 3641-3666 (2002)). Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.51 g of the cane bagasse sample, 0.53 g of sulfonated polystyrene (Dowex® 50WX2 resin, acid functionalization: 4.8 mmol/g, initial moisture content: 19.6% g H_2O / g dispensed catalyst), and 1.4 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for six hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate

constant for conversion of xylan to xylose was determined to be 0.1/hr. The first-order rate constant for conversion of glucan to soluble oligo-, di-, and mono-saccharides was determined to be < 0.01/hr. The number average degree of polymerization of residual cellulose was found to be DOP_N>300AHG units, indicating little or no digestion of crystalline cellulose in the biomass sample. Short-chain oligosaccharides were not detected. Unlike the digestion products depicted in Figure (1), the residual biomass exhibited little or no structural reduction in particle size.

Comparative Example B17: Attempted Hydrolysis of Sugarcane Bagasse with Sulfonated Polystyrene (Negative Control 2)

[00481] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.52 g of the cane bagasse sample, 0.55 g of sulfonated polystyrene (Amberlyst® 15, acid functionalization: 4.6 mmol/g, initial moisture content: 10.8% g H_2O / g dispensed catalyst), and 1.8 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for six hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be 0.1/hr. The first-order rate constant for conversion of glucan to soluble oligo-, di-, and mono-saccharides was determined to be < 0.01/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N> 300 AHG units, indicating little or no digestion of crystalline cellulose in the biomass sample. Short-chain oligosaccharides were not detected. Unlike the digestion products depicted in Figure (1), the residual biomass exhibited little or no structural reduction in particle size.

Comparative Example B18: Attempted Hydrolysis of Sugarcane Bagasse with Cross-linked Polyacrylic acid (Negative Control 3)

[00482] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g

dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.50 g of the cane bagasse sample, 0.50 g of polyacrylic acid beads (Amberlite® IRC86 resin, acid functionalization: 10.7 mmol/g, initial moisture content: 5.2% g H_2O / g dispensed catalyst), and 1.8 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for six hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be <0.05/hr. The first-order rate constant for conversion of glucan to soluble oligo-, di-, and mono-saccharides was determined to be < 0.001/hr. The number average degree of polymerization of residual cellulose was determined to be DOP_N>300 AHG units, indicating little or no digestion of crystalline cellulose in the biomass sample. Short-chain oligosaccharides were not detected. Unlike the digestion products depicted in Figure (1), the residual biomass exhibited little or no structural reduction in particle size.

Comparative Example B19: Attempted Hydrolysis of Sugarcane Bagasse with a Non-Acidic Ionomer as prepared in Example 2 (Negative Control 4)

[00483] Sugarcane bagasse (12.5% g H_2O/g wet bagasse, with a dry-matter composition of: 39.0% g glucan/g dry biomass, 17.3% g xylan / g dry biomass, 5.0% g arabinan / g dry biomass, 1.1% g galactan / g dry biomass, 5.5% g acetate / g dry biomass, 5.0% g soluble extractives / g dry biomass, 24.1% g lignin / g dry biomass, and 3.1% g ash / g dry biomass) was cut such that the maximum particle size was no greater than 1 cm. To a 15 mL cylindrical glass reaction vial was added: 0.50 g of the cane bagasse sample, 0.50 g of poly[styrene-co-3-methyl-1-(4-vinyl-benzyl)-3H-imidazol-1-ium chloride-co-divinylbenzene] (Catalyst as described in Example 2, Acid functionalization: 0.0 mmol/g, initial moisture content: 4.0% g H_2O / g dispensed polymer), and 1.8 mL of deionized H_2O. The reactants were mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the biomass. The resulting mixture was gently compacted to yield a solid reactant cake. The glass reactor was sealed with a phenolic cap and incubated at 115°C for six hours. Following the reaction, the product mixture was separated following the procedure described in Examples B2- B5. The first-order rate constant for conversion of xylan to xylose was determined to be <0.001/hr. No detectable amounts of soluble

oligo-, di-, and mono-saccharides were observed. It was determined that the number average degree of polymerization of the residual cellulose was DOP_N>300 AHG units, indicating little or no digestion of crystalline cellulose in the biomass sample. Short-chain oligosaccharides were not detected. Unlike the digestion products depicted in Figure (1), the residual biomass appeared physically unchanged from the input form.

Example B20: Preparation of a Saccharide Composition from Lignocellulosic Biomass using Catalyst described in Example 3

[00484] A lignocellulosic biomass is provided for saccharification using the Catalyst described in Example 3. The composition of the lignocellulosic biomass is determined using the methods described in Example B1 above.

[00485] To a 15 mL cylindrical glass reaction vial is added: 0.50 g of the lignocellulosic biomass sample, 0.30 g of Catalyst as prepared in Example 3, and 800μL of deionized H_2O. The reactants are mixed thoroughly with a glass stir rod to distribute the catalyst particles evenly throughout the lignocellulosic biomass. The resulting mixture is gently compacted to yield a solid reactant cake. The glass reactor is sealed with a phenolic cap and incubated at 120°C for four hours.

[00486] The cylindrical glass reactor is then cooled to room temperature and unsealed. 5.0 mL of distilled H_2O is added to the vial reactor and the resulting mixture of liquids and solids is agitated for 2 minutes by magnetic stirring. Following agitation, the solids are allowed to sediment for 30 seconds to produce the layered mixture. The solid catalyst is observed to form a layer at the bottom of the vial reactor. Lignin and residual biomass from the biomass is observed to form a solid layer above the solid catalyst. The short-chained beta-glucans is observed to form a layer of amorphous solids above the lignin and residual biomass. Finally, the soluble sugars are observed to form a liquid layer above the short-chained beta-glucans.

[00487] The supernatant and residual insoluble materials are then separated by decantation. The soluble-sugar content of hydrolysis products are determined by a combination of high performance liquid chromatography (HPLC) and spectrophotometric methods. HPLC determination of soluble sugars and oligosaccharides is performed on a Hewlett-Packard 1050 Series instrument that is equipped with a refractive index (RI) detector using a 30 cm x 7.8 mm Phenomenex HPB column with water as the mobile phase. The sugar column is protected by both a lead-exchanged sulfonated-polystyrene guard column and a tri-alkylammoniumhydroxide

anionic-exchange guard column. All HPLC samples are microfiltered using a 0.2 μm syringe filter prior to injection. Sample concentrations are determined by reference to a calibration generated from known standards.

[00488] The recovered hydrolysate is determined to contain a mixture of xylose, arabinose, and glucose in the proportions of about 10 : 1 : 1, with a total sugar concentration of 1% g sugars / g hydrolysate. The total concentration of 5-hydroxymethylfurfural, 2-furaldehyde, and levulinic acid is less than 0.05% g analyte / g hydrolysate. The total hydrolysate is concentrated by evaporation under vacuum to produce a solution with 10% g sugars / g hydrolysate.

