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(54) **POST-MODIFIED POLYCARBODIIMIDES**

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(57) **ABSTRACT**

A process of preparing a post-modified polycarbodiimide, the process includes combining a diisocyanate, a moisture scavenger, a monoisocyanate, and a catalyst in a reaction vessel; and heating the reaction vessel to a temperature and a time sufficient to form a capped polycarbodiimide wherein the capped polycarbodiimide has 0.25 wt % or less of free isocyanate groups; and the combining and heating are conducted in the absence of a solvent.

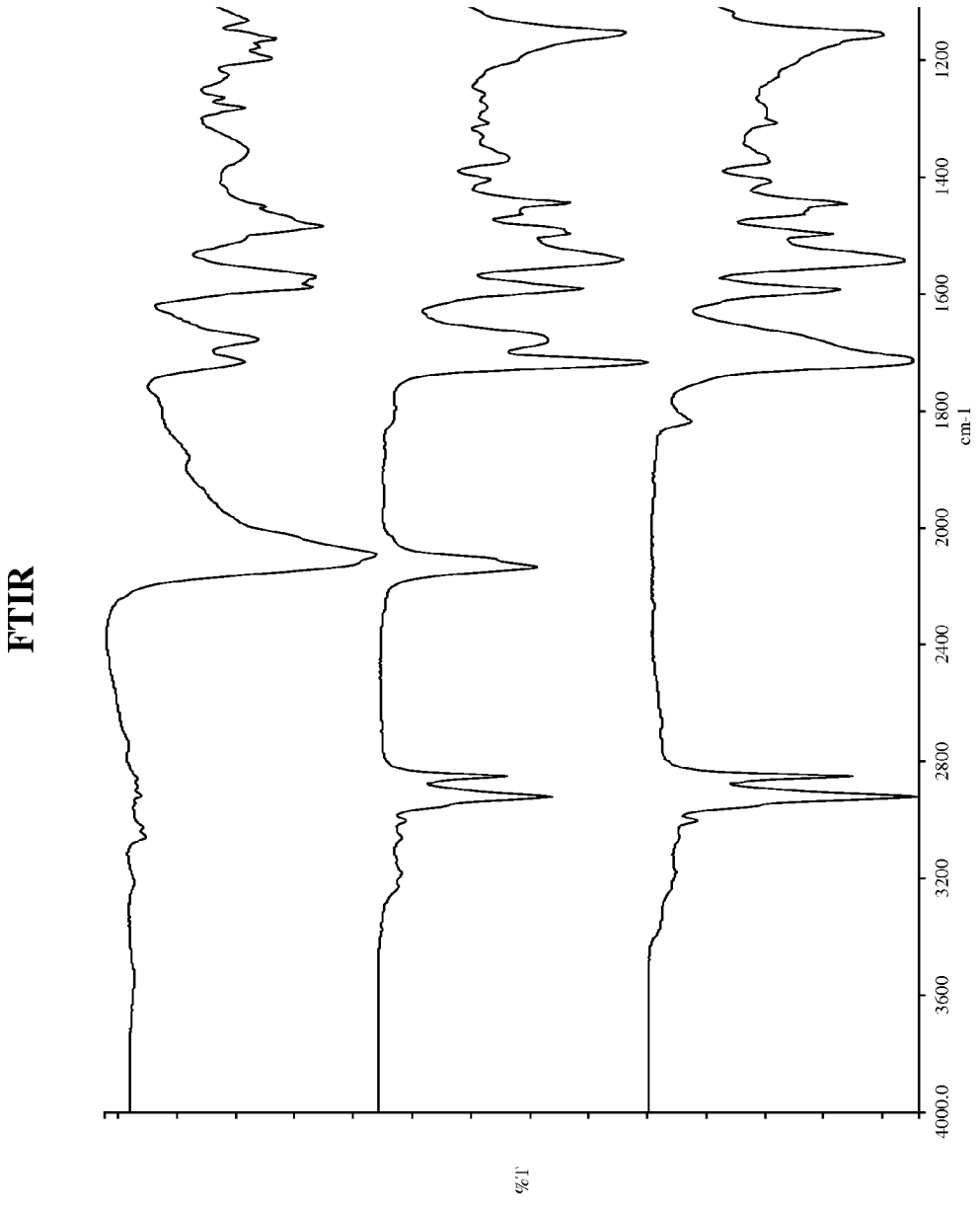


FIG. 1

POST-MODIFIED POLYCARBODIIMIDES

BACKGROUND OF THE DISCLOSURE

[0001] The present technology is generally related to modification of polycarbodiimides. Specifically, the technology is related to storage stable polycarbodiimides and their preparation in the absence of a solvent.

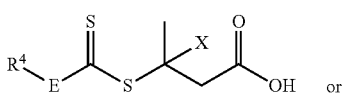
SUMMARY OF THE DISCLOSURE AND ADVANTAGES

[0002] In one aspect, a process is provided for preparing a capped polycarbodiimide, the process including combining in a reaction vessel a diisocyanate, a moisture scavenger, a monoisocyanate, and a catalyst to form a reaction mixture; and heating the reaction mixture to a temperature and for a time sufficient to form a capped polycarbodiimide, wherein the capped polycarbodiimide has 0.1 wt % or less of free isocyanate groups; and the combining and heating are conducted in the absence of a solvent. The capped polycarbodiimides are liquid materials that exhibit Newtonian Rheology.

[0003] In some embodiments, the capped polycarbodiimide has 0.075 wt % or less free isocyanate groups. In any of the above embodiments, the temperature may be from about 60° C. to about 120° C. In any of the above embodiments, the time may be from about 4 hours to about 48 hours. In any of the above embodiments, the diisocyanate may be a compound of formula ONC—R^1—CNO, wherein R^1 is a linking group. In any of the above embodiments, the monoisocyanate is a compound of formula ONC—R^2, wherein R^2 is an alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl. In any of the above embodiments, the capped polycarbodiimide may be a polycarbodiimide of formula: R^2—N═C═N—[R^1—N═C═N]$_n$—R^2, wherein R^1 is a linking group, R^2 is a alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl, and n is the polymer repeating unit. In the formula, n designates a repeating unit of the polymer. In any of the above embodiments, n may be from about 1 to about 30. In any of the above embodiments, n may be from about 1 to about 15.

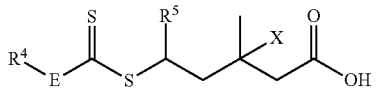
[0004] In any of the above embodiments, the process may also include contacting the capped polycarbodiimide with a monomeric acid. In any such embodiments, the monomeric acid may be a compound represented as $R^3C(O)OH$, wherein R^3 is a polymerizable group. In other such embodiments, the monomeric acid may be a fatty acid.

[0005] In another aspect, a polymer is provided, the polymer being the reaction product of any of the above capped polycarbodiimides and a monomeric acid. The monomeric acid may be a compound represented as $R^3C(O)OH$, wherein R^3 is a polymerizable group, or the monomeric acid may be a fatty acid. In any of the embodiments of the polymer, the polymer may be a chemical-cure (i.e. radically cured) and/or photocurable polymer. In some embodiments, the monomeric acid may be a group of formula



or

-continued



In the structure, R^4 may be C_1-C_{18} alkyl, E is absent or is S, X may be C_1-C_{18} alkyl, aryl, nitrile, or halide, R^5 may be a R^5 is alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl group, optionally substituted, and n is a repeat unit. In some embodiments, n' is from 1 to 30.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. **1** is a Fourier transform infrared spectrum of a polycarbodiimide in the top spectrum, partially modified in the middle spectrum, and a fully modified polycarbodiimide in the bottom spectrum, according to Examples 9 and 10.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0007] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).

[0008] As used herein, "about" will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, "about" will mean up to plus or minus 10% of the particular term.

[0009] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential.

[0010] In general, "substituted" refers to an alkyl, alkenyl, alkynyl, aryl, or ether group, as defined below (e.g., an alkyl group) in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to a carbon(s) or hydrogen(s) atom are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group will

be substituted with one or more substituents, unless otherwise specified. In some embodiments, a substituted group is substituted with 1, 2, 3, 4, 5, or 6 substituents. Examples of substituent groups include: halogens (i.e., F, Cl, Br, and I); hydroxyls; alkoxy, alkenoxy, alkynoxy, aryloxy, aralkyloxy, heterocyclyloxy, and heterocyclylalkoxy groups; carbonyls (oxo); carboxyls; esters; urethanes; oximes; hydroxylamines; alkoxyamines; aralkoxyamines; thiols; sulfides; sulfoxides; sulfones; sulfonyls; sulfonamides; amines; N-oxides; hydrazines; hydrazides; hydrazones; azides; amides; ureas; amidines; guanidines; enamines; imides; isocyanates; isothiocyanates; cyanates; thiocyanates; imines; nitro groups; nitriles (i.e., CN); and the like.

