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(54) **Title:** PHOTOCURABLE POLYMERS, PHOTOCURABLE POLYMER COMPOSITIONS AND LITHOGRAPHIC PROCESSES INCLUDING THE SAME

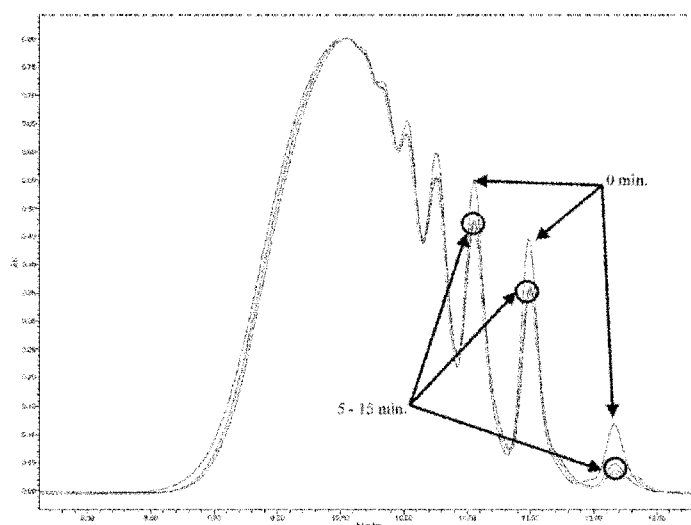


FIG 1

(57) **Abstract:** Described herein are photurable polymers that can be desirably used in photofabrication processes. Functionalized poly(aryl ether) ("PAE") polymers and photurable polymer compositions including the functionalized PAE polymers are described that can be desirably incorporated into lithographic processes in which light is used to cure the functionalized PAE polymers. The functionalized PAE polymers are functionalized with a linking group. The linking group is a polymerizable group, a photoinitiator group or a group that is reactive to oxiranes. The functionalized PAE polymer can be incorporated into a photurable polymer composition that can optionally include a photoinitiator. The photurable polymer compositions can be desirably used in photofabrication methods.

PHOTOCURABLE POLYMERS, PHOTOCURABLE POLYMER COMPOSITIONS AND LITHOGRAPHIC PROCESSES INCLUDING THE SAME

This application claims priority to U.S. provisional application No. 62/319936 filed April 8, 2016, the whole content of this application being incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

The invention relates to functionalized poly(aryl ether) polymers. The invention further relates to photocurable polymer compositions including the functionalized poly(aryl ether) polymers. Still further, the invention relates to lithographic methods to form 3-dimensional objects that incorporate the aforementioned photocurable polymer compositions.

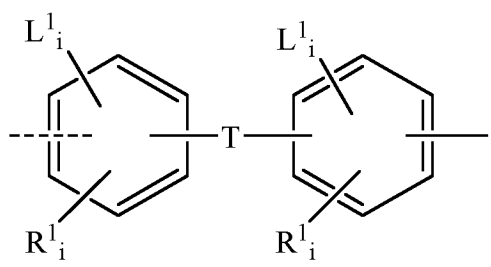
BACKGROUND OF THE INVENTION

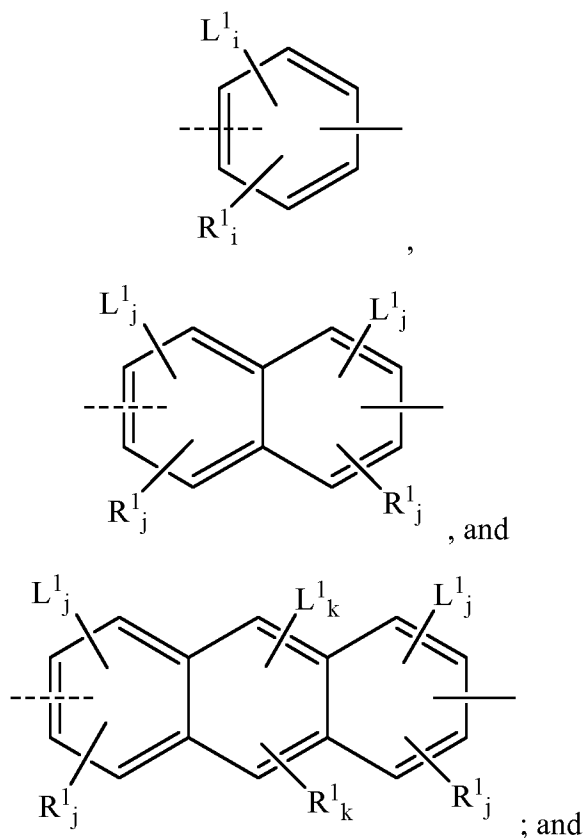
Lithographic process for the photofabrication of 3-dimensional articles from polymeric materials have found recent popularity due to their relative speed and simplicity. In general, lithographic processes involve the use of light to locally cure a polymerizable polymer composition at specific locations. The localized curing allows for the fabrication of 3-dimensional articles.

SUMMARY OF THE INVENTION

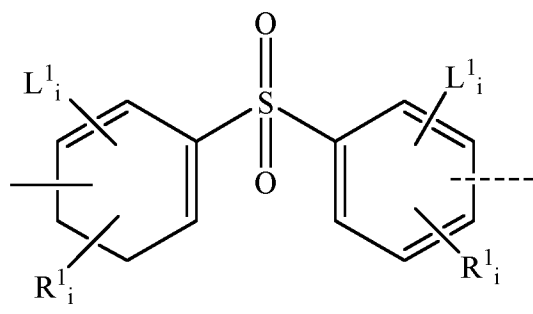
In a first aspect, the invention is directed to a functionalized poly(aryl ether) ("PAE") polymer including recurring unit (R_{PAES}) represented by the formula $--[M_A-O-M_S-O]--$ where,

- M_A is represented by a formula selected from the following group of formulae:





- M_S is represented by the following formula:



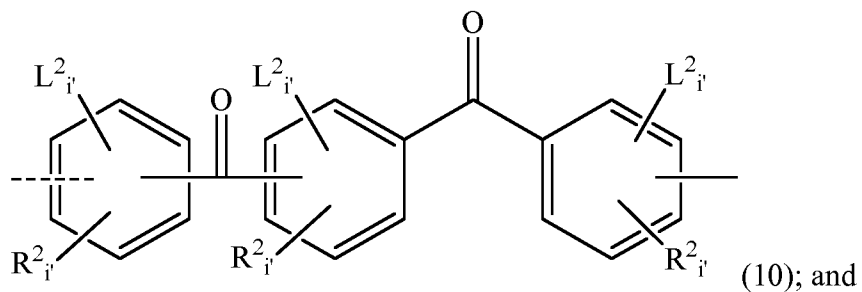
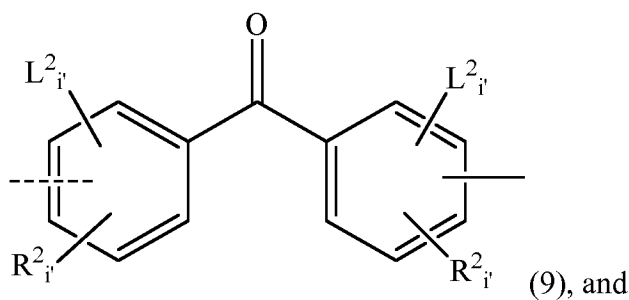
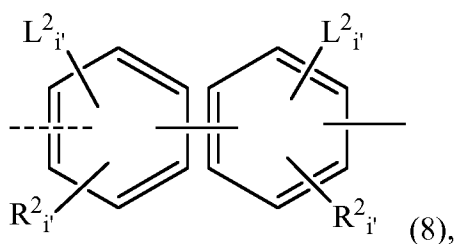
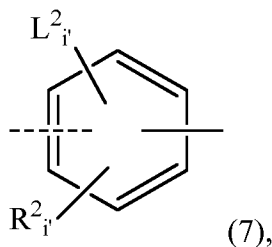
5 In the above, each R^1 is independently selected from the group consisting of a halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; each L^1 is a linker molecule independently
 10 selected from the group consisting of a radically polarizable group, a cationically polarizable group, a radical initiator group, and a oxirane reactive group; each i is an independently selected integer from 0 to 4; each j is an independently selected integer from 0 to 3; each k is an independently selected integer from 0 to 2; and T is selected from the group consisting of
 15 a bond, $-CH_2-$; $-O-$; $-SO_2-$; $-S-$; $-C(O)-$; $-C(CH_3)_2-$; $-C(CF_3)_2-$; $-C(=CCl_2)-$; $-C(CH_3)(CH_2CH_2COOH)-$; $-N=N-$; $-R^aC=CR^b-$, where each R^a and R^b , independently of one another, is a hydrogen or a C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, or C_6 - C_{18} -aryl group; $-(CH_2)_n-$

and $-(CF_2)_n-$ with n being an integer from 1 to 6; an aliphatic divalent group, linear or branched, of up to 6 carbon atoms; and combinations thereof.