Genetical Modification of Fermentation Hosts

[00489] To a freeze-dried knock-out strain of *E. coli* lacking genes Ec-rpiA, Ec-rpiB, Ec-rpiE, Ec-glcD, Ec-glcE, Ec-glcF, and EC-glcI, coding for ribose-5-phosphate isomerase, ribulose-5-phosphate 3-epimerase, glycolate oxidase and glyoxylate carboligase, is added 400uL of liquid LB medium with a Pasteur pipette to form a suspension that is mixed by vortexing for 30 seconds. The suspension is transferred to a culture tube containing 5mL of LB medium and incubated with shaking at 37°C for 24 hours to obtain a viable reconstituted cell stock (overnight culture). Electrocompetent cell stock is obtained by inoculating 1L of ½-NaCl LB media with the 5mL overnight culture and incubated with shaking at 37°C until log OD(600)=0.5, followed by incubating the cells in an ice water bath for 15 minutes. Two centrifuge bottles containing 12mL of 10% glycerol, 500 mL of sterile water, and a 50 mL conical tube are incubated on ice for 30 minutes. 500 mL of cells are poured into each of the pre-chilled centrifuge bottles and are pelletized at 6000xg for 15 minutes at 4°C. The supernatant is poured off from each centrifuge bottle and the cells are resuspended in 250 mL of ice-cold sterile water with vortexting, taking care to maintain the cells on ice. The cells are pelleted at 6000xg for 15 minutes at 4°C. The supernatant is poured off, and the pellets are resuspended in 2.5 mL of ice cold 10% glycerol by tituration, and combined into a 50 mL conical tube. The combined cells are pelleted at 600g for 15 minutes at 4°C and the supernantant is carefully removed. The pellet is finally resuspended in 2 mL of ice cold 10% glycerol and the suspension is separated into 80 μL aliquots into microfuge tubes and frozen in a -70°C bath.

Example C1: Genetically Modified Host for Converting D-Ribulose to Ethylene Glycol

[00490] 2 μL of a plasmid containing nucleic acid encoding the peptide sequence MVKPIIAPSI LASDFANLGC ECHKVINAGA DWLHIDVMDGHFVPNITLGQ

PIVTSLRRSVPRPGDASNTE KKPTAFFDCH MMVENPEKWV DDFAKCGADQ FTFHYEATQD PLHLVKLIKS KGIKAACAIK PGTSVDVLFE LAPHLDMALV MTVEPGFGGQ KFMEDMMPKV ETLRAKFPHL NIQVDGGLGK ETIPKAAKAG ANVIVAGTSV FTAADPHDVI SFMKEEVSKE LRSRDLLD

is inserted into the bottom of an eppendorf tube. 20 μL of immediately thawed electrocompetent cells from Example C1 are added to the tube and suspended by vortexing. The suspension is transferred into an electroporation cuvete and porated at 330 μF and 4 kOhm triggered at 410 V. The porated cells are transferred to a conical tube containing 1 mL of rich SOC media and incubated for 1 hour at 37°C with shaking. 150 μL of the recovered cells are plated with the plasmid-appropriate antibiotic and grown overnight at 37°C. A colony is picked using a culture loop, suspended in 5 mL of LB media and the appropriate activator, and incubated with shaking at 37°C for 4 hours.

Example C2: Genetically Modified Host for Converting a Saccharide Composition into a Fermentation Mixture Containing Ethanol

[00491] By way of non-limiting example, the following organisms can be used for one or more fermentation processes to convert a saccharide composition into ethanol. Any one, or a combination of two or more of these organisms, can be involved in a given biosynthetic pathway, and multiple biosynthetic pathways exist to produce ethanol.

[00492] Relevant organisms include *E. coli* K-12 substr. MG1655 (NCBI: 511145), *Clostridium acetobutylicum* ATCC 824 (NCBI: 272562), *Clostridium pasteurianum* (NCBI: 1501), *Neocallimastix sp. LM-2* (NCBI: 73818), *Zymomonas mobilis* (NCBI: 542), *Saccharomyces cerevisiae S288c* (NCBI: 559292), and *Zea mays* (NCBI: 4577).

Example C3: Genetically Modified Host for Converting a Saccharide Composition into a Fermentation Mixture Containing 1-Butanol and/or 2-Butanol

[00493] By way of non-limiting example, the following organisms can be used for one or more fermentation processes to convert a saccharide composition into 1-butanol and/or 2-butanol. Any one, or a combination of two or more of these organisms, can be involved in a given biosynthetic pathway, and multiple biosynthetic pathways exist to produce 1-butanol and/or 2-butanol.

[00494] Relevant organisms include Clostridium *acetobutylicum* (NCBI: 1488), *Clostridium acetobutylicum* ATCC 824 (NCBI: 272562), *Clostridium beijerinckii* (NCBI: 1520), *Clostridium saccarobutylicum* (NCBI: 169679); *E. coli* K-12 substr. MG1655 (NCBI: 511145), and *Euglena gracilis* (NCBI: 3039).

Example C4: Genetically Modified Host for Converting a Saccharide Composition into a Fermentation Mixture Containing 1-Propanol and/or 2-Propanol

[00495] By way of non-limiting example, the following organisms can be used for one or more fermentation processes to convert a saccharide composition into 1-propanol and/or 2-propanol. Any one, or a combination of two or more of these organisms, can be involved in a given biosynthetic pathway, and multiple biosynthetic pathways exist to produce 1-propanol and/or 2-propanol.

[00496] Relevant organisms include Clostridium *acetobutylicum* (NCBI: 1488), *Clostridium acetobutylicum* ATCC 824 (NCBI: 272562), *Clostridium beijerinckii* (NCBI: 1520), and *E. coli* (NCBI: 562).

Example C5: Genetically Modified Host for Converting a Saccharide Composition into a Fermentation Mixture Containing 1,2-Propanediol

[00497] By way of non-limiting example, the following organisms and enzymes can be used for one or more fermentation processes to convert a saccharide composition into 1,2-propanediol. Any one, or a combination of two or more of these organisms and enzymes, can be involved in a given biosynthetic pathway, and multiple biosynthetic pathways exist to produce 1,2-propanediol.

[00498] Relevant organisms include *E. coli* K-12 substr. MG1655 (NCBI: 511145), Enzyme EC 1.1.1.77, and Enzyme EC 4.2.1.28.