[0011] As used herein, "alkyl" groups include straight chain and branched alkyl groups having from 1 to about 20 carbon atoms, and typically from 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. As employed herein, "alkyl groups" include cycloalkyl groups as defined below. Alkyl groups may be substituted or unsubstituted. Examples of straight chain alkyl groups include methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, sec-butyl, t-butyl, neopentyl, and isopentyl groups. Representative substituted alkyl groups may be substituted one or more times with, for example, amino, thio, hydroxy, cyano, alkoxy, and/or halo groups such as F, Cl, Br, and I groups. As used herein the term haloalkyl is an alkyl group having one or more halo groups. In some embodiments, haloalkyl refers to a per-haloalkyl group. Alkylene groups are divalent alkyl groups.

[0012] Cycloalkyl groups are cyclic alkyl groups such as, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group has 3 to 8 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 5, 6, or 7. Cycloalkyl groups may be substituted or unsubstituted. Cycloalkyl groups further include polycyclic cycloalkyl groups such as, but not limited to, norbornyl, adamantyl, bornyl, camphenyl, isocamphenyl, and carenyl groups, and fused rings such as, but not limited to, decalinyl, and the like. Cycloalkyl groups also include rings that are substituted with straight or branched chain alkyl groups as defined above. Representative substituted cycloalkyl groups may be mono-substituted or substituted more than once, such as, but not limited to: 2,2-; 2,3-; 2,4-; 2,5-; or 2,6-disubstituted cyclohexyl groups or mono-, di-, or tri-substituted norbornyl or cycloheptyl groups, which may be substituted with, for example, alkyl, alkoxy, amino, thio, hydroxy, cyano, and/or halo groups.

[0013] Alkenyl groups are straight chain, branched or cyclic alkyl groups having 2 to about 28 carbon atoms, and further including at least one double bond. In some embodiments alkenyl groups have from 1 to 12 carbons, or, typically, from 1 to 8 carbon atoms. Alkenyl groups may be substituted or unsubstituted. Alkenyl groups include, for instance, vinyl, propenyl, 2-butenyl, 3-butenyl, isobutenyl, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl groups among others. Alkenyl groups may be substituted similarly to alkyl groups. Divalent alkenyl groups, i.e., alkenyl groups with two points of attachment, include, but are not limited to, CH—CH═CH_2, C═CH_2, or C═$CHCH_3$.

[0014] As used herein, "aryl", or "aromatic," groups are cyclic aromatic hydrocarbons that do not contain heteroatoms. Aryl groups include monocyclic, bicyclic and polycyclic ring systems. Thus, aryl groups include, but are not limited to, phenyl, azulenyl, heptalenyl, biphenylenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenyl, anthracenyl, indenyl, indanyl, pentalenyl, and naphthyl groups. In some embodiments, aryl groups contain 6 to 14 carbons, and in others from 6 to 12 or even 6 to 10 carbon atoms in the ring portions of the groups. The phrase "aryl groups" includes groups containing fused rings, such as fused aromatic-aliphatic ring systems (e.g., indanyl, tetrahydronaphthyl, and the like). Aryl groups may be substituted or unsubstituted.

[0015] Heteroaryl groups are aromatic ring compounds containing 5 or more ring members, of which, one or more is a heteroatom such as, but not limited to, N, P, O, and S. Unless expressly indicated otherwise, heteroaryl groups may be substituted or unsubstituted. Heteroaryl groups include, but are not limited to, groups such as pyrrolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, thiophenyl, benzothiophenyl, furanyl, benzofuranyl, indolyl, azaindolyl (pyrrolopyridyl), indazolyl, benzimidazolyl, imidazopyridyl (azabenzimidazolyl), pyrazolopyridyl, triazolopyridyl, benzotriazolyl, benzoxazolyl, benzothiazolyl, benzothiadiazolyl, imidazopyridyl, isoxazolopyridyl, thianaphthalenyl, purinyl, xanthinyl, adeninyl, guaninyl, quinolinyl, isoquinolinyl, tetrahydroquinolinyl, quinoxalinyl, and quinazolinyl groups.

[0016] Heterocyclyl groups include non-aromatic ring compounds containing 3 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S. In some embodiments, heterocyclyl groups include 3 to 20 ring members, whereas other such groups have 3 to 6, 3 to 10, 3 to 12, or 3 to 15 ring members. Heterocyclyl groups encompass unsaturated, partially saturated and saturated ring systems, such as, for example, imidazolyl, imidazolinyl and imidazolidinyl groups. Unless expressly indicated otherwise, heterocyclyl groups may be substituted or unsubstituted. Heterocyclyl groups include, but are not limited to, aziridinyl, azetidinyl, pyrrolidinyl, imidazolidinyl, pyrazolidinyl, thiazolidinyl, tetrahydrothiophenyl, tetrahydrofuranyl, dioxolyl, furanyl, thiophenyl, pyrrolyl, pyrrolinyl, imidazolyl, imidazolinyl, pyrazolyl, pyrazolinyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, thiazolinyl, isothiazolyl, thiadiazolyl, oxadiazolyl, piperidyl, piperazinyl, morpholinyl, thiomorpholinyl, tetrahydropyranyl, tetrahydrothiopyranyl, oxathiane, dioxyl, dithianyl, pyranyl, pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, dihydropyridyl, dihydrodithiinyl, dihydrodithionyl, homopiperazinyl, quinuclidyl, indolyl, indolinyl, isoindolyl, azaindolyl (pyrrolopyridyl), indazolyl, indolizinyl, benzotriazolyl, benzimidazolyl, benzofuranyl, benzothiophenyl, benzthiazolyl, benzoxadiazolyl, benzoxazinyl, benzodithiinyl, benzoxathiinyl, benzothiazinyl, benzoxazolyl, benzothiazolyl, benzothiadiazolyl, benzo[1,3]dioxolyl, pyrazolopyridyl, imidazopyridyl (azabenzimidazolyl), triazolopyridyl, isoxazolopyridyl, purinyl, xanthinyl, adeninyl, guaninyl, quinolinyl, isoquinolinyl, quinolizinyl, quinoxalinyl, quinazolinyl, cinnolinyl, phthalazinyl, naphthyridinyl, pteridinyl, thianaphthalenyl, dihydrobenzothiazinyl, dihydrobenzofuranyl, dihydroindolyl, dihydrobenzodioxinyl, tetrahydroindolyl, tetrahydroindazolyl, tetrahydrobenzimidazolyl, tetrahydrobenzotriazolyl, tetrahydropyrrolopyridyl, tetrahydropyrazolopyridyl,

tetrahydroimidazopyridyl, tetrahydrotriazolopyridyl, and tetrahydroquinolinyl groups. Representative substituted heterocyclyl groups may be mono-substituted or substituted more than once, such as, but not limited to, pyridyl or morpholinyl groups, which are 2-, 3-, 4-, 5-, or 6-substituted, or disubstituted with various substituents such as those listed above.

[0017] Provided herein are post-modified polycarbodiimides. As described further below, a polycarbodiimide may be post-polymerization modified (i.e. "post-modified" or "post-modification") by reaction with a monomeric acid. There are two types of post-modified polycarbodiimides described herein. The polycarbodiimides have long pot-lives. For example, the pot-life may be greater than 1 year. As used herein, the term "pot-life" indicates that the composition maintains a molecular weight, flowability, and reactivity over the described time period at room temperature. In the above example of the pot-life of greater than 1 year, this includes, but is not limited to, pot-lives of at least 16 months, 18 months, 2 years, 30 months, 3 years, 42 months, or 4 years.

[0018] The first type is a photo-curable, or chemically-curable polycarbodiimide. The photo-curable polycarbodiimides are formed by reaction of a polycarbodiimide with a photo-curable monomeric acid, such that the post-modification product retains the photo-curable character of the monomeric acid. Such materials may be used in a wide variety of applications where photo-curing is desirable. For example, the post-modified polycarbodiimides may be used in sealants, elastomers, coatings, or adhesives. Coatings may include inks. Chemically-curable materials are those that may be cured via free radical mechanisms, or catalyzed mechanisms.

[0019] The second type of post-modified polycarbodiimide is a fatty acid-modified polycarbodiimide. The fatty acid-modified polycarbodiimides are formed by reaction of a polycarbodiimide with a fatty acid, to incorporate the greasy, longer chain fatty acid residues into the polycarbodiimide. The fatty acids may be saturated, monounsaturated, or polyunsaturated. Such fatty acid post-modified polycarbodiimides may be used in a wide variety of applications where radical curing is desirable, such as in alkyd resins. For example, the fatty acid post-modified polycarbodiimides may be used as wood coatings, pigment dispersants, oil field applications.

[0020] For either type of post-modified polycarbodiimide, the reactions used to prepare the materials are conducted in the absence of solvent, or other solvent-type monomers. For example, the reactions avoid the use of solvents such as, but not limited to, methylene chloride, chloroform, trichloroethylene, hexachloroethylene, carbon tetrachloride, benzene, toluene, xylene, ethyl acetate, butyl acetate, or the like. In some embodiments, the reaction also avoids the use of "solvent" monomers beyond the monomeric acid. Such solvent monomers include, but are not limited to, styrene, α-methylstyrene, vinyl alcohol, vinyl esters, glycols, glycol esters, amides, and vinyl amides. All of the materials in the reaction pot are either the polycarbodiimide (or mixture of any two or more polycarbodiimides) or monomeric acid (or mixture of any two or more monomeric acids), along with any processing aid such as, but not limited to, moisture scavengers and/or catalysts. Catalyst residue from the catalyst used to prepare the polycarbodiimide may be present.