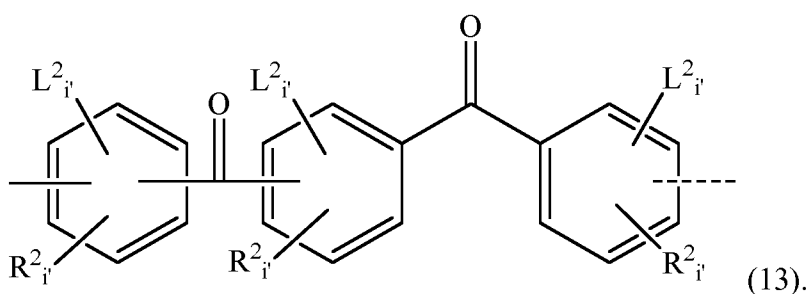
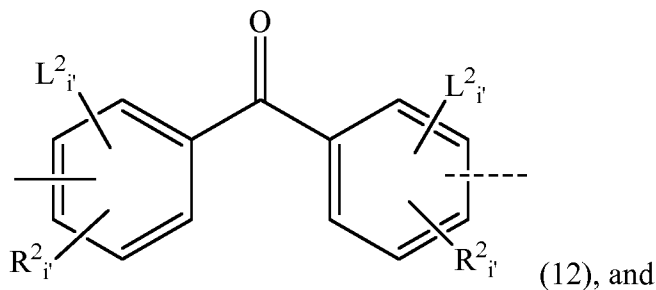
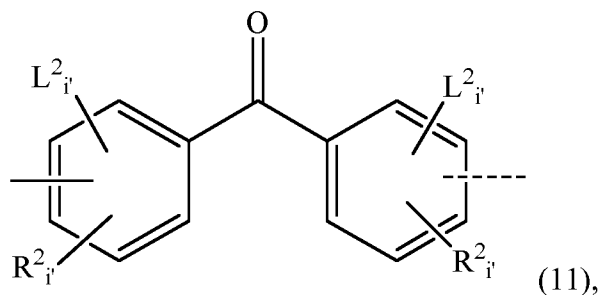
In another aspect, the invention is directed to a functionalized PAE polymer including recurring unit (R_{PAEK}) represented by the formula $--[M_B-O-M_K-O]--$

5 where

- M_B is represented by a formula selected from the following group of formulae



- M_K is represented by a formula selected from the following group of formulae:



In the above, each R^2 is independently selected from the group consisting of a
 5 halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide,
 alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal
 phosphonate, alkyl phosphonate, amine and quaternary ammonium; each L^2 is a linker
 molecule independently selected from the group consisting of radically polarizable group, a
 cationically polarizable group, a radical initiator group, and a oxirane reactive group; and
 10 each i' is an independently selected integer from 0 to 4.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plot of the elution time vs intensity for a PPSU polymer functionalized with
 terminal olefin, before and after exposure to various temperatures and times.

DETAILED DESCRIPTION OF THE INVENTION

Described herein are photocurable polymers that can be desirably used in
 photofabrication processes. In particular, functionalized PAE polymers and photocurable
 polymer compositions including the functionalized PAE polymers that are described can be
 desirably incorporated into lithographic processes in which light is used to cure the

functionalized PAE polymers. The functionalized PAE polymers are functionalized with a linking group. The linking group is a polymerizable group, a photoinitiator group or a group that is reactive to oxiranes (“oxirane reactive group”). The functionalized PAE polymer can be incorporated into a photocurable polymer composition that can optionally include a photoinitiator. The photocurable polymer compositions can be desirably used in photofabrication methods.

Current polymerizable polymer compositions used in lithographic processes utilize polymers which, after curing, have moderate thermal stability. For example, such cured polymers exhibit significant thermal degradation at elevated temperatures for example, at above 300 °C, 350 °C or 400 °C. Concomitantly, 3-dimensional articles formed from the polymerizable polymer compositions are suitable only in relatively low temperature applications. While the switch to polymerizable polymers having higher thermal stability, higher hydrolytic resistance and mechanical performance like poly(aryl ether) is desirable, they exhibit two main limitations: they are too viscous and require very high processing temperatures to get a desired flow or they don’t have functionalities that can react in presence of UV, alone or as a component photocurable polymer composition.

Lithographic processes involve the use of light to cure the photocurable polymer composition. In one embodiment, the lithographic process can be a stereolithography (“SLA”) process. In SLA processes, the photocurable polymer composition in a liquid form is placed in a reservoir and light is directed at the polymer composition. The light induces polymerization or crosslinking of the photocurable polymer at least at a portion of where the light contacts the photocurable polymer composition. In another embodiment, the lithographic process can be a continuous liquid interface production (“CLIP”) process. In CLIP processes, a continuous sequence of light images (*e.g.*, generated by a digital light projector) is projected through an oxygen-permeable, light-transparent window below a liquid bath of the photocurable polymer composition. The amount of oxygen permitted in the liquid bath is controlled and the oxygen acts to inhibit the photocurable polymer composition from curing (*e.g.* polymerizing or cross-linking) in certain areas and allowing other regions of the photocurable polymer composition that are exposed to light to cure. Correspondingly, the oxygen creates a “dead zone” within the liquid bath where curing does not take place when the liquid bath is exposed to light. While CLIP is described using oxygen as a curing inhibitor, other inhibitors (and correspondingly, inhibitor permeable membranes) can be used. CLIP processing is further described in WO 2014/126837 to Desimone *et al.*, filed October 2, 2014 and incorporated by reference herein. In both SLA and CLIP processes, the

light preferably comprises ultraviolet ("UV") light having a wavelength from about 10 nanometers to about 400 nm. In some embodiments of CLIP and SLA, the UV light is UV laser light.

The photocurable resin composition is a liquid phase composition and includes a functionalized PAE polymer. The PAE polymer is a low molecular weight polymer. In some embodiments, the PAE polymer can have a number average molecular weight (" M_n ") of no more than about 20,000 g/mol, no more than about 15,000 g/mol or no more than about 10,000 g/mol. In some such embodiments, the PAE polymer has a M_n of no less than about 1,000 g/mol or no less than about 2,000 g/mol. The number average molecular weight can be measured using gel permeation chromatography ("GPC") using the polystyrene standard.

In embodiments of interest herein, the PAE polymer is functionalized with a linking group selected from a polymerizable group, a photoinitiator group or an oxirane reaction group. The polymerizable group can be a radically polymerizable group or a cationically polymerizable group. Radically polymerizable groups refer to groups that cause a polymerization reaction or crosslinking reaction upon irradiation with light in the presence of a radical photoinitiator. Cationically polymerizable groups refer to groups that cause a polymerization reaction or crosslinking reaction upon irradiation with light in the presence of a cationic photoinitiator. In embodiments in which the linking group is a photoinitiator, the photoinitiator is preferably a radical photoinitiator. A radical photoinitiator refers to a compound that decomposes and evolves radicals to initiate radical polymerization upon exposure to light. In embodiments in which the linking group is an oxirane reactive group, the oxirane reactive group is defined as a group that can react with an oxirane group. In some embodiments, the photocurable polymer composition can include an oxirane containing polymer that can be a PAE polymer or another monomer or polymer of another type. Regardless of the particular choice of linking group, the polymerization reaction or crosslinking reaction can occur between different PAE polymer chains, internally within the same PAE polymer chain or between a PAE chain and another polymer chain in the photocurable polymer composition having a composition distinct from the PAE polymer. For example, with respect to radically polymerizable linking groups, the reaction can take place between a radical formed by UV excitation of a radical photoinitiator and a C=C double bond of a functionalized PAE. As another example, with respect to cationically polymerizable linking groups, the reaction can take place between the product formed by the UV excitation of an onium salt and an epoxy of a functionalized PAE.