Example C6: Genetically Modified Host for Converting a Saccharide Composition into a Fermentation Mixture Containing Lactic Acid

[00499] By way of non-limiting example, *Arabidopsis thalania col* (NCBI: NIL) can be used for one or more fermentation processes to convert a saccharide composition into lactic acid. Additional organisms and enzymes can be involved in a given biosynthetic pathway, and multiple biosynthetic pathways exist to produce lactic acid.

Fermentation of Saccharide Compositions

Example D1: Fermentation to Ethylene Glycol

[00500] The concentrated hydrolysate from Example B20 is sterilized by autoclaving for 30 minutes at 110°C and titrated to pH 6 using sodium hydroxide (NaOH). 2.5 mL of LB media and 2.5 mL of hydrolysate is added to a culture tube. The tube is inoculated with the engineered host from Example C1, initiated, and grown with continuous shaking at 37°C for 24 hours. Following growth, the sample is shocked to 100°C for 5 minutes and spun down to collect the cell mass pellet. The production of ethylene glycol is measured by HPLC by diluting a 100 uL sample from the supernatant to 1mL and filtering through a 0.2 um syringe filter. The concentration of ethylene glycol is determined by HPLC to be at least 1 g / g.

Example D2: Purification of Ethylene Glycol

[00501] The fermentation supernatant produced from Example D1 is loaded onto a column containing a poly-acrylic acid cationic exchange resin and eluted with double distilled H_2O and concentrated under vacuum at 80°C to produce a solution containing at least 80% ethylene glycol in water.

Example D3: Fermentation to Propylene Precursors

[00502] The concentrated hydrolysate from any of Examples C2 to C6 is sterilized by autoclaving for 30 minutes at 110°C and titrated to pH 6 using sodium hydroxide (NaOH). 2.5 mL of LB media and 2.5 mL of hydrolysate is added to a culture tube. The tube is inoculated with the engineered host selected from Examples C2 to C6, initiated, and grown with continuous shaking at 37°C for 24 hours. Following growth, the sample is shocked to 100°C for 5 minutes and spun down to collect the cell mass pellet. The production of propylene precursor is measured by HPLC by diluting a 100 uL sample from the supernatant to 1mL and filtering through a 0.2 um syringe filter. The concentration of propylene precursor is determined by HPLC to be at least 1 g / g.

Example D4: Purification of Propylene Precursors

[00503] The fermentation supernatant produced from Example D3 is loaded onto a column containing a poly-acrylic acid cationic exchange resin and eluted with double distilled H_2O and

concentrated under vacuum at 80°C to produce a solution containing at least 30% polypropylene precursor in water.

CLAIMS

WHAT IS CLAIMED IS:

1. A method of producing an ethylene glycol compound, comprising:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone;

c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition comprises at least one of glucose, galactose, fructose, xylose, and arabinose; and

d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture comprising an ethylene glycol compound, or a chemical intermediate between the saccharide composition and the ethylene glycol compound, or a mixture thereof.

2. The method of claim 1, further comprising isolating the ethylene glycol compound from the fermentation product mixture.

3. The method of claim 1, wherein the ethylene glycol compound is selected from monoethylene glycol, diethylene glycol, and polyethylene glycol.

4. The method of claim 1, wherein the saccharide composition comprises at least two of glucose, galactose, fructose, xylose, and arabinose.

5. The method of claim 1, wherein the saccharide composition comprises xylose and the

chemical intermediate is selected from one or more of xylulose, xylulose-5-phosphate, ribulose-5-phosphate, ribulose, ribulose-1-phosphate, glycolaldehyde, and 2-dihydroxyacetone phosphate.

6. The method of claim 5, wherein the saccharide composition comprises xylose and the chemical intermediate is selected from one or more of xylulose-5-phosphate, ribulose-1-phosphate, and 2-dihydroxyacetone phosphate.

7. The method of claim 1, wherein the saccharide composition comprises xylose and the chemical intermediate is selected from xylonate, 2-dehydro-3-deoxy- pentonate, and glycoaldehyde.

8. The method of claim 1, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme selected from xylose isomerase, xylulokinase, ribulose phosphate 3-epimerase, phosphoribulokinase, ribulose-5-phosphate kinase, ribulokinase, ribulose-phosphate aldolase, and 1,2-propanediol oxidoreductase.

9. The method of claim 1, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme selected from xylose dehydrogenase, xylonate dehydratase, 2-dehydro-3-deoxy- pentonate aldolase and glycoaldehyde reductase.

10. The method of claim 1, wherein the chemical intermediate is selected from glyceraldehyde, 2-phosphoglycerate, 3-phosphoglycerate, glycerate, serine, hydroxypyruvate, ethanolamine, and glycolaldehyde.

11. The method of claim 1, wherein the ethylene glycol compound is suitable for use in a polymer that is recyclable, at least partially bio-degradable, or a combination thereof.

12. The method of claim 1, wherein the fermentation host is genetically modified to convert

xylose to ribulose, and ribulose to the ethylene glycol compound or the chemical intermediate.

13. The method of claim 1, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one ethylene glycol pathway enzyme.

14. The method of claim 13, wherein the ethylene glycol pathway enzyme is selected from a serine aminotransferase, a serine decarboxylase, a serine oxidoreductase, a hydroxypyruvate decarboxylase, a glycoaldehyde reductase, an ethanolamine aminotransferase, an ethanolamine oxidoreductase, a hydroxypyruvate reductase, a glycerate decarboxylase, a 3-phosphoglycerate phosphatase, a glycerate kinase, a 2-phosphoglycerate phosphatase, a glycerate-2-kinase, and a glyceraldehyde dehydrogenase.

15. The method of claim 1, wherein the ethylene glycol pathway enzyme is selected from a glycerate dehydrogenase, a glycolaldehyde reductase, a hydroxypyruvate decarboxylase, a hydroxypyruvate isomerase, and a glyoxylate carboligase.

16. The method of claim 1, wherein the ethylene glycol pathway enzyme is selected from a glycolyl-CoA transferase, a glyoxylate reductase, a glycolyl-CoA synthetase, a glycolyl-CoA reductase, a glycolaldehyde reductase, a glycolate reductase, a glycolate kinase, a phosphotransglycolylase, a glycolylphosphate reductase, and a glycolyl-CoA reductase.

17. An ethylene glycol compound produced according to the method of claim 1.

18. A method of producing a bio-based polymer comprising a terephthalate component and a diol component, comprising:

a) providing a terephthalate component;

b) providing a diol component comprising an ethylene glycol compound, wherein at least a portion of the ethylene glycol compound is produced according to the method of any one of claims 1 to 16; and

c) reacting the terephthalate component and the diol component to produce a bio-based

polymer.

19. The method of claim 18, wherein the terephthalate component comprises terephthalic acid, dimethylterephthalate, isophthalic acid, or a combination thereof.