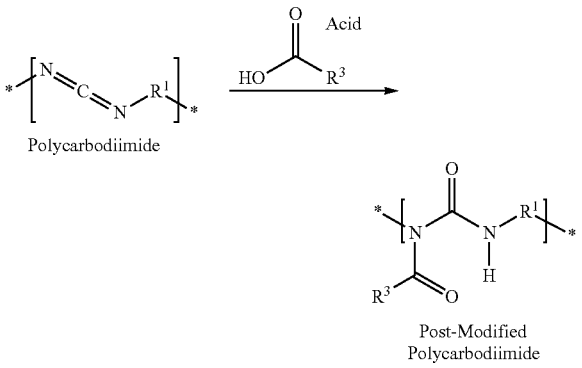
[0021] In any of the above embodiments, the moisture scavenger may be triphenylphosphite. In any of the above embodiments, the catalyst may be phospholene oxide, or any of the catalysts described in U.S. Pat. No. 6,489,503, incorporated herein by reference.

[0022] The post-modified polycarbodiimides are also liquid materials at room temperature that exhibit Newtonian behavior. That is, the liquids have a constant viscosity at different shear rates. The post-modified polycarbodiimides may have, for example, a number average molecular weight range from about 400 to about 6000 for an acrylic modified polycarbodiimide, from about 600 to about 13000 for an oleic acid modified polycarbodiimide, from about 400 to about 1200 for a hybrid polycarbodiimide (as defined below). The molecular weight will vary depending on the specific monomeric acid used to modify the capped polycarbodiimide.

[0023] The polycarbodiimides are made by a process such that they lack residual isocyanate (NCO) groups, or at least have a very high percentage of —N═C═N— linkages in comparison to residual NCO groups. By one measure, any remaining NCO groups are so few as to be undetectable by infrared spectroscopy methods. For example, polycarbodiimides may have 0.3 wt % or fewer free NCO groups. In some embodiments, there are 0.1 wt % or fewer free NCO groups. In other embodiments, there are 0.075 wt % or fewer free NCO groups. In yet further embodiments, there are no free NCO groups.

[0024] In one aspect, a post-modified polycarbodiimide is formed in a process generally described in Scheme 1.

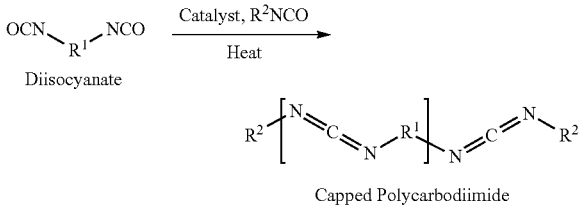
Scheme 1:



[0025] In Scheme 1, a polycarbodiimide is reacted with a monomeric acid ($R^3C(O)OH$), which may be a polymerizable acid, to form a post-modified polycarbodiimide. The polycarbodiimide is a capped polycarbodiimide at the "*" positions in the illustrated compounds. As used herein, a "capped polycarbodiimide" is a polycarbodiimide that is free of isocyanate groups. The caps on the polycarbodiimide may be aliphatic or aromatic caps derived from monoisocyanates. For example, groups such as, but not limited to, butyl, (trialkoxysilyl)propyl, 3-isopropenyl-α,α-dimethylbenzyl, phenyl, naphthyl, p-toluene sulfonyl, and tolyl may be used. The capped groups remain in the post-modified material as an O- or N-acyl urea group.

[0026] The polycarbodiimide may be prepared according to the reaction described in Scheme 2.

Scheme 2:



[0027] In the reaction described in Scheme 2, the capped polycarbodiimide is prepared in process that includes combining in a reaction vessel a diisocyanate, a moisture scavenger, a monoisocyanate, and a catalyst to form a reaction mixture. The reaction mixture is then heated to a temperature and for a time sufficient to form the capped polycarbodiimide. In the process of the preparation, the capped polycarbodiimide has 0.25 wt % or less of free isocyanate groups; and the combining and heating steps of the process are conducted in the absence of a solvent. In some embodiments, the capped polycarbodiimide has 0.1 wt % or less of free isocyanate groups. During the process of forming the capped polycarbodiimide, the diisocyanate, monoisocyanate, moisture scavenger, and catalyst may be added to a reactor all together or in any order. In one embodiment, the diisocyanate, monoisocyanate, and moisture scavenger are added together and heated prior to addition of the catalyst.

[0028] In the process, the temperature during heating may be from about 30° C. to about 200° C., according to some embodiments. In other embodiments, the temperature is from about 60° C. to about 120° C. In yet other embodiments, the temperature is from about 100° C. to about 110° C. The time may be from about 2 hours to 48 hours. In some embodiments, the time is from about 4 hours to 20 hours. In other embodiments, the time is from about 4 hours to 14 hours.

[0029] In Schemes 1 and 2 for forming a post-modified polycarbodiimide, R^1 is a linking group, which in the diisocyanate is the group on which the isocyanates are located. Also included in the reaction medium is a monoisocyanate (R^2NCO) that results in the end groups capping the polycarbodiimide R^1 and R^2 may individually be alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl. In some embodiments, of the above compounds, R^1 and R^2 may individually be a C_1-C_{12} alkyl, C_1-C_{12} cycloalkyl, a C_6-C_{12} aromatic, a C_6-C_{12} heterocyclyl, or a C_6-C_{12} heteroaryl group. For example, R^1 and R^2 may individually be a methylene, ethylene, propylene, isopropylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decalinylene, dodecylene, 1,2-cyclohexylene, 1,3-cyclohexylene, 1,4-cyclohexylene, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, tolyl, or xylyl. In some preferred embodiments, R^1 is an aryl group. For example, R^1 may preferably be phenyl, tolyl, or xylyl. In some preferred embodiments, R^2 is an aryl group. For example, R^2 may preferably be phenyl, tolyl, or xylyl.

[0030] In some embodiments, R^2 is methyl, ethyl, propyl isopropyl, butyl, pentyl hexyl, heptyl, octyl, nonyl, decalinyl, dodecyl, tetradecyl, hexadecyl, octadecyl, cyclohexyl, phenyl, tolyl, tolyl isomers, 2,2-diphenyl, 2,2-diphenylethyl, phenylsulfonyl, toluenesulfonyl phenyl isomers, 3-isopropenyl-α,α-dimethylbenzyl, 3-(triethoxysilyl)propyl, 4-(chlorosulfonyl)phenyl, chlorosulfonyl, 1-naphthalene, 2-naphthalene, 1-(1-naphthyl)ethyl, 4-phenylazophenyl, 2,6-diisopropylphenyl, benzyl, 2-benzylphenyl, 4-benzylphenyl, benzophenone, 4-benzyloxyphenyl, 2-methyoxyphenyl, 3-methyoxyphenyl, 4-methoxyphenyl, 2-phenoxyphenyl, 3-phenoxyphenyl, 4-phenoxyphenyl, 2-biphenylyl, 4-biphenylyl, 4-chloro-2-phenoxy, 5-chloro-2-phenoxy, 4-pentylphenyl, 4-butyl-2-methylphenyl, 2-ethyl-6-isopypylphenyl, 1-admantyl, 2,3-dimethoxyphenyl, 2,5-dimethoxyphenyl, 3,4-dimethoxyphenyl, 2,6-dimethoxyphenyl, 4-t-butylphenyl, 4-sec-butylphenyl, 4-butylphenyl, 4-phenylbutyl, 4-ethylphenethyl, 2,6-diethylphenyl, 1,2,3,4-tetrahydronaphthalene, 3,4,5-trimethoxyphenyl, 2,4-dimethoxybenzyl, 1-ethoxy-2-methoxyphenyl, 3-phenylpropyl, 2-ethyl-6-methylphenyl, 1-methyl-2-methylbenzoate, ethylbenzoate isomers, 5-indanyl, 1,1,3,3-tetramethylbutyl, 4-(dimethylamino)phenyl, 2-ethylhexyl, phenylethyl, methylbenzyl isomers, 3,5-dimethylphenyl, 3,5-bis(trifluoromethyl)phenyl, 4-bromo-2-ethylphenyl, fluorophenethyl isomers, nitrophenyl isomers, fluorophenyl isomers, fluorobenzyl isomers, fluorotolyl isomers, chloromethylphenyl isomers, bromtolyl isomers, bromophenyl isomers, cyanophenyl isomers, trifluorophenyl isomers, fluorotrifluoromethyl isomers, benzoyl chloride isomers, chlorophenylisomers, bromophenyl isomers, iodophenyl isomers, nitrotolyl isomers, chlorophenethyl isomers, methylbenzoate isomers, dichlorophenethyl isomers, methyl bezonitrile isomers, or methoxybenzyl isomers.