The PAE polymer is functionalized with the linking group within the polymer backbone (“internal functionalization”) or at the ends of the PAE polymer chain (“terminal functionalization”). For example, with respect to internal functionalization, one or more of the recurring units of the PAE polymer that are not disposed at the end of the PAE polymer chain can be functionalized with a linking group. As another example, with respect to terminal functionalization, one or both ends of the PAE polymer chain can be functionalized with a linking group.

The functionalized PAE polymers can be incorporated into curable polymer compositions. Depending on the selected linking group, the curable polymer composition can optionally include a photoinitiator and other polymers distinct from the PAE polymer. Upon excitation with light and at a reaction temperature suitable for polymerization/cross-linking, the PAE polymer can undergo polymerization or cross-linking with itself or other distinct polymers in the polymer compositions. The PAE polymer compositions can therefore be desirably incorporated into lithographic processes in which light (*e.g.* UV light) is used to cure a polymer composition.

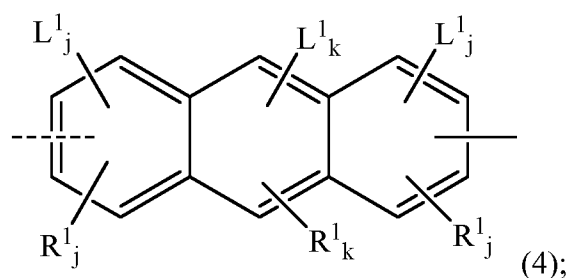
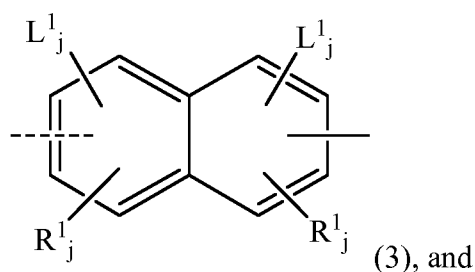
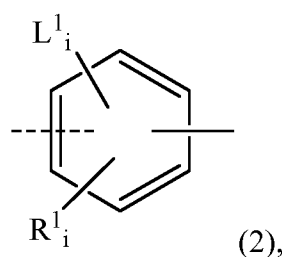
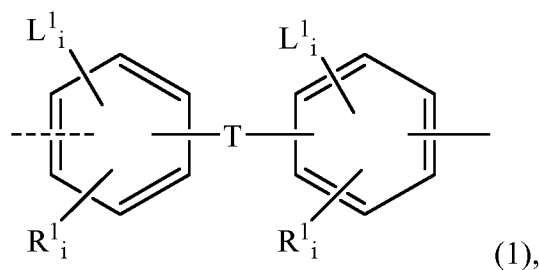
The Photocurable Polymer

The Polymer

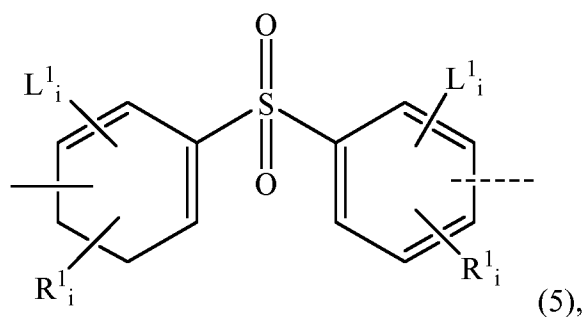
The polymerizable compositions contain a functionalized poly(aryl ether) (“PAE”) polymer. As used herein, a PAE polymer refers to any polymer having at least 50 mole percent (“mol. %”) recurring unit (R_{PAE}) containing an arylene group and an ether group (-O-). In some embodiments, the PAE polymer can have at least 60 mol.%, at least 70 mol.%, at least 80 mol.%, at least 90 mol.%, at least 95 mol.%, at least 99 mol.% or at least 99.9 mol.% recurring unit (R_{PE}). The PAE polymers of interest herein are low molecular weight polymers. In embodiments in which the PAE polymer is internally functionalized with a linker molecule, one or more of the recurring units (R_{PAE}) that are not disposed at the end of the PAE polymer chain is functionalized with a linker molecule.

In some embodiments, the PAE polymer can be a poly(aryl ether sulfone) (“PAES”) polymer or a poly(aryl ether ketone) (“PAEK”) polymer. As used herein, a PAES polymer refers to any PAE polymer where recurring unit (R_{PAE}) contains, in addition to the arylene group and ether group (-O-), a sulfone group [-SO₂-]. For clarity, recurring unit (R_{PAE}) is referred to as “(R_{PAES})”, when the PAE polymer is a PAES polymer.

Recurring unit (R_{PAES}) can be represented by the formula $--[M_A-O-M_S-O]--$, where the dashed bonds represent bonds to adjacent repeat units. M_A is represented by a formula selected from the following group of formulae:



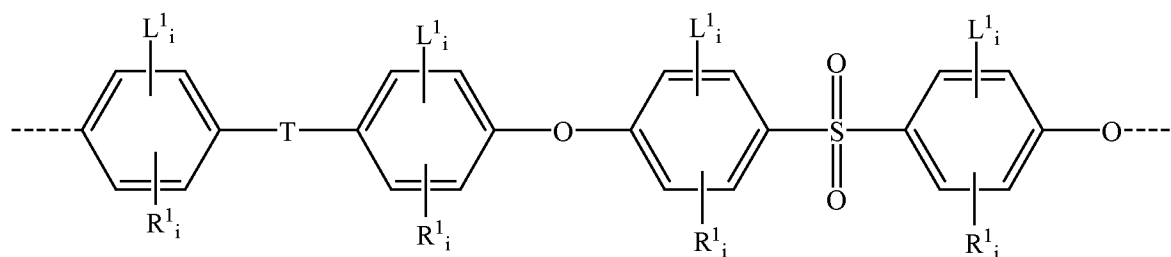
and M_S is represented by the following formula:



10 where each R^1 is independently selected from the group consisting of a halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl

phosphonate, amine and quaternary ammonium; each L^1 is a linker molecule independently selected from the group consisting of a polarizable group, a UV initiating group, and a oxirane reactive group; each i is an independently selected integer from 0 to 4; each j is an independently selected integer from 0 to 3; each k is an independently selected integer from 0 to 2; and T is selected from the group consisting of a bond, $-\text{CH}_2-$; $-\text{O}-$; $-\text{SO}_2-$; $-\text{S}-$; $-\text{C}(\text{O})-$; $-\text{C}(\text{CH}_3)_2-$; $-\text{C}(\text{CF}_3)_2-$; $-\text{C}(=\text{CCl}_2)-$; $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{COOH})-$; $-\text{N}=\text{N}-$; $-\text{R}^a\text{C}=\text{CR}^b-$, where each R^a and R^b , independently of one another, is a hydrogen or a C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, or C_6 - C_{18} -aryl group; $-(\text{CH}_2)_n-$ and $-(\text{CF}_2)_n-$ with n being an integer from 1 to 6; an aliphatic divalent group, linear or branched, of up to 6 carbon atoms; and combinations thereof. As used herein, the dashed bonds represent a bond to an adjacent recurring unit.

In some embodiments, the PAES polymer can be represented by the following formula:

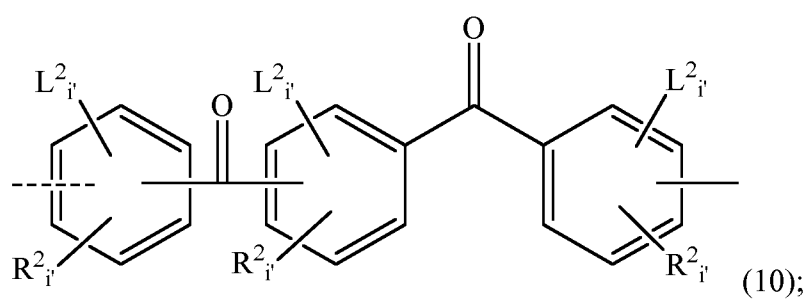
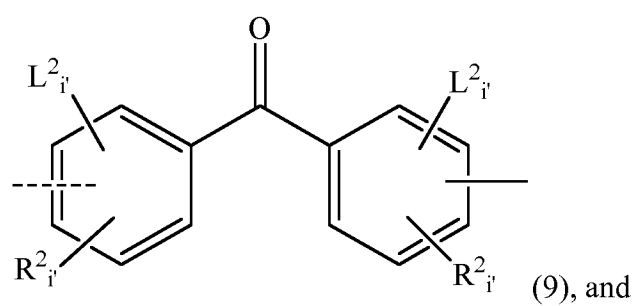
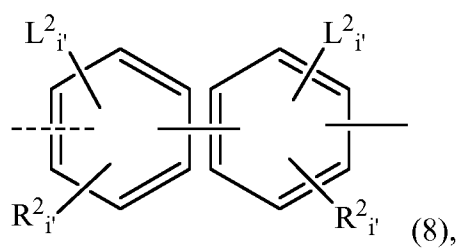
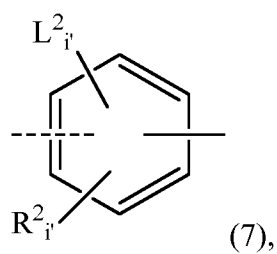


(6).