20. The method of claim 18, wherein at least a portion of the ethylene glycol component is produced from cellulosic material.

21. The method of claim 18, wherein the ethylene glycol compound is selected from monoethylene glycol, diethylene glycol, and polyethylene glycol.

22. A method of producing a propylene-containing compound, comprising:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone;

c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition comprises at least one of glucose, galactose, fructose, xylose, and arabinose;

d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more ompounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more compounds;

e) isolating the one or more compounds from the fermentation mixture; and

f) converting the one or more compounds to the propylene-containing compound.

23. The method of claim 22, further comprising producing polypropylene from the propylene-containing compound.

24. The method of claim 22, wherein the saccharide composition comprises at least one of glucose, xylose, and arabinose.

25. The method of claim 22, wherein the saccharide composition comprises at least two of glucose, galactose, fructose, xylose, and arabinose.

26. The method of claim 22, wherein the fermentation host is genetically modified to convert ribulose to ribulose-1-phosphate, then convert -ribulose-1-phosphate to glycoaldehyde and DHAP.

27. The method of 26, wherein the fermentation host is genetically modified to convert DHAP to one or more compounds selected from 1,2-propane diol, lactic acid, and 1-propanol.

28. The method of 27, wherein the one or more compounds are converted into a propylene-containing compound.

29. The method of claim 22, wherein the saccharide composition comprises one or more sugars selected from glucose, galactose, arabinose, and xylose, and the chemical intermediate is selected from glucose-6-phosphate, ribulose-1-phosphate, and 2-dihydroxyacetone phosphate.

30. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from ribulose 5-phosphate 4-epimerase, arabinose isomerase, arabinose 1-dehydrogenase, ribulokinase, ribulose 5-phosphate 4-epimerase, fucose, fuculokinase, methylglyoxal synthase, glyceraldehyde 3-phosphate, methylglyoxal reductase, 1,2-propanediol dehydrogenase, glycerol dehydrogenase, propanediol dehydratase, propanol dehydrogenase, propanediol dehydratase, CoA-dependent propionaldehyde dehydrogenase, phosphate propanoyltransferase, propionate kinase, 1,2-propanediol oxidoreductase, aldehyde dehydrogenase, glycerol-1-phosphate dehydrogenase, glycerol-3-phosphate dehydrogenase, sugar phosphatase, dihydroxyacetone kinase, glycerol dehydrogenase, glycerol dehydratase, γ-glutamyl-γ-aminobutyraldehyde dehydrogenase, and 1,3-propanediol dehydrogenase.

31. The method of claim 22, wherein the saccharide composition comprises glucose or galactose, and the chemical intermediate is selected from glucose-6-phosphate, 2-dihydroxyacetone phosphate, and glycoaldehyde.

32. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from ribulose-phosphate aldolase and ribulose 5-phosphate 4-epimerase.

33. The method of claim 22, wherein the saccharide composition comprises xylose, and the chemical intermediate is selected from xylulose-5-phosphate, ribulose-1-phosphate and 2-dihydroxyacetone phosphate.

34. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from arabinose isomerase, arabinose 1-dehydrogenase, ribulokinase, ribulose 5-phosphate 4-epimerase, and ribulose-phosphate aldolase.

35. The method of claim 22, wherein the saccharide composition comprises arabinose, and the chemical intermediate is selected from ribulose-5 phosphate, ribulose-1-phosphate and 2-dihydroxyacetone phosphate.

36. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from fucose, fuculokinase, and ribulose-phosphate aldolase.

37. The method of claim 22, wherein the saccharide composition comprises arabinose and the chemical intermediate is selected from ribulose, ribulose-1-phosphate and 2-dihydroxyacetone phosphate.

38. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from methylglyoxal reductase, 1,2-propanediol dehydrogenase, glycerol dehydrogenase, propanediol dehydratase, and propanol dehydrogenase.

39. The method of claim 22, wherein the chemical intermediate is selected from 1,2-propanediol, methyl glyoxal, lactaldehyde, and lactic acid.

40. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from 1,2-propanediol oxidoreductase and aldehyde dehydrogenase.

41. The method of claim 22, wherein the chemical intermediate is selected from 2-dihydroxyacetone phosphate, glycerol, 3-proprionaldehyde, and 1,3-propane diol.

42. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least one propylene pathway enzyme selected from glycerol-1-phosphate dehydrogenase, glycerol-3-phosphate dehydrogenase, sugar phosphatase, dihydroxyacetone kinase, glycerol dehydrogenase, glycerol dehydratase, γ-glutamyl-γ-aminobutyraldehyde dehydrogenase, and 1,3-propanediol dehydrogenase.

43. The method of claim 22, wherein the propylene-containing compound is suitable for use in a polymer that is recyclable, at least partially bio-degradable, or a combination thereof.

44. The method of claim 22, wherein the fermentation host is genetically modified to comprise at least one exogenous nucleic acid encoding at least two propylene pathway enzymes.

45. A method of producing a saccharide composition suitable for use in preparing one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, comprising:

a) providing a cellulosic material;

b) contacting the cellulosic material with a polymer catalyst,

wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic

group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone; and

c) degrading at least a portion of the cellulosic material to produce a saccharide composition, wherein the saccharide composition comprises at least one C5 saccharide and at least one C6 saccharide in a ratio suitable for fermentation to produce one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol.

46. The method of claim 45, further comprising d) combining the saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol.

47. The method of claim 46, further comprising e) isolating the one or more compounds from the fermentation mixture.

48. The method of claim 47, further comprising f) converting the one or more compounds to the propylene-containing compound.

49. A composition comprising the saccharide composition of claim 45 and a fermentation host under conditions such that one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol are capable of being produced.

50. A propylene-containing compound produced according to the method of claim 22.

51. A method of producing an ethylene glycol compound, comprising: combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising the ethylene glycol compound, by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone,

wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose.

52. A product containing an ethylene glycol compound produced by the step of combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising the ethylene glycol compound, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose.

53. A bio-based polymer comprising a terephthalate component and a diol component, wherein the diol component comprises an ethylene glycol compound, and wherein the bio-based polymer is produced by reacting the terephthalate component and the diol component to produce a bio-based polymer.

54. The bio-based polymer of claim 53, wherein the bio-based polymer is used to produce one or more products selected from vehicle components, electronics, plastic bottles and food packaging.

55. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from bottles, dishes, utensils, packaging, non-stick cookware, coffee pots, refridgerator components, microwave casing and components, household implement handles and other components, surface laminates, toothbrushes, and hair dryers.

56. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce

one or more products selected from toilets, sinks, bathroom fixtures, plumbing piping and systems, lighting fixtures, flooring, carpeting, rugs, and laminates, furniture, windows and frames, insulation cosmetics, handbags, tote bags, and luggage.

57. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from textiles, clothing, shoes and soles, fabrics, upholstery, curtains and window treatments, coverings, rope, string, and high performance fibers.

58. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from surgical and medical implements, and medical implants and devices.

59. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from casings, screens and components for applicances, computers, printers, cellular phones and other mobile devices, TVs, and vehicle components.

60. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from laboratory equipment, chemical bottles, drums and carboys, and packaging for commercial products or shipping.

61. The bio-based polymer of claim 53, wherein the the bio-based polymer is used to produce one or more products selected from gaskets, bearings, valves, seals, pumps, knobs, piping, sealants, adhesives, resins, foams, coatings, tapes, brushes, and paints, dyes, and pigments.

62. A method of producing an propylene containing compound, comprising:

a) combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more compounds, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a

portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose, and

b) converting the one or more compounds to the propylene-containing compound.

63. A product containing a propylene-containing compound produced by the step of combining a saccharide composition with a fermentation host to produce a fermentation product mixture comprising one or more compounds selected from ethanol, lactic acid, 1,2-propanediol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, or a chemical intermediate between the saccharide composition and the one or more compounds, wherein the saccharide composition is produced by contacting a cellulosic material with a polymer catalyst, wherein the polymer catalyst comprises acidic monomers and ionic monomers connected to form a polymeric backbone, wherein a plurality of the acidic monomers independently comprise at least one Bronsted-Lowry acid, wherein one or more of the acidic monomers comprises a linker connecting the Bronsted-Lowry acid to the polymeric backbone, wherein a plurality of ionic monomers independently comprise at least one nitrogen-containing cationic group or phosphorous-containing cationic group, and wherein one or more of the ionic monomers comprises a linker connecting the nitrogen-containing cationic group or the phosphorous-containing cationic group to the polymeric backbone, under conditions such that at least a portion of the cellulosic material is degraded to produce a saccharide composition comprising at least one of glucose, galactose, fructose, xylose, and arabinose.

64. The product of claim 63, wherein the propylene-containing compound is converted into a polypropylene-containing compound.

65. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from plastic bottles, food containers, packaging, household and kitchenware, bags, furniture, insulation, toys, vehicle components, chemical drums and totes, and piping.

66. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from vehicle components, electronics, plastic bottles and food packaging.

67. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from bottles, dishes, utensils, packaging, non-stick cookware, coffee pots, refridgerator components, microwave casing and components, household implement handles and other components, surface laminates, toothbrushes, and hair dryers.

68. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from toilets, sinks, bathroom fixtures, plumbing piping and systems, lighting fixtures, flooring, carpeting, rugs, and laminates, furniture, windows and frames, insulation cosmetics, handbags, tote bags, and luggage.

69. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from textiles, clothing, shoes and soles, fabrics, upholstery, curtains and window treatments, coverings, rope, string, and high performance fibers.

70. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from surgical and medical implements, and medical implants and devices.

71. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from casings, screens and components for applicances, computers, printers, cellular phones and other mobile devices, TVs, and vehicle components.

72. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from laboratory equipment, chemical bottles, drums and carboys, and packaging for commercial products or shipping.

73. The polypropylene-containing compound of claim 64, wherein the polypropylene is used to produce one or more products selected from gaskets, bearings, valves, seals, pumps, knobs, piping, sealants, adhesives, resins, foams, coatings, tapes, brushes, and paints, dyes, and pigments.