[0031] Illustrative diisocyantes include, but are not limited to, m-phenylene diisocyanate; 2,4-toluene diisocyanate; 2,6-toluene diisocyanate; hexamethylene diisocyanate; 1,4-phenylene diisocyanate; tetramethylene diisocyanate; cyclohexane-1,4-diisocyanate; hexahydrotoluene diisocyanate; methylenediisocyanate; 2,6-diisopropylphenyl isocyanate; m-xylylene diisocyanate; dodecyl isocyanate; 3,3'-dichloro-4,4'-diisocyanato-1,1'-biphenyl; 1,6-diisocyanato-2,2,4-trimethylhexane; 3,3'-dimethoxy-4,4'-biphenylene diisocyanate; 2,2-diisocyanatopropane; 1,3-diisocyanatopropane; 1,4-diisocyanatobutane; 1,5-diisocyanatopentane; 1,6-diisocyanatohexane; 2,3-diisocyanatotoluene; 2,4-diisocyanatotoluene; 2,5-diisocyanatotoluene; 2,6-diisocyanatotoluene; isophorone diisocyanate; hydrogenated methylene bis(phenylisocyanate); naphthalene-1,5-diisocyanate; 1-methoxyphenyl-2,4-diisocyanate; 1,4-diisocyanatobutane; 4,4'-biphenylene diisocyanate; 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate; 4,4',4"-triphenylmethane triisocyanate; toluene-2,4,6-triisocyanate; 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate; polymethylene polyphenylene polyisocyanate; or a mixture of any two or more thereof. In a preferred embodiment, the diisocyanate is 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, or a mixture of 2,4- and 2,6-toluene diisocyanate. In some embodiments, the diisocyanate includes 100% 2,4-toluene diisocyanate; 80% 2,4-toluene diisocyanate, 20% 2,6-toluene diisocyanate; or 65% 2,4-toluene diisocyanate, 35% 2,6-toluene diisocyanate.

[0032] Illustrative monoisocyanates, R^2NCO, that may be used in forming the polycarbodiimide, include, but are not limited to, chlorosulfonyl isocyanate; trichloromethyl isocyanate; trichloroacetyl isocyanate; trichloroacetyl isocyanate; chloroacetyl isocyanate; vinyl isocyanate; methyl isocyanatoformate; 2-bromoethyl isocyanate; 2-chloroethyl isocyanate; 2-chloroethyl isocyanate; ethyl isocyanate; isocyanato(methoxy)methane; allyl isocyanate; ethyl isocyana-

toformate; 3-chloropropyl isocyanate; isopropyl isocyanate; propyl isocyanate; (trimethylsilyl)isocyanate; isocyanatocyclobutane; ethyl isocyanatoacetate; methyl (2s)-2-isocyanatopropanoate; butyl isocyanate; tert-butyl isocyanate; 1,1-dimethoxy-2-isocyanatoethane; cyclopentyl isocyanate; 2-isocyanato-2-methyl-propionic acid methyl ester; ethyl 3-isocyanatopropionate; (r)-(−)-3-methyl-2-butyl isocyanate; 1-isocyanato-2,2-dimethylpropane; 1-isocyanato-3-methylbutane; 3-isocyanatopentane; pentyl isocyanate; 1-ethoxy-3-isocyanatopropane; pentafluorophenyl isocyanate; 4-bromo-2,6-difluorophenyl isocyanate; 2,4,6-tribromophenyl isocyanate; 2,3,4-trifluorophenyl isocyanate; 2,4,5-trifluorophenyl isocyanate; 4-bromo-1-chloro-2-isocyanatobenzene; 4-bromo-2-fluorophenyl isocyanate; 1-chloro-3-fluoro-2-isocyanatobenzene; 2-chloro-3-fluorophenyl isocyanate; 3-chloro-4-fluorophenyl isocyanate; 4-chloro-2-fluorophenyl isocyanate; 5-chloro-2-nitrophenyl isocyanate; 2,4-dichlorophenyl isocyanate; 2,6-dichlorophenyl isocyanate; 3,4-dichlorophenyl isocyanate; 3,5-dichlorophenyl isocyanate; 2-fluoro-4-iodophenyl isocyanate; 4-fluoro-2-nitrophenyl isocyanate; 2,4-difluorophenyl isocyanate; 2,4-difluorophenyl isocyanate; 2,5-difluorophenyl isocyanate; 2,6-difluorophenyl isocyanate; 3,4-difluorophenyl isocyanate; 3,5-difluorophenyl isocyanate; 2,1,3-benzothiadiazol-4-yl isocyanate; 3,5-dinitrophenyl isocyanate; 3,5-dinitrophenyl isocyanate; 2-bromophenyl isocyanate; 3-bromophenyl isocyanate; 4-bromophenyl isocyanate; 2-chlorophenyl isocyanate; 3-chlorophenyl isocyanate; 3-chlorophenyl isocyanate; 4-chlorophenyl isocyanate; 2-chlorobenzenesulfonyl isocyanate; 4-(chlorosulfonyl)phenyl isocyanate; 4-chlorobenzenesulfonyl isocyanate; 2-fluorophenyl isocyanate; 3-fluorophenyl isocyanate; 4-fluorophenyl isocyanate; 4-fluorobenzenesulfonyl isocyanate; 2-iodophenyl isocyanate; 3-iodophenyl isocyanate; 4-iodophenyl isocyanate; 2-nitrophenyl isocyanate; 3-nitrophenyl isocyanate; 4-nitrophenyl isocyanate; phenyl isocyanate; phenyl isocyanate; benzenesulfonyl isocyanate; 2-isocyanatoethyl methacrylate; (isocyanatomethyl)cyclopentane; cyclohexyl isocyanate; 2-isocyanato-3-methyl-butyric acid methyl ester; butyl isocyanatoacetate; ethyl 4-isocyanatobutyrate; methyl (2s)-2-isocyanato-4-(methylsulfanyl)butanoate; hexyl isocyanate; 4-bromo-2-(trifluoromethyl)phenyl isocyanate; 2-chloro-4-(trifluoromethyl)phenyl isocyanate; 2-chloro-6-(trifluoromethyl)phenyl isocyanate; 4-chloro-3-(trifluoromethyl)phenyl isocyanate; 5-chloro-2-isocyanatobenzonitrile; 5-fluoro-2-isocyanatobenzonitrile; 2-fluoro-3-(trifluoromethyl)phenyl isocyanate; 2-fluoro-5-(trifluoromethyl)phenyl isocyanate; 3-fluoro-5-(trifluoromethyl)phenyl isocyanate; 4-fluoro-2-(trifluoromethyl)phenyl isocyanate; 4-fluoro-3-(trifluoromethyl)phenyl isocyanate; 3-isocyanatobenzoyl chloride; 4-isocyanatobenzoyl chloride; 2-(trifluoromethyl)phenyl isocyanate; 3-(trifluoromethyl)phenyl isocyanate; 4-(trifluoromethyl)phenyl isocyanate; 4-(trifluoromethylthio)phenyl isocyanate; 2-(trifluoromethoxy)phenyl isocyanate; 4-(trifluoromethoxy)phenyl isocyanate; 3-cyanophenyl isocyanate; 4-cyanophenyl isocyanate; 4-bromo-2-chloro-6-methylphenyl isocyanate; 2,4-dichlorobenzyl isocyanate; 3,4-dichlorobenzyl isocyanate; 2-(difluoromethoxy)phenyl isocyanate; 4-(difluoromethoxy)phenyl isocyanate; benzoyl isocyanate; 3,4-(methylenedioxy)phenyl isocyanate; phenyl isocyanatoformate; 4-bromo-3-methylphenyl isocyanate; 4-bromobenzyl isocyanate; 2-(chloromethyl)phenyl isocyanate; 2-chloro-5-methylphenyl isocyanate; 2-chloro-6-methylphenyl isocyanate; 2-chlorobenzyl isocyanate; 3-chloro-2-methylphenyl isocyanate; 3-chloro-4-methylphenyl isocyanate; 4-(chloromethyl)phenyl isocyanate; 4-chlorobenzyl isocyanate; 5-chloro-2-methylphenyl isocyanate; 5-chloro-2-methoxyphenyl isocyanate; 2-fluoro-5-methylphenyl isocyanate; 2-fluorobenzyl isocyanate; 3-fluoro-2-methylphenyl isocyanate; 3-fluoro-4-methylphenyl isocyanate; 3-fluorobenzyl isocyanate; 4-fluoro-3-methylphenyl isocyanate; 4-fluorobenzyl isocyanate; 5-fluoro-2-methylphenyl isocyanate; 4-fluorobenzyl isothiocyanate; 2-methyl-3-nitrophenyl isocyanate; 2-methyl-4-nitrophenyl isocyanate; 4-methyl-2-nitrophenyl isocyanate; 5-methyl-2-nitrophenyl isocyanate; 2-methoxy-4-nitrophenyl isocyanate; 4-methoxy-2-nitrophenyl isocyanate; benzyl isocyanate; m-tolyl isocyanate; o-tolyl isocyanate; p-tolyl isocyanate; 2-methoxyphenyl isocyanate; 3-methoxyphenyl isocyanate; 4-methoxyphenyl isocyanate; o-toluenesulfonyl isocyanate; p-toluenesulfonyl isocyanate; cycloheptyl isocyanate; cyclohexanemethyl isocyanate; 6-isocyanatohexanoic acid methyl ester; methyl (2s)-2-isocyanato-4-methylpentanoate; ethyl 2-isocyanato-4-(methylthio) butyrate; (r)-(−)-2-heptyl isocyanate; (s)-(+)-2-heptyl isocyanate; heptyl isocyanate; 3,5-bis(trifluoromethyl)phenyl isocyanate; 2-isocyanato-5-methylbenzonitrile; 4-isocyanatobenzyl cyanide; 2,4-dichlorophenethyl isocyanate; 3,4-dichlorophenethyl isocyanate; 4-acetylphenyl isocyanate; methyl 2-isocyanatobenzoate; methyl 3-isocyanatobenzoate; methyl 4-isocyanatobenzoate; (s)-(−)-1-(4-bromophenyl)ethyl isocyanate; 4-bromo-2,6-dimethylphenyl isocyanate; 4-bromo-2-ethylphenyl isocyanate; (r)-(+)-1-(4-chlorophenyl)ethyl isocyanate; 3-chlorophenethyl isocyanate; 4-chlorophenethyl isocyanate; (r)-(+)-1-(4-fluorophenyl)ethyl isocyanate; (s)-(−)-1-(4-fluorophenyl)ethyl isocyanate; 2-fluorophenethyl isocyanate; 4-fluorophenethyl isocyanate; 2,3-dimethyl-6-nitrophenyl isocyanate; 4-ethoxy-2-nitrophenyl isocyanate; 2,5-dimethylphenyl isocyanate; 2,6-dimethylphenyl isocyanate; 2-methylbenzyl isocyanate; 3,5-dimethylphenyl isocyanate; 3-methylbenzyl isocyanate; 4-ethylphenyl isocyanate; 4-methylbenzyl isocyanate; phenethyl isocyanate; 2-methoxy-5-methylphenyl isocyanate; 2-methoxybenzyl isocyanate; 3-ethoxyphenyl isocyanate; 3-methoxybenzyl isocyanate; 4-methoxybenzyl isocyanate; 1-isocyanato-2,3-dimethoxybenzene; 2,4-dimethoxyphenyl isocyanate; 2,5-dimethoxyphenyl isocyanate; 2,6-dimethoxyphenyl isocyanate; 3,4-dimethoxyphenyl isocyanate; 3,5-dimethoxyphenyl isocyanate; 4-(dimethylamino)phenyl isocyanate; ethyl 2-isocyanato-4-methylvalerate; ethyl 6-isocyanatohexanoate; (r)-(−)-2-octyl isocyanate; (s)-(+)-2-octyl isocyanate; 1,1,3,3-tetramethylbutyl isocyanate; 2-ethylhexyl isocyanate; octyl isocyanate; 5-ethyl-2-isocyanatobenzonitrile; (s)-(+)-1-indanyl isocyanate; 5-indanyl isocyanate; trans-2-phenylcyclopropyl isocyanate; 3,4-methylenedioxyphenethyl isocyanate; ethyl 2-isocyanatobenzoate; ethyl 3-isocyanatobenzoate; ethyl 4-isocyanatobenzoate; methyl 3-isocyanato-2-methylbenzoate; 3-bromo-2,4,6-trimethylphenyl isocyanate; (r)-(+)-1-phenylpropyl isocyanate; (s)-(−)-1-phenylpropyl isocyanate; 2-ethyl-6-methylphenyl isocyanate; 3-phenylpropyl isocyanate; (r)-(+)-1-(3-methoxyphenyl)ethyl isocyanate; (r)-(+)-1-(4-methoxyphenyl)ethyl isocyanate; (s)-(−)-1-(3-methoxyphenyl)ethyl isocyanate; 1-ethoxy-4-isocyanato-2-methoxybenzene; 2,4-dimethoxybenzyl isocyanate; 3,4,5-trimethoxyphenyl isocyanate; (r)-(−)-2-nonyl isocyanate; (s)-(+)-2-nonyl isocyanate; 1-naphthyl isocyanate; 2-naph-