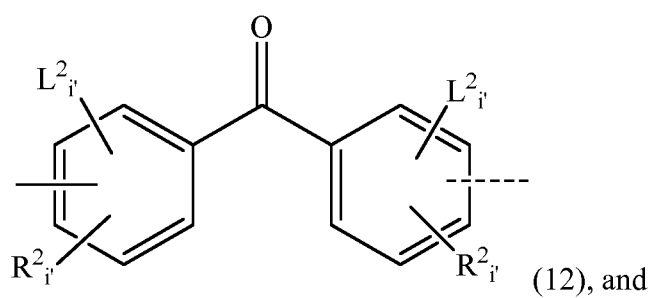
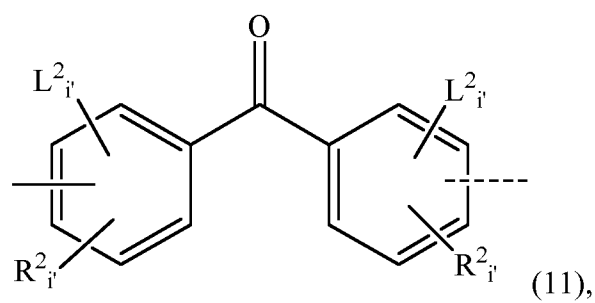
In some such embodiments, the PAES polymer can be a polysulfone ("PSU") polymer, a poly(ether sulfone) ("PESU") polymer, or a poly(phenyl sulfone) ("PPSU") polymers. For example, referring to Formula (6), when T is a bond, $-\text{SO}_2-$ and $-\text{C}(\text{CH}_3)_2-$, the PAES polymer is a PPSU polymer, PESU polymer and PSU polymer, respectively. In some embodiments in which the PAES polymer is a PPSU, PESU or PSU polymer, for each R_i , i is zero; in other such embodiments, for each L_i , i is zero; and in yet other such embodiments each i zero.

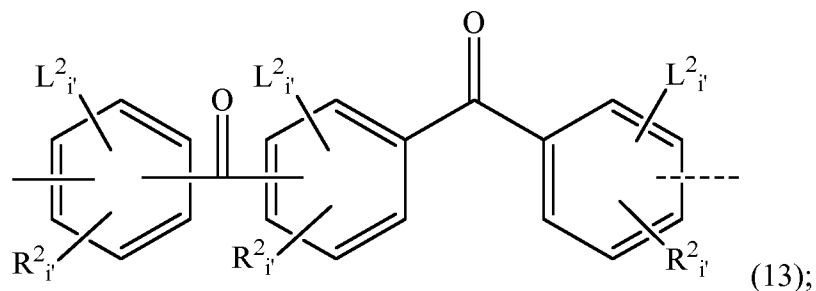
As discussed above, in some embodiments, the PAE polymer can be a PAEK polymer. As used herein, a PAEK polymer refers to any PAE polymer where recurring unit (R_{PAE}) contains, in addition to the arylene group and ether group ($-\text{O}-$), a carbonyl group [$-\text{C}(=\text{O})-$]. For clarity, recurring unit (R_{PAE}) is referred to as " (R_{PAEK}) ", when the PAE polymer is a PAEK polymer.

Recurring unit (R_{PAEK}) can be represented by the formula $--[\text{M}_\text{B}-\text{O}-\text{M}_\text{K}-\text{O}]--$. M_B is represented by a formula selected from the following group of formulae:



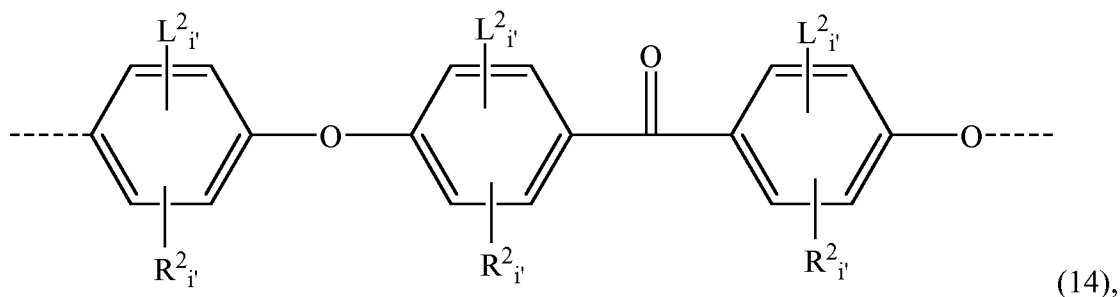
5 and M_K is represented by a formula selected from the following group of formulae:



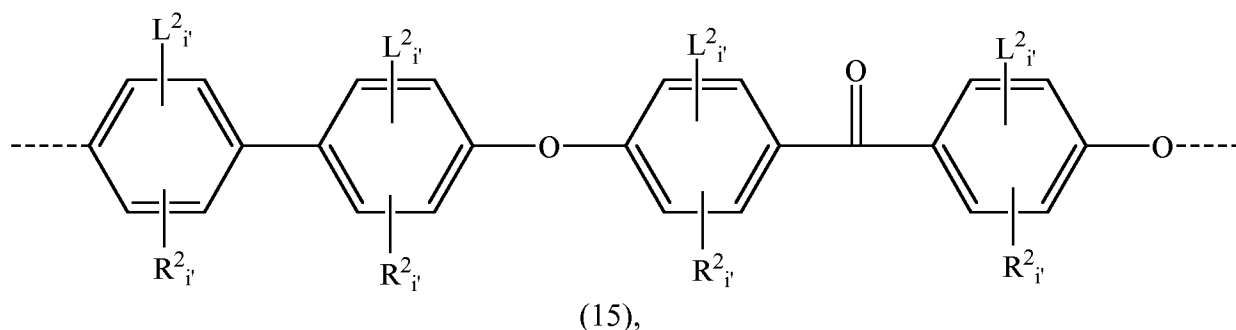


where each R^2 is independently selected from the group consisting of a halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium; each L^2 is a linker molecule independently selected from the group consisting of a polarizable group, a UV initiating group, and a oxirane reactive group; each i' is an independently selected integer from 0 to 4.

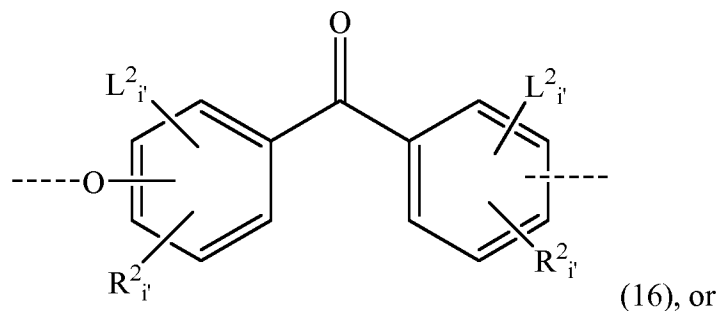
In some embodiments, the PAEK polymer can be a poly(ether ether ketone) ("PEEK") polymer, with recurring unit (R_{PAEK}) represented by the following formula:



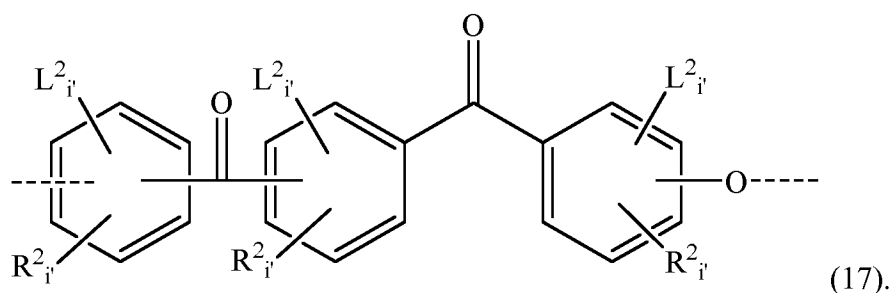
a poly(ether diphenyl ether ketone) ("PEDEK") polymer, with recurring unit (R_{PAEK}) represented by the following formula:



a poly(ether ketone) ("PEK") polymer, with recurring unit (R_{PAEK}) represented by the following formula:



a poly(ether ketone ketone) (“PEKK”) polymer, with recurring unit (R_{PAEK}) represented by the following formula:



5 For clarity, in the aforementioned embodiments in which the PAEK polymer is a PEEK, PEK, PEKK or PEDEK polymer, recurring unit (R_{PAEK}) is referred to as (R_{PEEK}), (R_{PEK}), (R_{PEKK}), and (R_{PEDEK}), respectively. In some embodiments in which the PAEK polymer is represented by one of the Formulas (14) – (17) above, for each $R^i_{i'}$, i' is zero; in other such embodiments, for each $L^i_{i'}$, each i' is zero; and in yet further embodiments, each i' is zero.

10

In some embodiments, in which the functionalized PAE polymer is a PAEK polymer, the polymer can comprise about 1 mol% to about 99 mol% of a first selection of recurring units from the group consisting of (R_{PEEK}), (R_{PEK}), (R_{PEKK}) and (R_{PEDEK}) and about 1 mol% to about 99 mol% of a second selection of recurring units from the group consisting of (R_{PEEK}), (R_{PEK}), (R_{PEKK}), and (R_{PEDEK}), such that the first and second selections are different (*e.g.* the PAEK polymer is at least a copolymer). In some such embodiments, the PAEK polymer can comprise about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, or about 70 mol% recurring unit (R_{PEEK}) and, respectively, about 90 mol%, about 80 mol%, about 70 mol%, about 60 mol%, about 50 mol%, about 40 mol%, or about 30 mol% recurring unit (R_{PEDEK}). While the aforementioned examples pertain to recurring unit (R_{PEEK}), and (R_{PEDEK}), a person of ordinary skill in the art will recognize that the same ranges can apply to any two distinct recurring units selected from the group consisting of (R_{PEEK}), (R_{PEK}), (R_{PEKK}) and (R_{PEDEK}).

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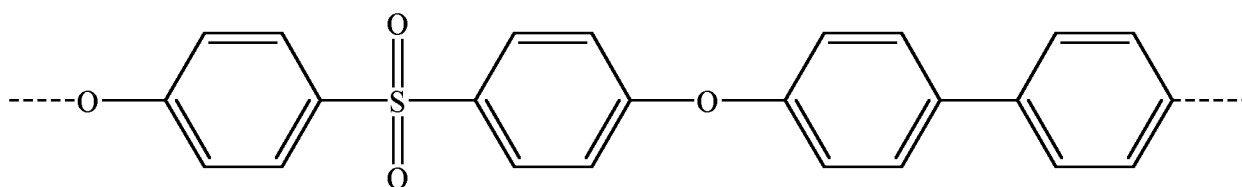
As discussed above, in some embodiments, the PAE polymers can be terminally functionalized. In some such embodiments, the functionalized PAE polymers can be represented by a formula selected from the following group of formulae:



where P_{PAES} is a PAES polymer having recurring unit (R_{PAES}) represented by the formula -- $[M_A-O-M_S-O]$ --, as described above, and P_{PAEK} is a PAEK polymer having recurring unit (R_{PAEK}) represented by the formula -- $[M_B-O-M_K-O]$ --, as described above. In Formulas (18A) - (18D), M_A^* , M_B^* , M_S^* and M_K^* are identical to M_A , M_B , M_S and M_K , respectively, with the exception that L^1 , i , j , and k are replaced by L^{1*} , i^* , j^* , and k^* respectively; L^2 and i' are replaced by L^{2*} and i'^* respectively; each L^{1*} and L^{2*} is a linking group independently selected from the group consisting of a polarizable group, a UV initiating group, and a oxirane reactive group; each i^* and i'^* is an independently selected integer from 0 to 4; each j^* is an independently selected integer from 0 to 3; and each k^* is an independently selected integer from 0 to 2. Accordingly, the M_A^* , M_B^* , M_S^* and M_K^* are identical to M_A , M_B , M_S and M_K , respectively, with the exception that the number of, positioning of, and composition of the linking groups may be different.

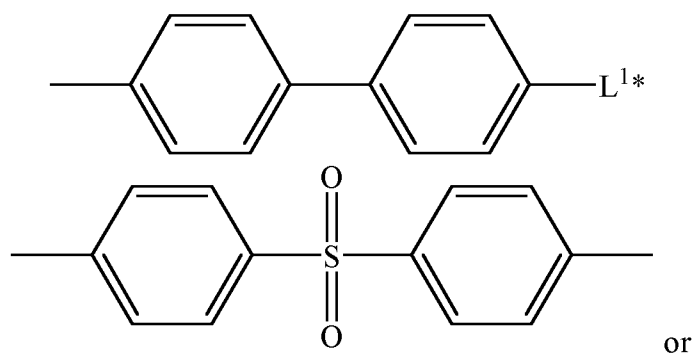
In some embodiments the functionalized PAE polymer is functionalized PAES polymer where

a) R_{PAES} is represented by

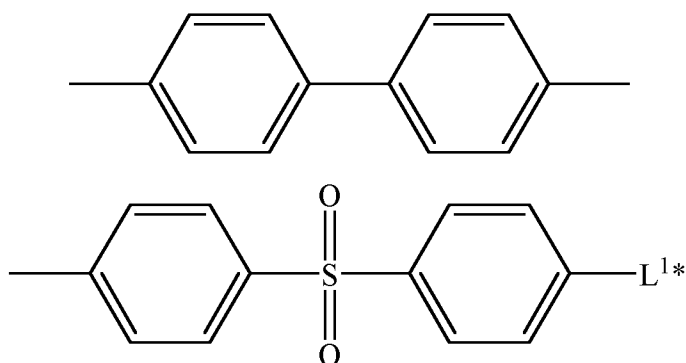


and

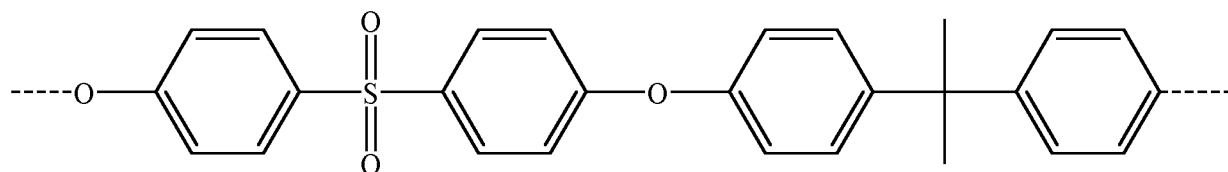
i. the PAES polymer is represented by Formula (18A) with M_A^* and M_S^* respectively represented by



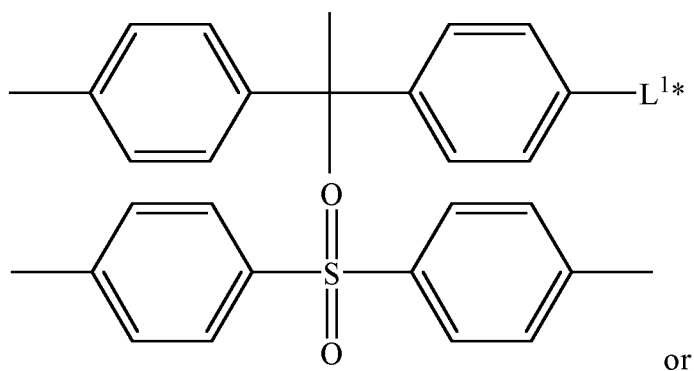
- ii. the PAES polymer is represented by Formula (18B) with MA* and MS* respectively represented by