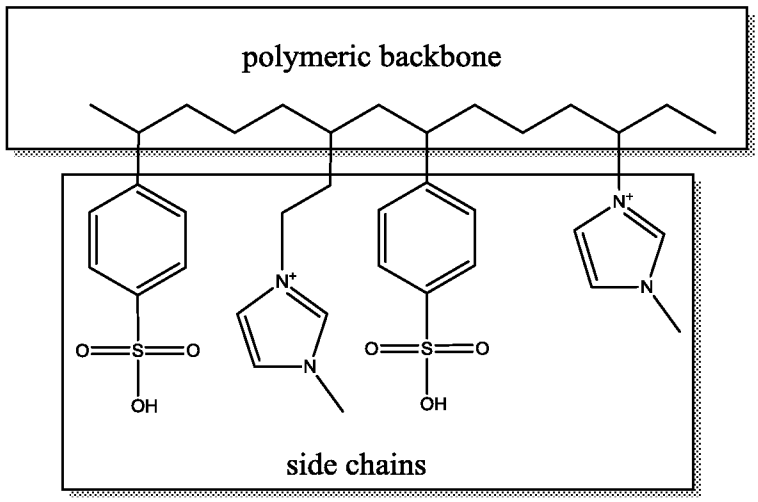

polymeric backbone
side chains

FIG. 1

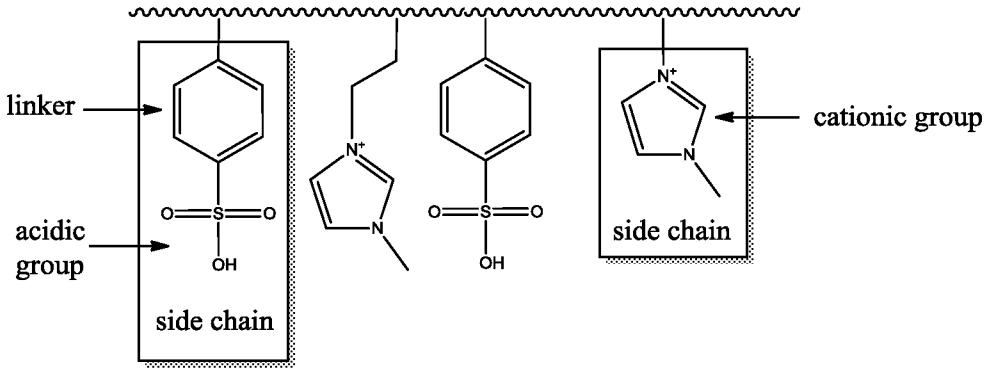

linker
acidic group
side chain
side chain
cationic group

FIG. 2

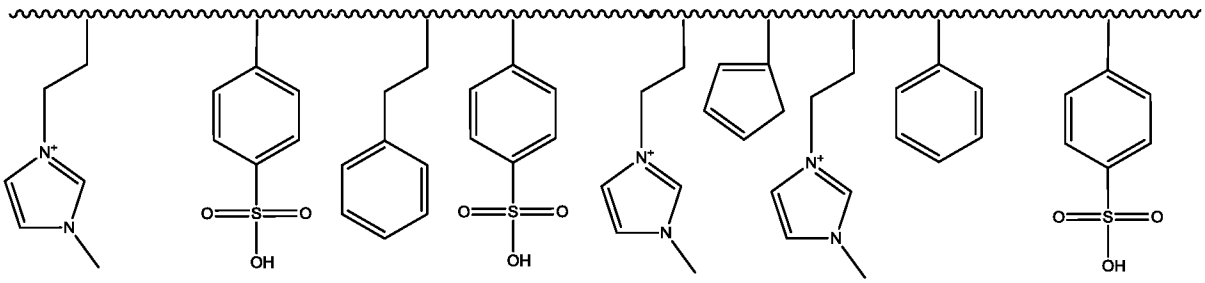


FIG. 3A

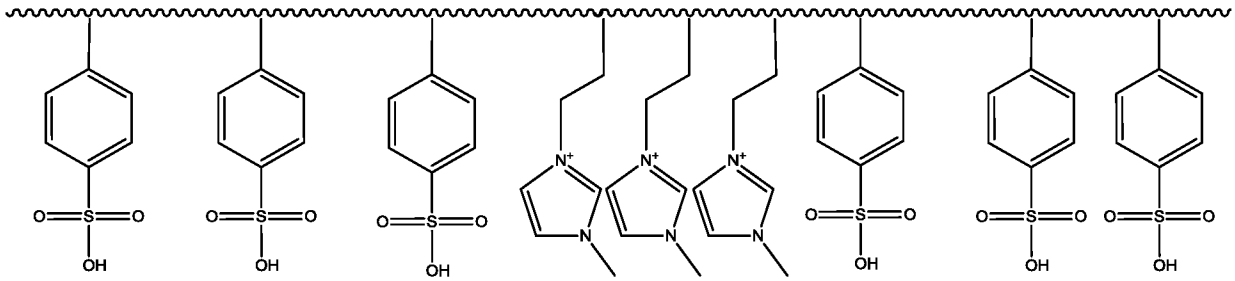


FIG. 3B

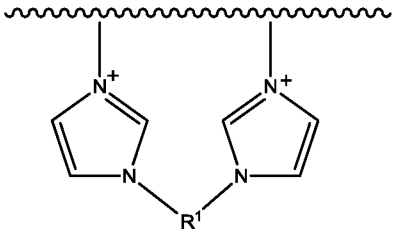


FIG. 4A

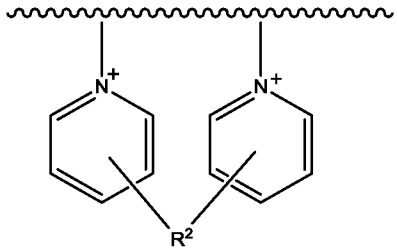


FIG. 4B

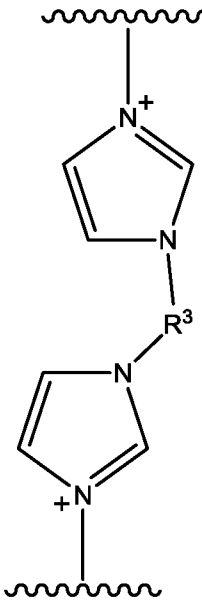


FIG. 5A

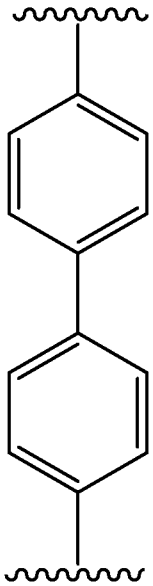


FIG. 5B

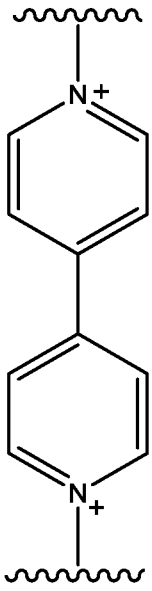


FIG. 5C