thyl isocyanate; dimethyl 2-isocyanatoterephthalate; dimethyl 5-isocyanatoisophthalate; 1-isocyanato-1,2,3,4-tetrahydronaphthalene; ethyl (4-isocyanatophenyl)acetate; 2,6-diethylphenyl isocyanate; 4-butylphenyl isocyanate; 4-ethylphenethyl isocyanate; 4-phenylbutyl isocyanate; 4-sec-butylphenyl isocyanate; 4-tert-butylphenyl isocyanate; 2,3-dimethoxyphenethyl isocyanate; 2,5-dimethoxyphenethyl isocyanate; 3,4-dimethoxyphenethyl isocyanate; 3,4,5-trimethoxybenzyl isocyanate; 1-adamantyl isocyanate; ethyl 4-(isocyanatomethyl)cyclohexanecarboxylate; decyl isocyanate; 8-(isocyanatomethyl)-6h-[1,3]dioxolo[4,5-g]chromen-6-one; 2-ethyl-6-isopropylphenyl isocyanate; 4-butyl-2-methylphenyl isocyanate; 4-pentylphenyl isocyanate; undecyl isocyanate; 4-chloro-2-phenoxyphenyl isocyanate; 5-chloro-2-phenoxyphenyl isocyanate; 2-biphenylyl isocyanate; 4-biphenylyl isocyanate; 3-phenoxyphenyl isocyanate; 4-phenoxyphenyl isocyanate; p-phenylazophenyl isocyanate; 1-(1-naphthyl)ethyl isocyanate; (1r,2r)-(−)-2-benzyloxycyclopentyl isocyanate; 4,4'-oxybis(phenyl isocyanate); 9h-fluoren-2-yl isocyanate; 9h-fluoren-9-yl isocyanate; 4-isocyanatobenzophenone; 2-benzylphenyl isocyanate; 4-benzylphenyl isocyanate; diphenylmethyl isocyanate; 4-(benzyloxy)phenyl isocyanate; (1r,2r)-(−)-2-benzyloxycyclohexyl isocyanate; (1s,2s)-(+)-2-benzyloxycyclohexyl isocyanate; 2,2-diphenylethyl isocyanate; 2-(4-biphenyl)ethyl isocyanate; 4'-isocyanatobenzo-15-crown-5; 2,5-di-tert-butylphenyl isocyanate; tetradecyl isocyanate; n-fmoc-isocyanate; 3,3-diphenylpropyl isocyanate; 2,2-bis(4-isocyanatophenyl)hexafluoropropane; hexadecyl isocyanate; or octadecyl isocyanate. Mixtures of any two or more monoisocyanates may also be used.

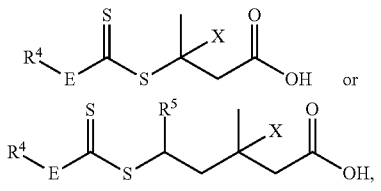
[0033] In the compounds in Schemes 1 and 2, the monomeric acid is illustrated as a compound of formula $R^3C(O)OH$. In the formula, R^3 is alkyl, alkenyl, or a group of formula $—CH_2C(X)(CH_3)(CH_2CHR^5)_xSC(S)ER^4$, wherein E is absent or S, R^4 is alkyl or alkenyl, R^5 is alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl, and x is from 0 to 20. In some embodiments, R^3 is an alkyl. In some embodiments, R^3 is an alkenyl. In some embodiments, R^3 is a group of formula $—CH_2C(X)(CH_3)(CH_2CHR^5)_nSC(S)ER^4$. Mixtures of any two or more such monomeric acids may be used as the monomeric acid. In one embodiment, the monomeric acid comprises a compound represented as $R^3C(O)OH$, wherein R^3 is a C_8-C_{24} alkyl, a C_8-C_{24} alkylene, or a group of formula $—CH_2C(X)(CH_3)(CH_2CHR^5)_nSC(S)SR^4$, wherein E is absent or s, R^4 is a C_1-C_{12} alkyl, a C_2-C_{12} alkenyl, R^5 is phenyl or tolyl, and x is from 0 to 30.

[0034] In the compounds in Schemes 1 and 2, the acid may be a monomeric acid, where the carboxyl group of the acid in conjunction with R^3 forms a photo-curable group, or alternatively, the acid is a fatty acid. In other words, in some embodiments, the polymerizable group, R^3, provides photo-curable properties to the polymer. Thus, when the monomeric acid is added to the polycarbodiimide, R^3 may be preserved and is not involved in the reaction to form the post-modified polycarbodiimide. However, upon UV exposure, the photo-curable R^3 may react to form higher molecular weight polymers, or cross-links between polymers. Accordingly, R^3, alone, or in conjunction with the carboxyl group of the acid may be a photo-curable group. Illustrative examples of photo-curable groups include, but are not limited to, vinyl groups and allylic groups.

[0035] As another alternative, the monomeric acid used in the process may be a fatty acid. For example, some fatty acids may be represented as $R^3C(O)OH$, where R^3 is a C_8-C_{24} alkyl or a C_8-C_{24} alkylene. Illustrative examples of such fatty acids include, but are not limited to, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linolaidic acid, α-linolenic acid, arachidonic acid, eicosapentaenoic acid, euricic acid, or docosahexaenoic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, or cerotic acid. A mixture of any two or more such acids may also be used.