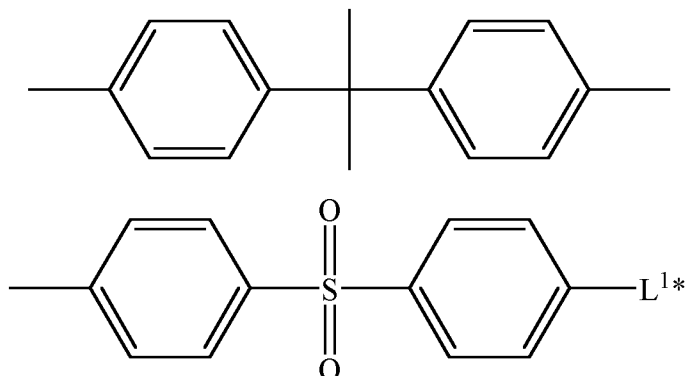
- b) R_{PAES} is represented by



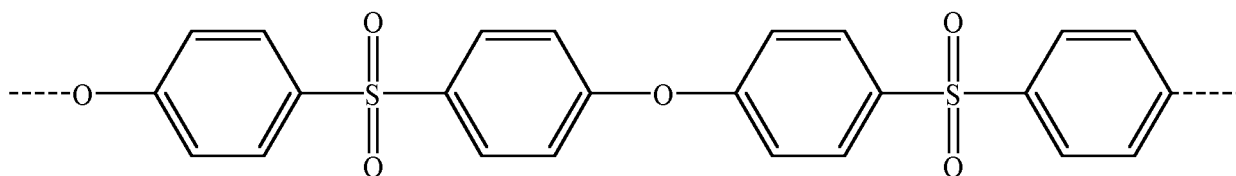
- i. the PAES polymer is represented by Formula (18A) with M_A* and M_S* respectively represented by



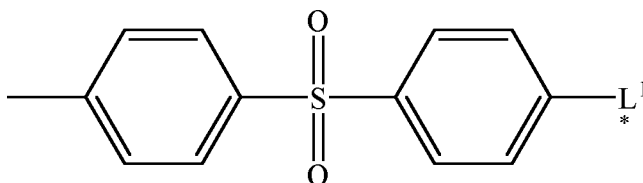
- ii. the PAES polymer is represented by Formula (18B) with MA* and MS* respectively represented by



- 5 c) R_{PAES} is represented by



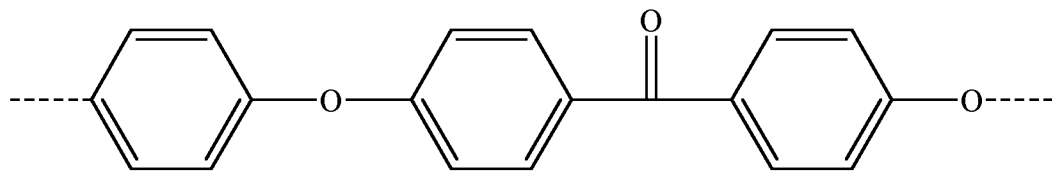
and the PAES polymer is represented by Formula (18A) or (18B), with M_A^* and M_S^* both represented by



In some embodiments according to a) – c) above, P_{PAES} comprises from 1 to 50 repeat units R_{PAES} and, in further such embodiments, P_{PAES} consists essentially of or consists of repeat units R_{PAES} .

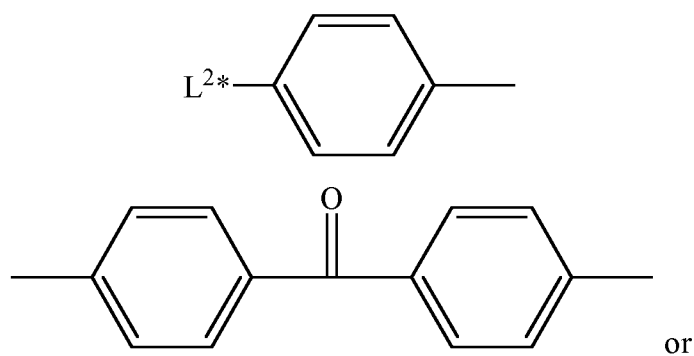
In some embodiments the functionalized PAE polymer is functionalized PAEK polymer where

- d) R_{PAEK} is represented by



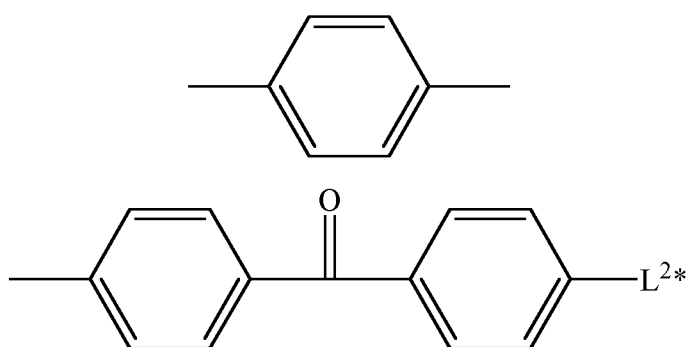
and

- i. the PAEK polymer is represented by Formula (18C) with M_B^* and M_K^* respectively represented by

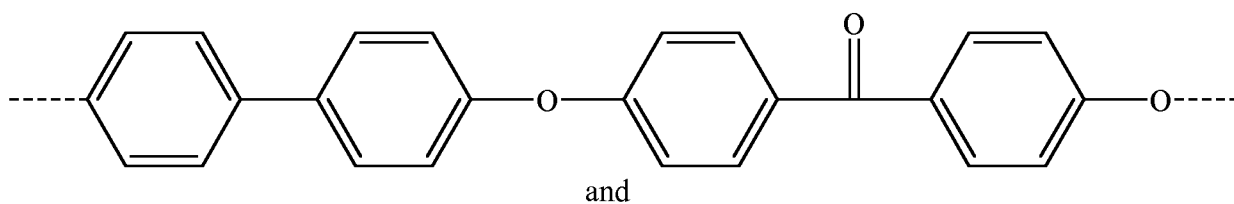


- ii. the PAEK polymer is represented by Formula (18D) with M_B^* and M_K^* respectively represented by

5

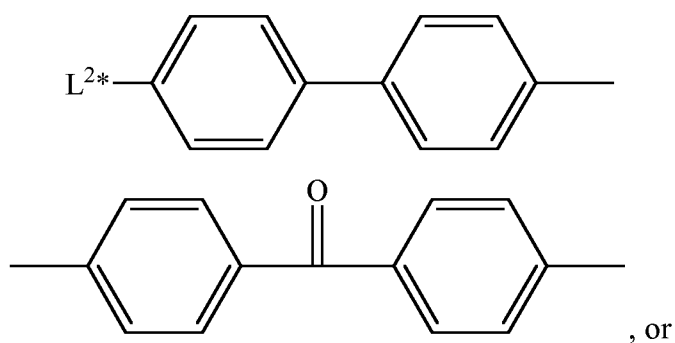


- e) R_{PAEK} is represented by



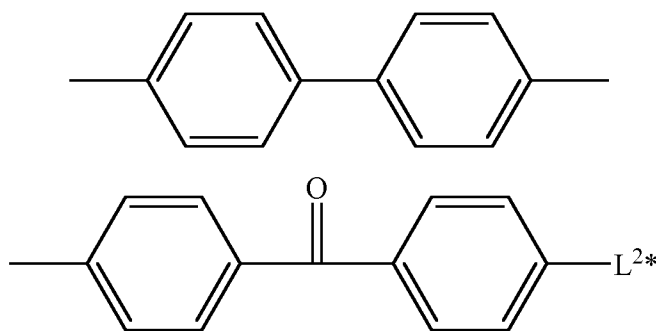
10

- i. the PAEK polymer is represented by Formula (18C) with M_B^* and M_K^* respectively represented by



15

- ii. the PAEK polymer is represented by Formula (18D) with M_B^* and M_K^* respectively represented by