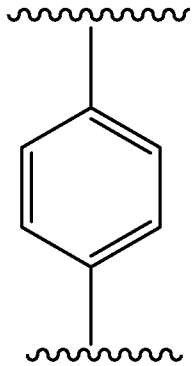


FIG. 5D

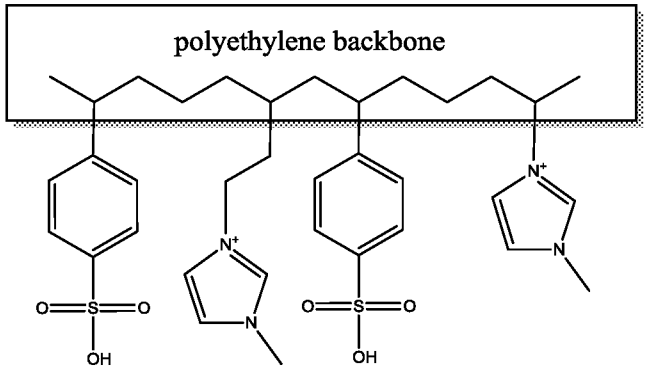

polyethylene backbone
O
S
O
OH
N+
N

FIG. 6A

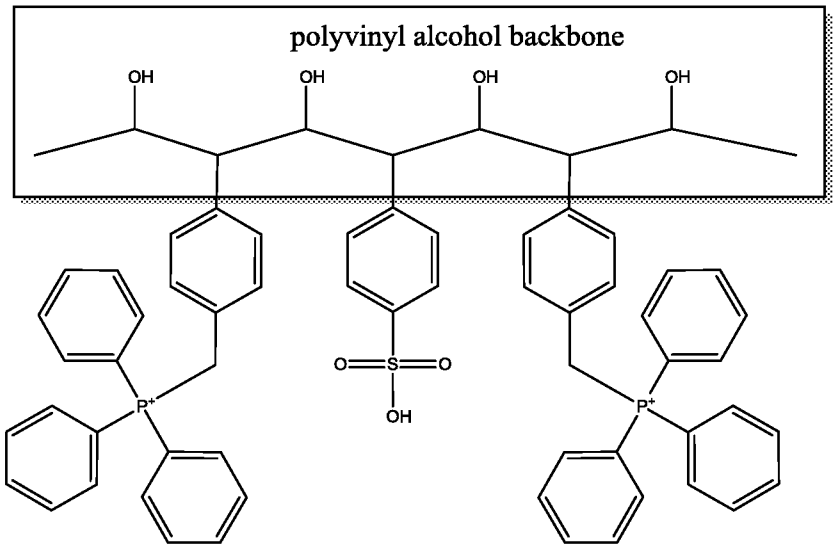

polyvinyl alcohol backbone
OH
OH
OH
OH
O
S
O
OH
P+
P+

FIG. 6B

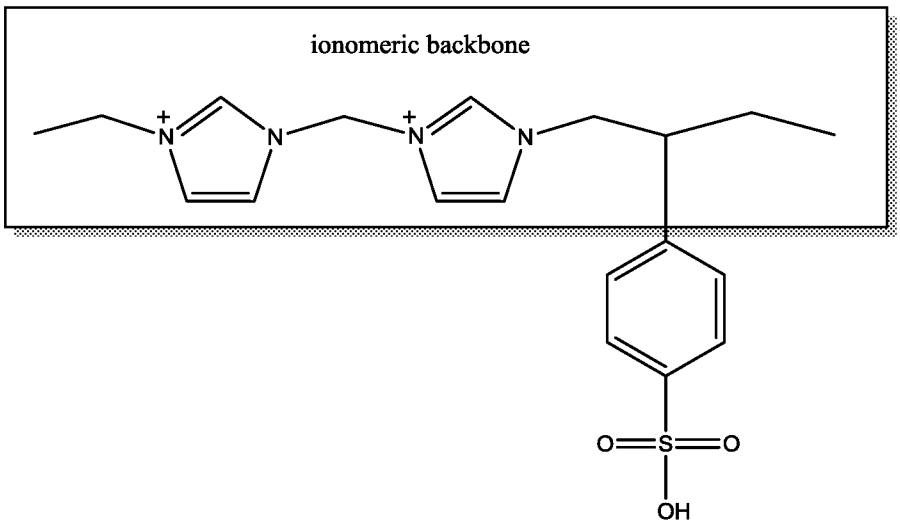


FIG. 6C

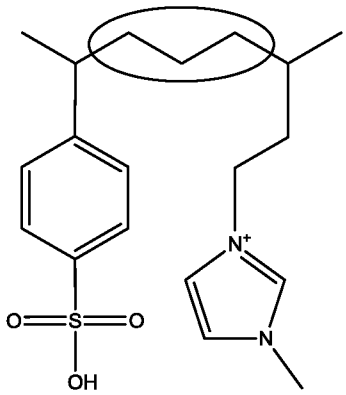


FIG. 7A

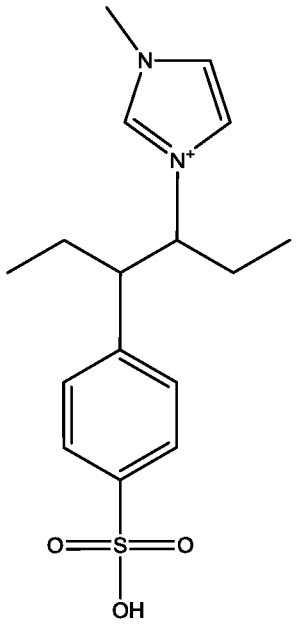


FIG. 7B

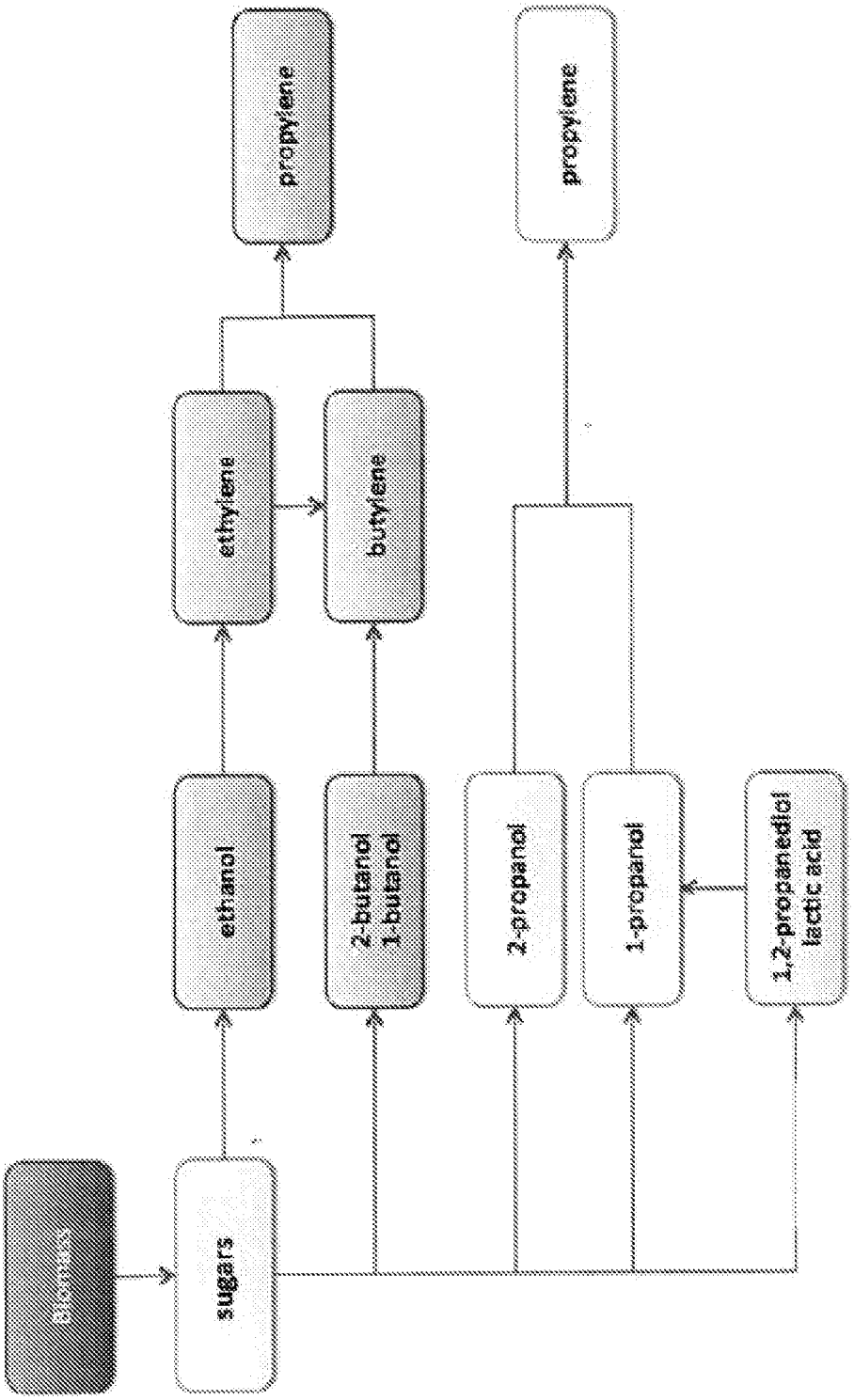

biomass
sugars
ethanol
2-butanol
1-butanol
2-propanol
1-propanol
1,2-propanediol
lactic acid
ethylene
butylene
propylene
propylene