[0036] Alternatively, the monomeric acid used in the process may be a mixture of a vinyl acid (i.e. where R^3 is an alkylene as described herein) and a fatty acid. Where the monomeric acid is such a mixture, the ratio of vinyl acid to fatty acid may range from 0.01:9.99 to 9.90:0.01 by weight.

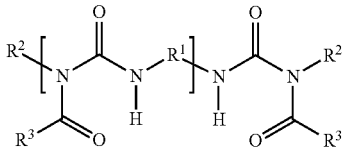
[0037] In yet a further embodiment, the monomeric acid may be a thiocarbonate acid of formula:



or such a thiocarbonate acid may be using in combination with any of the monomeric acids, including vinyl acids and fatty acids, described herein. In the above thiocarbonate acid, E is absent or is S, R^4 may be C_1-C_{18} alkyl, X is alkyl, aryl, nitrile, or halide, and x is the repeat group associate with the addition of a vinyl monomer, and R^5 may be an R^5 is alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl group, or a substituted group. In some embodiments, R^5 may be functionalized with an acid or ester groups. Illustrative examples of the thiocarbonate acid include, but are not limited to, 2-(4-methoxyphenylcarbonothioylthio)-ethanoic acid; 2-(phenylcarbonothioylthio)-propanoic acid; 2-(dodecylthiocarbonothioylthio)-2-methyl-propionic acid; 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid; 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid; and 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid, a trithiocarbonate acid terminated-polystyrene, -polyacrylate, -polymethacrylate, -polyvinylpyridine, -polyvinylthiophene, -polyvinylformamide, -polyvinylimidazole, or co-polymer thereof or a mixture of any two or more thereof. Where the monomeric acid is the poly thiocarbonate acid, R^5 may be derived from a vinylic monomer such as, but not limited to, styrene, α-methylstyrene, isobutyl acrylate, hydroxyethyl caprolactone acrylate, hexyl acrylate, isodecyl acrylate, lauryl acrylate, behenyl acrylate, allyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, tert.-butylaminoethyl methacrylate, lauryl methacrylate, stearyl methacrylate, behenyl methacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, triethylene glycol dimethacrylate, diethylene glycol dimethacrylate, PEG 200 dimethacrylate, trimethylolpropane trimethacrylate, 2-ethylhexyl acrylate, N-vinylcarbazole, 1-vinylimidazole, 2-vinylpyridine, n-vinylformamide,

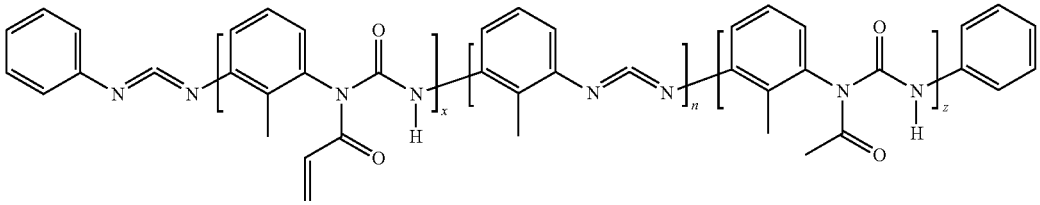
vinyl 2-ethylhexanoate, 2-vinylthiophene, butyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate, methacrylic acid, acrylic acid, methyl methacrylate, acrylamide, divinylbenzene, 1,6-hexanediol diacrylate, 4-tert-butylcyclohexyl acrylate, trimethylolpropane triacrylate, 4-hydroxybutyl acrylate, dicyclopentadienyl acrylate, phenoxyethyl acrylate, hydroxypropyl acrylate, TMI (META) unsaturated aliphatic isocyanate.

[0038] In another aspect, the post-modified polycarbodiimide of Scheme 1 is provided. Such a polymer may be of the formula:



Post-Modified Polycarbodiimide

In the formulas, R^1, R^2, and R^3 are as defined above. In some embodiments, R is an arylene, R^2 is a vinyl group, and R^3 is a C_8-C_{24} alkyl or C_8-C_{24} alkylene. The bracketing indicates the repeat unit of the polymer. For example, in one embodiment, the polymer is:



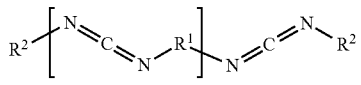
In this structure, x, y, and z indicate the repeat units in the polymer. Individually, x, y, and z may range from 0 to 30. In some embodiments, the sum of x, y, and z may be from 5 to 50. In some embodiments, the sum of x, y, and z may be from 10 to 35. In some embodiments, the sum of x, y, and z may be about 29.

[0039] In any of the above embodiments, the post-modified polycarbodiimides may have a weight average molecular weight of from about 300 to about 30,000 g/mol. In some embodiments, the weight average molecular weight is from about 300 to about 20,000 g/mol. In some embodiments, the weight average molecular weight is from about 300 to about 10,000 g/mol. In some embodiments, the weight average molecular weight is from about 300 to about 2,500 g/mol.

[0040] In one aspect, a process of preparing a post-modified polycarbodiimide is provided. The process includes contacting a capped polycarbodiimide with a monomeric acid to form a mixture which is solvent-free. Furthermore, the process of contacting the monomeric acid with the post-modified polycarbodiimide may be catalyst free. In other words, the mixture may contain only the capped polycarbodiimide, or mixture of capped polycarbodiimides, and the monomer acid, or mixture of monomeric acids. The mixture may also include any catalyst residue from the catalyst that may have been employed in the preparation of the capped polycarbodiimide.

[0041] The process conditions are quite mild. The contacting may be conducted at, or about, room temperature. For example, the temperature of the process may be from about 25° C. to about 40° C. In some embodiments, the process is conducted at a temperature of about 25° C. to about 30° C. There may be an exothermic response as the acid and polycarbodiimide proceeds that may be managed through cooling and controlled addition of the acid.

[0042] As above in the post-modified polycarbodiimides, the process uses a capped polycarbodiimide that may be a polymer of formula:



Capped Polycarbodiimide.

In the capped polycarbodiimide, R^1 is a linking group, and R^2 is an end cap derived from a monoisocyanate. In various embodiments, the linking group is alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl. For example, R^1 and R^2 may individually be a C_1-C_{12} alkyl, C_1-C_{12} cycloalkyl, a C_6-C_{12} aromatic, a C_6-C_{12} heterocyclyl, or a C_6-C_{12} heteroaryl. Illustrative examples of R^1 and R^2 include, but are not limited to, methylene, ethylene, propylene, isopropylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decalinylene, dodecylene, 1,2-cyclohexylene, 1,3-cyclohexylene, 1,4-cyclohexylene, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, a tolyl, or a xylyl. In some preferred embodiments, R^1 is an arylene group. For example, R^1, in some embodiments, is 1,3-phenylene, 1,4-phenylene, a tolyl, or a xylyl. For example, R^2, in some embodiments, is 1,3-phenylene, 1,4-phenylene, a tolyl, or a xylyl.

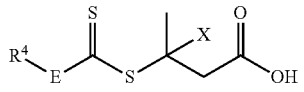
[0043] The monomeric acid used in the process may be a compound represented as $R^3C(O)OH$, wherein R^3 is a polymerizable group. For example, the polymerizable group may be an alkylene group, such as a vinyl group. Illustrative monomeric acids include, but are not limited to, acrylic acid, methacrylic acid, vinylphosphoric acid, or 4-vinylphenylboronic acid.

[0044] Where a post-modified polycarbodiimide is formed from a monomeric acid of formula $R^3C(O)OH$, the post-modified polycarbodiimide may be a photo and/or chemical-curable polymer. That is, illustrative monomeric acids such as acrylic acid and methacrylic acid are photo and/or chemical-curable materials. Because the vinyl group, which imparts photo and/or chemical-curable character, does not

take part in the reaction with the polycarbodiimide, the photo- and/or chemical curable character of the moiety containing the vinyl group is maintained in the post-modified polycarbodiimide. Such a group may be exploited in further uses of the post-modified polycarbodiimide when used in photo and/or chemical-cure applications.

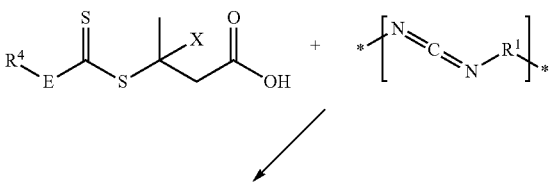
[0045] Alternatively, the monomeric acid using the process may be a fatty acid. For example, some fatty acids may be represented as $R^3C(O)OH$, where R^3 is a C_8-C_{24} alkyl or a C_8-C_{24} alkylene. Illustrative examples of such fatty acids include, but are not limited to, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, α-linolenic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid, euricic acid, or docosahexaenoic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, or cerotic acid. Higher unsaturation in the fatty acid (e.g. linoleic (2 double bonds) or linolenic (3 double bonds)) may provide additional sites of chemical, i.e. radical, cure materials.