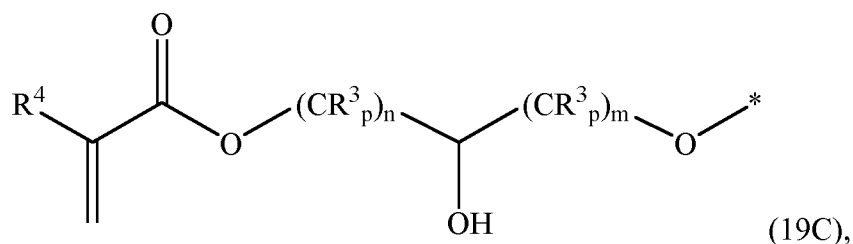
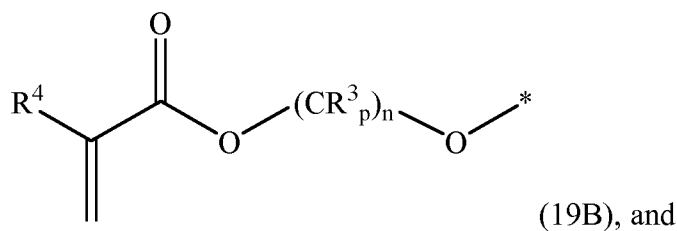
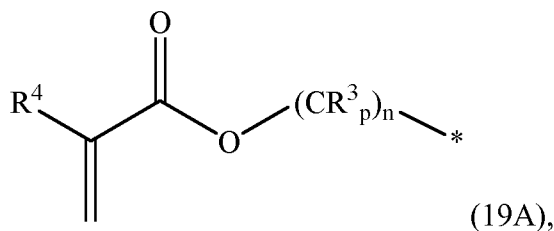


In some embodiments according to d) – e) above, P_{PAEK} comprises from 1 to 50 repeat units R_{PAEK} and, in further such embodiments, P_{PAES} consists essentially of or consists of repeat units R_{PAES} . For clarity, embodiments a) – e) above are hereinafter referred to as Embodiments a) – e), respectively.

The Linking Group

The polymerizable polymers are functionalized with a linking group. During UV polymerization, the linking group forms covalent bonds with other polymerizable polymers in a liquid state at the reaction temperature. For the polymerizable PAE polymers of interest herein, the reaction temperature can be from about 0 °C to about 300 °C, from about 10 °C to about 280 °C, or from about 20 °C to about 250 °C. The linking group can be a polymerizable group, such as a radically polymerizable group or a cationically polymerizable group, or a UV initiator such as a radical photoinitiator group or cationic photoinitiator group. In some embodiments, the linker molecule can be an oxirane reactive group.

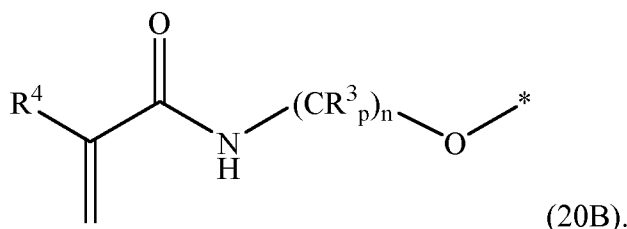
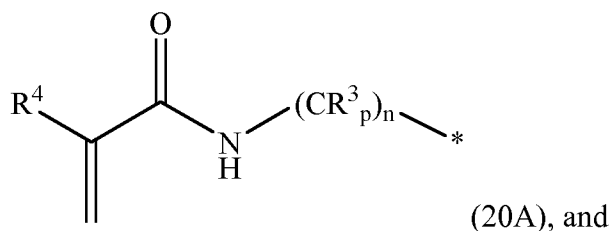
In some embodiments, the linking group is a polymerizable group, such as a radically polymerizable group or a cationically polymerizable group. A radically polymerizable group is a group that induces a polymerization reaction upon irradiation by light in the presence of a radical photoinitiator (described below). Desirable radically polymerizable groups include, but are not limited to, acrylates, acrylamides, olefins (*e.g.* α -olefin), maleimides, styrenes, vinyls and norbornenes. In embodiments in which the radically polymerizable group is an acrylate group, linking group (L) can be represented by a formula selected from the following group of formulae:



where R^4 and each R^3 are independently selected from the group consisting of a hydrogen and
 5 a linear or branched a C_1 - C_{12} -alkyl group; p is an independently selected integer from 0 to 2;
 n and m are independently selected integers from 0 to 15 and “*” indicates the bond to M_A ,
 M_S , M_B , M_K , M_A^* , M_S^* , M_B^* , or M_K^* . In some embodiments in which the polymerizable
 PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit
 (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently
 10 represented by a Formula (19A) - (19C). In some such embodiments, each p is zero. In some
 Embodiments a) – e) above, L^{1*} and L^{2*} are independently represented by a Formula (19A) -
 (19C). In some such embodiments, each L^{1*} is the same and each L^{2*} is the same. In further
 such embodiments, each p is zero.

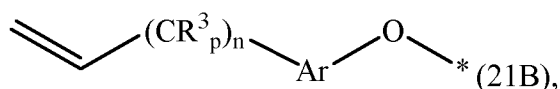
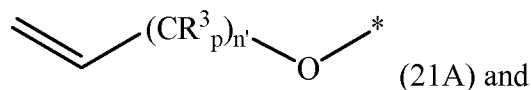
The PAE polymer can be functionalized with the acrylate linking group by reacting
 15 the corresponding acryloyl halide or acrylate reactant with a functional hydroxyl group on the
 PAE polymer. Specific examples of acryloyl halide and acrylate reactants include, but are
 not limited to, acryloyl chloride/methacryloyl chloride, 2-chloroethyl acrylate/methacrylate,
 2-ethylacryloyl chloride, ethyl 2-(bromomethyl)acrylate, methyl acrylate/methacrylate, ethyl-
 2-propyl acrylate/methacrylate, ethyl 2-ethylacrylate/methacrylate, methyl
 20 2-(chloromethyl)acrylate, phenylacrylate/methacrylate, pentafluorophenyl
 acrylate/methacrylate, 2-tetrahydropyranyl acrylate/methacrylate, tert-butyl
 methacrylate/acrylate, 3-chloro-2-hydroxypropyl methacrylate, or glycidyl
 methacrylate/acrylate.

In embodiments in which the radically polymerizable group is an acrylamide group, linking group (L) can be represented by one of the following formulae:



5 The PAE polymer can be functionalized with the acrylamide linking group by reacting the corresponding acryloyl halide with a functional amine group on the PAE polymer. Specific acryloyl halides include, but are not limited to, those described above with respect to acrylate linking groups. In some embodiments in which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK})
 10 according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by a Formula (20A) or (20B). In some such embodiments, each p is zero. In some Embodiments a) – c) above, L^{1*} and L^{2*} are independently represented by a Formula (20A) or (20B). In some such embodiments, each L^{1*} is the same and each L^{2*} is the same. In further such embodiments, each p is zero.

15 In embodiments, in which the radically polymerizable group is an olefin group, linking group (L) can be represented by one of the following formulae:

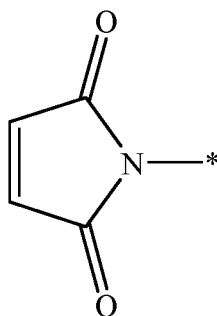


where Ar is selected from the group consisting of a benzyl group, a naphthyl group and an anthracenyl group and n' is an integer from 1 to 15. In some embodiments in which the linking group is an olefin group, each p is equal to 0, n is equal to 2 and n' is equal to 2 in Formulas (21A) and (21B). The PAE polymer can be functionalized with the olefin linking groups by reaction with an –OH functional group on the PAE polymer, for instance by (a) nucleophilic substitution in presence of a base like potassium carbonate or sodium carbonate
 25 with 4-bromo-1-butene or (b) by acylation using acethylene or (c) by reaction with a halide

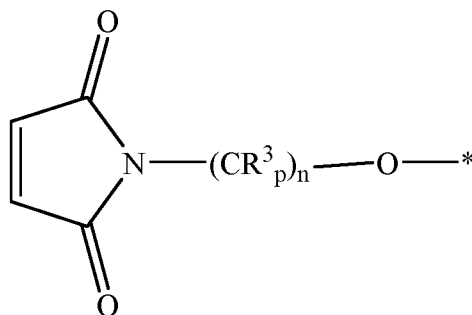
functional group on the PAE polymer with 3-butene-1-ol. In some embodiments in which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by the Formula (21A) or Formula (21B). In some such

5 embodiments, each p is zero. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently selected from Formula (21A) and (21B). In some such embodiments, each L^{1*} is the same and each L^{2*} is the same. In further such embodiments, each p is zero.