FIG. 8

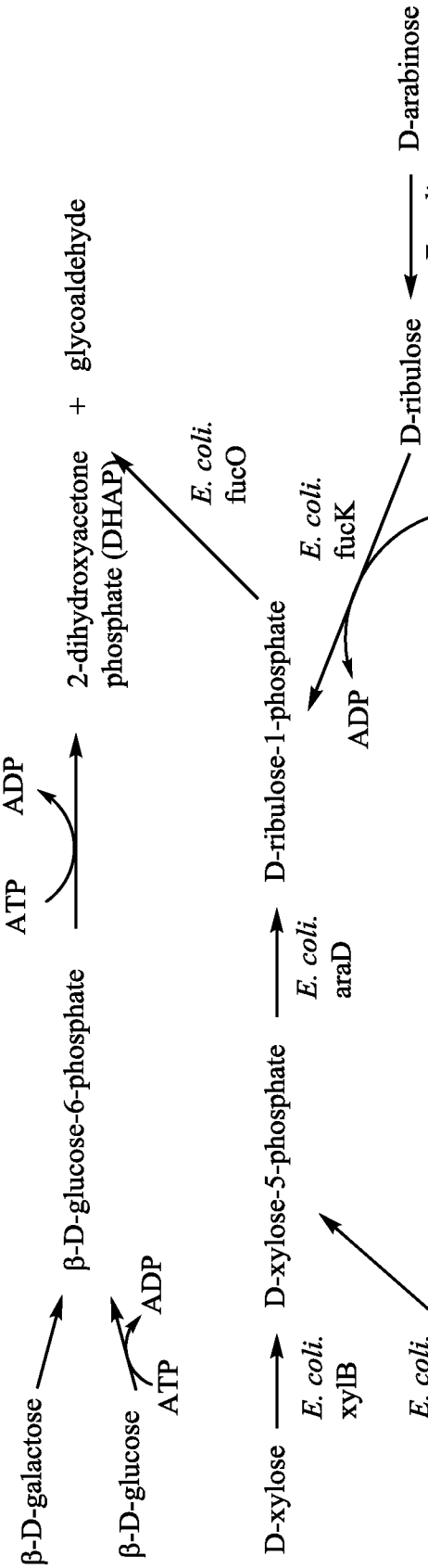

β-D-galactose
β-D-glucose
ATP
ADP
β-D-glucose-6-phosphate
ATP
ADP
2-dihydroxyacetone phosphate (DHAP)
+
glycoaldehyde
E. coli. fucO
D-xylose
E. coli. xylB
D-xylose-5-phosphate
E. coli. araD
D-ribulose-1-phosphate
E. coli. fucK
ATP
ADP
D-ribulose
E. coli. fucI
D-arabinose
E. coli. araD
ATP
ADP
L-ribulose-5-phosphate
E. coli. araB
L-ribulose
E. coli. araA
L-arabinose

FIG. 9

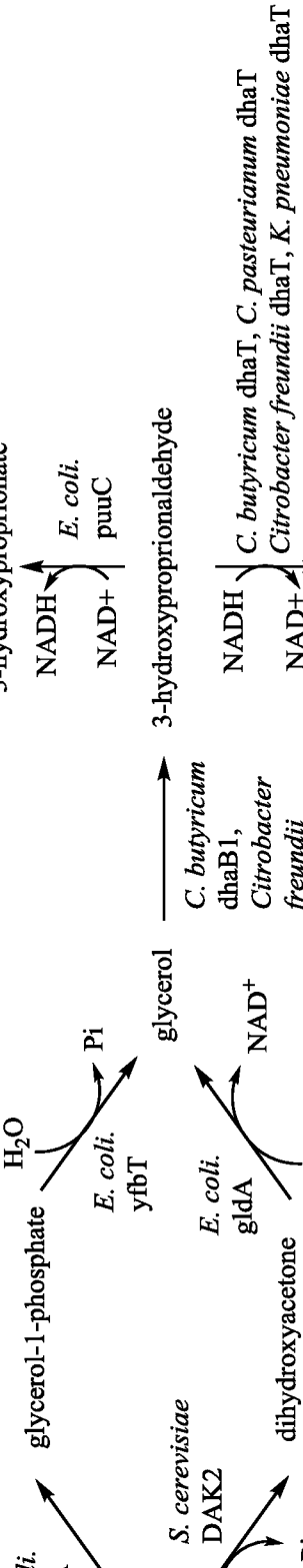

3-hydroxyproprionate
NADH
NAD+
E. coli.
puuC
3-hydroxyproprionaldehyde
NADH
NAD+
C. butyricum dhaT, C. pasteurianum dhaT
Citrobacter freundii dhaT, K. pneumoniae dhaT
1,3-propanediol
C. butyricum
dhaB1,
Citrobacter
freundii
dhaB, dhaC,
dhaE
glycerol
Pi
H2O
E. coli.
yfbT
glycerol-1-phosphate
E. coli.
GpsA
DHAP
H2O
S. cerevisiae
DAK2
Pi
dihydroxyacetone
E. coli.
gldA
NAD+
NADH

FIG. 10

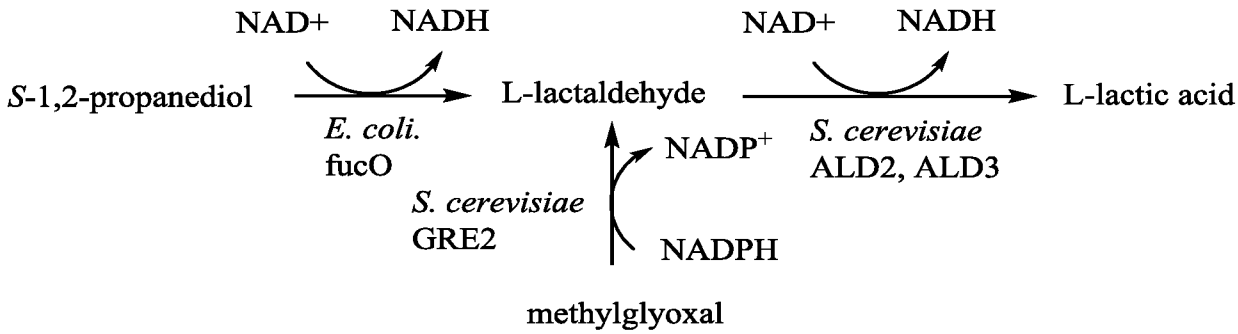

NAD+
NADH
NAD+
NADH
S-1,2-propanediol
L-lactaldehyde
L-lactic acid
E. coli.
fucO
S. cerevisiae
ALD2, ALD3
NADP+
S. cerevisiae
GRE2
NADPH
methylglyoxal

FIG. 11