[0046] In another embodiment, the monomeric acid may be an thiocarbonate acid of formula:

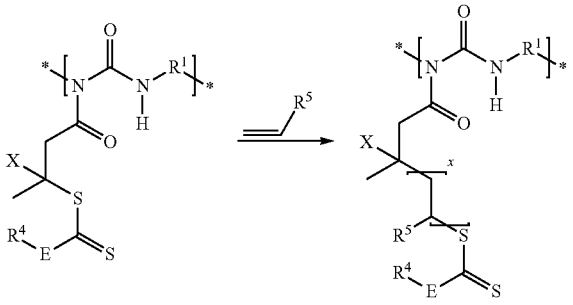


In the structure, E is absent or is S, R^4 may be C_1-C_{18} alkyl, and X is alkyl, aryl, nitrile, or halide. Illustrative examples of the thiocarbonate acid include, but are not limited to, 2-(4-methoxyphenylcarbonothioylthio)-ethanoic acid; 2-(phenylcarbonothioylthio)-propanoic acid; 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid; 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid; 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid; and 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid, a thiocarbonate acid, or a trithiocarbonate acid terminated-polystyrene, -polyacrylate, -polymethacrylate, -polyvinylpyridine, -polyvinylthiophene, -polyvinylformamide, -polyvinylimidazole, or co-polymer thereof, or a mixture of any two or more thereof.

[0047] In another embodiment, in the process, the capped polycarbodiimide may be reacted with any of the above monomeric acids to form the post-modified polycarbodiimide. The post-modified polycarbodiimide may then be further modified with a vinylic monomer to provide a hybrid polymer. Such an embodiment may be illustrated by the following scheme, using a thiocarbonate acid as an illustrative monomeric acid, but where any of the monomeric acids may be used.



-continued



In this embodiment and in the scheme, the vinylic monomer is represented as $H_2C{=}CHR^5$, where R^5 is an alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl group, an x is the repeat unit in the polymer. The value of x may be 0 (where the vinylic monomer is not present), or x may be from 1 to 50. In some embodiments, x is from 1 to 15. Vinylic monomers may include, but are not limited to, styrene and α-methylstyrene, isobutyl acrylate, hydroxyethyl caprolactone acrylate, hexyl acrylate, isodecyl acrylate, lauryl acrylate, behenyl acrylate, allyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, tert.-butylaminoethyl methacrylate, lauryl methacrylate, stearyl methacrylate, behenyl methacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, triethylene glycol dimethacrylate, diethylene glycol dimethacrylate, PEG 200 dimethacrylate, trimethylolpropane trimethacrylate, 2-ethylhexyl acrylate, N-vinylcarbazole, 1-vinylimidazole, 2-vinylpyridine, n-vinylformamide, vinyl 2-ethylhexanoate, 2-vinylthiophene, butyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate, methacrylic acid, acrylic acid, methyl methacrylate, acrylamide, divinylbenzene, 1,6-hexanediol diacrylate, 4-tert-butylcyclohexyl acrylate, trimethylolpropane triacrylate, 4-hydroxybutyl acrylate, dicyclopentadienyl acrylate, phenoxyethyl acrylate, hydroxypropyl acrylate, and TMI (META) unsaturated aliphatic isocyanate. As an alternative on this process, where a thiocarbonate acid is the monomeric acid, it may initially be modified with the vinylic monomer (to form a thiocarbonate-polyvinylic-acid as a monomeric acid) prior to reaction with the post-modified polycarbodiimide.

[0048] The polycarbodiimide used in the processes may be prepared or commercially obtained. The polycarbodiimide may be a polymer derived from a monomer of formula ONC—R^1—CNO, in the absence of a solvent, where R^1 is as defined above in any of the embodiments. In some embodiments, R is an arylene group such as, but not limited to, phenylene, tolylene, or xylylene.

[0049] As introduced above, the capped polycarbodiimide may be prepared by combining in a reaction vessel a diisocyanate, a moisture scavenger, a monoisocyanate, and a catalyst to form a reaction mixture; and heating the reaction reaction mixture to a temperature and for a time sufficient to form a capped polycarbodiimide. The diisocyanate, moisture scavenger, and a monoisocyanate are as described above and below. The capped polycarbodiimide prepared, has 0.25 wt % or less of free isocyanate groups, and, in the process, the combining and heating are conducted in the absence of a solvent.

[0050] In the process, illustrative temperatures are from about 30° C. to about 200° C. In some embodiments, the temperature is from about 60° C. to about 120° C. In yet other embodiments, the temperature is from about 100° C. to about 110° C.

[0051] The present invention, thus generally described, will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting of the present invention.

EXAMPLES

Example 1

[0052] Preparation of a toluene diisocyanate-based polycarbodiimide. An 80:20 mixture of the 2,4- and 2,6-isomers of toluene diisocyanate (492.7 g) was placed in a flask with triphenyl phosphite (TPP, 1.0 g), and the flask was then heated to 70° C. At temperature, phenyl isocyanate (505.3 g) and phospholene oxide (5% solution in toluene, 1.0 g) were added, and the flask was heated to 106° C. for 7 hours. Additional phospholene oxide (0.3 g) was then added and the flask heated to 110° C. for another 7 hours. The amount of residual NCO groups (expressed as F_{NCO} (free NCO)) was 0.56 wt %.

Example 2

[0053] Alternative preparation of a toluene diisocyanate-based polycarbodiimide. An 80:20 mixture of the 2,4- and 2,6-isomers of toluene diisocyanate (492.7 g) was placed in a flask with triphenyl phosphite (TPP, 1.0 g), and the flask was then heated to 70° C. At temperature, phenyl isocyanate (505.3 g) was added, and the flask contents stirred until the temperature was again at 70° C. At temperature, phospholene oxide (5% solution in toluene, 1.0 g) was added, and the flask was heated to 106° C. for 8.5 hours. F_{NCO} was 0.79 wt %.

Example 3

[0054] Alternative preparation of a toluene diisocyanate-based polycarbodiimide. An 80:20 mixture of the 2,4- and 2,6-isomers of toluene diisocyanate (492.7 g) was placed in a flask with triphenyl phosphite (TPP, 1.0 g), and the flask was then heated to 70° C. At temperature, phenyl isocyanate (505.3 g) was added, and the flask contents stirred until the temperature was again at 70° C. At temperature, phospholene oxide (5% solution in toluene, 1.5 g) was added, and the flask was heated to 120° C. for 1 hour. At this time 1.5 g of phospholene oxide (5% solution in toluene) was added, and the flask was heated to 120° C. for 4 hours. Two different runs provided F_{NCO} values of 0.28 wt % and 0.44 wt %. It is noteworthy that in such samples, the F_{NCO} may be attributable to both residual monomer and polymer NCO content. However, the overall amount of NCO content attributable to free TDI (toluene diisocyanate) is less than 0.1 wt %.

Example 4

[0055] In other examples, the procedure of Example 3 may be followed with ratios of 2,4-toluene diisocyanate:2,6-toluene diisocyanate ranging from 100:0 to 65:35.

Example 5

[0056] Complete conversion of a toluene diisocyanate-based polycarbodiimide (carbodiimide-acrylic acid) (Example 1) to a UV and/or chemical curable resin. A toluene diisocyanate-based polycarbodiimide from Example 1 (5 g) was reacted with acrylic acid (2 g) by mechanical mixing at ambient temperature. The reaction was instantaneous and exothermic. The disappearance of the carbodiimide was monitored by infrared spectroscopy. Upon completion a post-modified polycarbodiimide was obtained.

Example 6

[0057] Partial conversion of a toluene diisocyanate-based polycarbodiimide (carbodiimide-acrylic acid) (Example 1) to a UV and/or chemical curable resin. A toluene diisocyanate-based polycarbodiimide from Example 1 (2.0 g) was reacted with acrylic acid (0.5 g) by mechanical mixing at ambient temperature. The reaction was instantaneous and exothermic. A decrease in the vibration of the carbodiimide was monitored by infrared spectroscopy to determine extent of the reaction. Upon completion a post-modified polycarbodiimide containing carbodiimide, N-acylurea of acrylic acid was obtained.

Example 7

[0058] Partial conversion of a toluene diisocyanate-based polycarbodiimide (carbodiimide-acrylic acid-tripropyneglycol diacrylate) (Example 1) to a UV and/or chemical curable resin. A toluene diisocyanate-based polycarbodiimide from Example 1 (1.0 g) was reacted with acrylic acid (0.24 g), tripropylene glycol diacrylate (0.25 g) by mechanical mixing at ambient temperature. The reaction was instantaneous and exothermic. A decrease in the vibration of the carbodiimide was monitored by infrared spectroscopy to determine extent of the reaction. Upon completion a post-modified polycarbodiimide containing carbodiimide, N-acylurea and tripropylene glycol diacrylate was obtained.

Example 8

[0059] Partial conversion of a toluene diisocyanate-based polycarbodiimide (carbodiimide-acrylic acid-trimethylolpropane triacrylate) (Example 1) to a UV and/or chemical curable resin. A toluene diisocyanate-based polycarbodiimide from Example 1; 1.0 g was reacted with acrylic acid (0.24 g), trimethylol propane triacrylate (0.25 g) by mechanical mixing at ambient temperature. The reaction was instantaneous and exothermic. A decrease in the vibration of the carbodiimide was monitored by infrared spectroscopy to determine extent of the reaction. Upon completion a post-modified polycarbodiimide containing carbodiimide, N-acylurea and TMPTA was obtained.

Comparative Example 1

[0060] Conversion of a commercial polycarbodiimide ZOLIDINE® XL-29SE to a UV curable resin. ZOLIDINE® XL-29SE (10 g) was reacted with acrylic acid (0.89 g) in an orbital shaker at ambient temperature. The reaction was slow and it took 24 hours for the disappearance of the carbodiimide (as monitored by infrared spectroscopy) indicating the completion of the reaction. Upon completion a post-modified polycarbodiimide was obtained.

Example 9

[0061] Oleic acid modified toluene diisocyanate-based polycarbodiimide (carbodiimide-Oleic acid 1:1 wt ratio). A toluene diisocyanate-based polycarbodiimide from Example 1 (100.0 g) was reacted with oleic acid (100.0 g) in Parr Pressure reactor at 600 rpm at ambient temperature. The reaction was instantaneous (<10 minutes) and exothermic. Formation of N-acyl was monitored by infrared spectroscopy to determine the extent of the reaction (FIG. **1**, middle spectrum). Upon completion a post-modified polycarbodiimide was obtained.

Example 10

[0062] Oleic acid modified toluene diisocyanate-based polycarbodiimide (carbodiimide-oleic acid 1:2.5 wt ratio). A toluene diisocyanate-based polycarbodiimide from Example 1 was reacted with oleic acid in a 1:2.5 wt ratio in a Parr Pressure reactor at 600 rpm at ambient temperature. The reaction was instantaneous (<10 min) and exothermic. Formation of N-acyl was monitored by infrared spectroscopy to determine the extent of the reaction. In FIG. **1**, the top spectrum is the polycarbodiimide, middle is of partially reacted and the bottom spectrum is the fully modified spectrum. Note the changes, in the region of about 2100 cm^{-1} (—N═C═N—) to about 1600 cm^{-1} (—N(H)C(O)NC(O)(R)-). Upon completion a post-modified polycarbodiimide was obtained.

Example 11

[0063] Post-modified toluene diisocyanate-based polycarbodiimide (carbodiimide-fatty acid-acrylic acid-tripropylene glycol diacrylate). A toluene diisocyanate-based polycarbodiimide from Example 1 (1.0 g) was reacted with acrylic acid (0.24 g) tripropylene glycol diacrylate (0.25 g) and oleic acid (1.0 g) by vigorous mechanical mixing at ambient temperature. The reaction was instantaneous (<10 min) and exothermic. Formation of N-acyl was monitored by infrared spectroscopy to determine the extent of the reaction. Upon completion a post-modified polycarbodiimide containing carbodiimide, N-acylurea (acrylic acid and oleic acid) and tripropylene glycol diacrylate was obtained.

Example 12

[0064] Post-modified toluene diisocyanate-based polycarbodiimide (carbodiimide-Fatty acid based resin Pamolyn 380). A toluene diisocyanate-based polycarbodiimide from Example 1 (4.0 g) was reacted with commercially available fatty acid based resin Pamolyn 380 (4.0 g) by vigorous mechanical mixing at ambient temperature. The reaction was instantaneous (<10 min) and exothermic. Formation of N-acyl was monitored by infrared spectroscopy to determine the extent of the reaction. Upon completion a post-modified polycarbodiimide was obtained.

Example 13

[0065] Post-modified toluene diisocyanate-based polycarbodiimide (carbodiimide-fatty acid-tung oil). A toluene diisocyanate-based polycarbodiimide from Example 1 (2.0 g) was reacted with oleic acid (2.0 g) and tung oil (0.5 g) by vigorous mechanical mixing at ambient temperature. The reaction was instantaneous (<10 min) and exothermic. Formation of N-acyl was monitored by infrared spectroscopy to determine the extent of the reaction. Upon completion a post-modified polycarbodiimide was obtained.

[0066] While certain embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

[0067] The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising," "including," "containing," etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the claimed technology. Additionally, the phrase "consisting essentially of" will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase "consisting of" excludes any element not specified.

[0068] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds compositions or biological systems, which can of course vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0069] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0070] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0071] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0072] Other embodiments are set forth in the following claims.

1. A process of preparing a capped polycarbodiimide, the process comprising:

combining in a reaction vessel a diisocyanate, a moisture scavenger, a monoisocyanate, and a catalyst to form a reaction mixture; and

heating the reaction mixture to a temperature and for a time sufficient to form a capped polycarbodiimide;

wherein:

the capped polycarbodiimide has 0.25 wt % or less of free isocyanate groups;

the capped polycarbodiimide is a liquid at 25° C.; and

the combining and heating are conducted in the absence of a solvent.

2. A process as set forth in claim **1** wherein the capped polycarbodiimide has 0.1 wt % or less free isocyanate groups.

3. A process as set forth in claim **1** wherein the temperature is from about 30° C. to about 200° C.

4. A process as set forth in claim **1** wherein the diisocyanate is a compound of formula ONC—R^1—CNO, wherein R^1 is a C_1-C_{12} alkyl, C_1-C_{12} cycloalkyl, a C_6-C_{12} aromatic, a C_6-C_{12} heterocyclyl, or a C_6-C_{12} heteroaryl linking group.

5. A process as set forth in claim **1** wherein the diisocyanate comprises 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, or a mixture of 2,4- and 2,6-toluene diisocyanate.

6. A process as set forth in claim **1** wherein the monoisocyanate is a compound of formula ONC—R^2, wherein R^2 is a alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl and/or R^2 is a C_1-C_{12} alkyl, C_1-C_{12} cycloalkyl, a C_6-C_{12} aromatic, a C_6-C_{12} heterocyclyl, or a C_6-C_{12} heteroaryl.

7. A process as set forth in claim **1** wherein the capped polycarbodiimide is a material of formula: R^2—N═C═N—[R^1—N═C═N]$_n$—R^2, wherein R^1 is alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl, R^2 is a alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl, and n is the polymer repeating unit.

8. A process as set forth in claim **7** wherein R^1 is methylene, ethylene, propylene, isopropylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decalinylene, dodecylene, 1,2-cyclohexylene, 1,3-cyclohexylene, 1,4-cyclohexylene, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, or tolyl and/or R^2 is methyl, ethyl, propyl isopropyl, butyl, pentyl hexyl, heptyl, octyl, nonyl, decalinyl, dodecyl, cyclohexyl, phenyl, or tolyl.

9. A process as set forth in claim **7** wherein n is from about 1 to about 30.

10. A process as set forth in claim **1** further comprising contacting the capped polycarbodiimide with a monomeric acid, or a mixture of two or more monomeric acids.

11. A process as set forth in claim **10** wherein the monomeric acid comprises a compound represented as R^3C(O)OH, wherein R^3 is alkyl, alkenyl, or a group of formula —$CH_2C(X)(CH_3)(CH_2CHR^5)_xSC(S)ER^4$, and wherein E is absent or S, R^4 alkyl or alkenyl, R^5 is alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl, and x is from 0 to 20.

12. (canceled)

13. A process as set forth in claim **10** wherein the monomeric acid comprises acrylic acid, methacrylic acid, vinylphosphonic acid, 4-vinylphenylboronic acid, or a fatty acid and/or the monomeric acid comprises a saturated fatty acid, a monounsaturated fatty acid, or a polyunsaturated fatty acid.

14. A process as set forth in claim **10** wherein the monomeric acid is a photo-curable and/or chemical-curable monomeric acid.

15. A process as set forth in claim **10** wherein the monomeric acid is a mixture of any two or more of a vinyl acid and a fatty acid wherein a ratio of the vinyl acid to the fatty acid is from 9.99:0.01 to 0.01:9.99.

16. A process as set forth in claim **7** wherein n is from 2 to 14.

17. A process as set forth in claim **1** wherein the moisture scavenger is triphenylphosphite and/or the catalyst is phospholene oxide.

18. A polymer comprising the reaction product of a capped polycarbodiimide and a monomeric acid.

19. A polymer as set forth in claim **18** wherein the capped polycarbodiimide is a material of formula: R^2—N═C═N—[R^1—N═C═N]$_n$—R^2, wherein

R^1 is methylene, ethylene, propylene, isopropylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decalinylene, dodecylene, 1,2-cyclohexylene, 1,3-cyclohexylene, 1,4-cyclohexylene, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, or tolyl;

R^2 is a alkyl, cycloalkyl, aromatic, heterocyclic, or heteroaryl, and n is the polymer repeating unit; and

the monomeric acid is a compound represented as R^3C(O)OH, wherein R^3 is alkyl, alkenyl, or a group of formula —$CH_2C(X)(CH_3)(CH_2CHR^5)_xSC(S)ER^4$, and wherein E is absent or S, R^4 alkyl or alkenyl, R^5 is alkyl, aryl, aralkyl, —OC(O)alkyl, —C(O)Oalkyl, —OC(O)aryl, —C(O)Oaryl, heteroaryl, heterarylalkyl, heterocyclyl, or heterocyclylalkyl, and x is from 0 to 20.

20. A polymer as set forth in claim **18** wherein the polymer is a photo-curable and/or chemical-curable polymer.

21. A polymer as set forth in claim **19** wherein n is from 2 to 14.

* * * * *