In embodiments in which the radically polymerizable group is a maleimide group, linking group (L) can be represented by one of the following formulae:



(22A) and



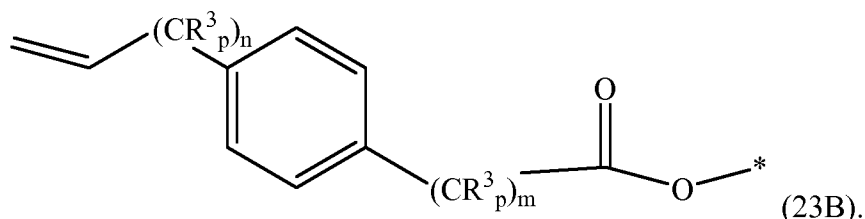
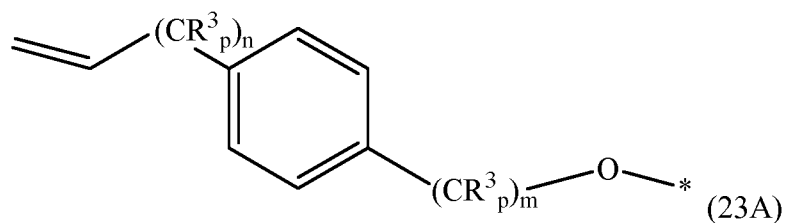
(22B).

In some embodiments, in which the linking group is a maleimide group, each p equals 0. The PAE polymer can be functionalized with a maleimide group by reacting maleic anhydride with with amine functional groups on the PAE polymer. In some embodiments in

15 which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by the Formula (22A) or Formula (22B). In some such embodiments, each p is zero. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently selected from Formula (22A) and (22B). In some such embodiments, each L^{1*}

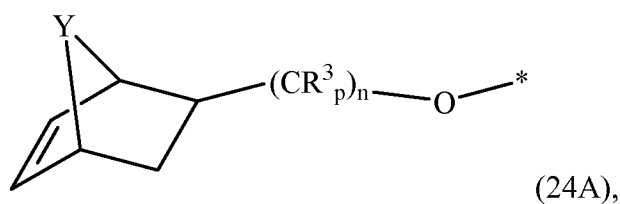
20 is the same and each L^{2*} is the same. In further such embodiments, each p is zero.

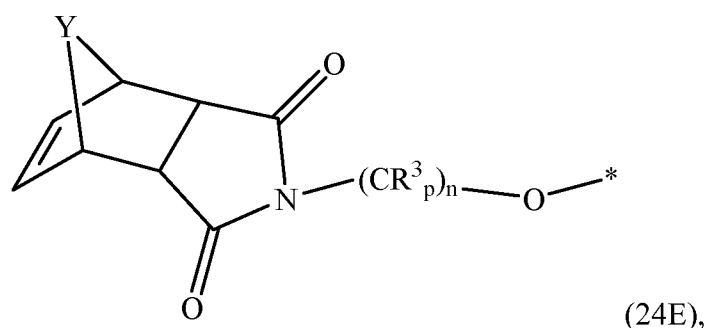
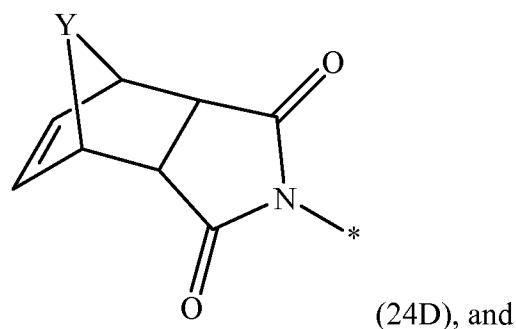
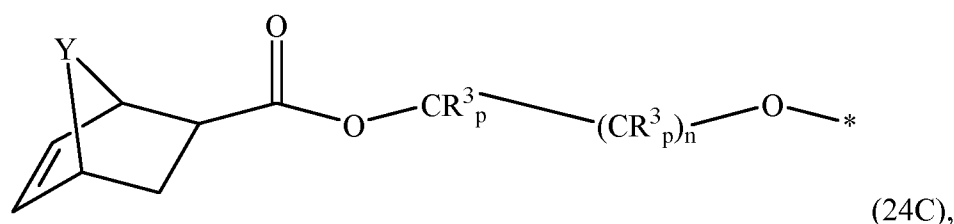
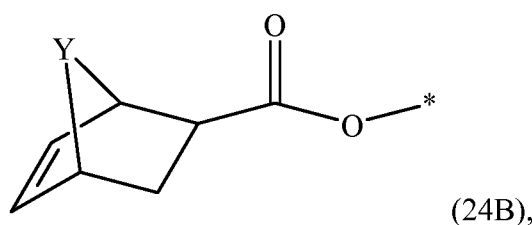
In embodiments in which the radically polymerizable group is a styrene group, linking group (L) can be represented by one of the following formulae:



In some embodiments in which linking group (L) is represented by Formula (23A) or (23B), each p is zero and, in further embodiments, n and m are zero. The PAE polymer can be functionalized with a styrene group by reacting a vinylbenzyl halide or vinylbenzoyl halide reactant with an -OH group on the PAE polymer in presence of a base like potassium carbonate or sodium carbonate or by reacting a vinylbenzyl hydroxyl with a halogen (-Cl or -F) group on the PAE polymer in presence of a base like potassium carbonate or sodium carbonate. Specific a vinylbenzyl and vinylbenzoyl halides include, but are not limited to, 4-Vinylbenzyl chloride. Specific vinylbenzyl hydroxyl include, but are not limited to 4-hydroxystyrene. In some embodiments in which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by the Formula (23A) or Formula (23B). In some such embodiments, each p is zero. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently selected from Formula (23A) and (23B). In some such embodiments, each L^{1*} is the same and each L^{2*} is the same. In further such embodiments, each p is zero.

In embodiments in which the radically polymerizable group is a norbornene group, linking group (L) can be represented by a formula selected from the following group of formulae:





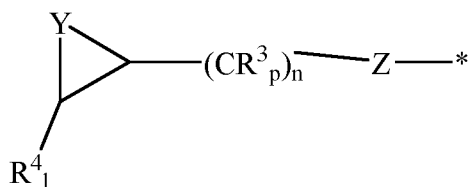
5 where Y is and oxygen or a -CH₂- group. In some embodiments in which linking group (L) is represented by Formula (24A), (24C), or (24F), each p is zero and, in further such embodiments, each n is also zero. The PAE polymer can be functionalized with a norbornene group by reacting an alkyl halide or carboxylic acid terminated norbornene or a norbornene acyl halide with an -OH functional group on the PAE polymer. The PAE polymer can also

10 be functionalized with a norbornene group by reacting norbornene anhydride or norbornene ketone with amine or alkyl amine functional groups on the PAE polymer. Desirable norbornene reactants include, but are not limited to halide terminated norbornenes, norbornene acyl halides or carboxylic acid like 5-Norbornene-2-carboxylic acid, 5-Norbornene-2-endo-acetic acid, and norbornene anhydrides or norbornene ketones like 5-Norbornene-2,3-

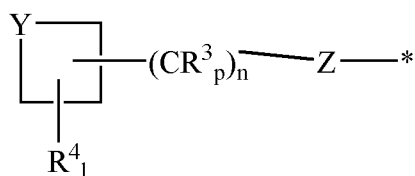
15 dicarboxylic acid or 5-Norbornene-2,3-dicarboxylic anhydride, 2-Benzoyl-5-norbornene. In some embodiments in which the polymerizable PAE polymer comprises recurring unit

(R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L¹ and each L² is independently represented by any one of the Formulas (24A) to (24E). In some such embodiments, each p is zero. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently selected from any one of Formulas (24A) to (24E). In some such embodiments, each L^{1*} is the same and each L^{2*} is the same. In further such embodiments, each p is zero.

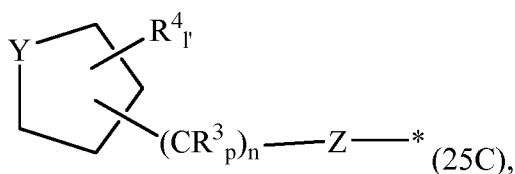
As discussed above, in some embodiments, the linking group is a cationically polymerizable group. A cationically polymerizable group is a group that induces a polymerization reaction upon irradiation by light in the presence of a cationic photoinitiator (described below). Desirable cationically polymerizable groups include, but are not limited to, epoxides, vinyl ethers, propenyl ethers, siloxanes, oxetanes, cyclic acetals and formals, cyclic sulfides, lactones and lactams. In some embodiments, the cationically polymerizable group can be represented by a formula selected from the following group of formulae:



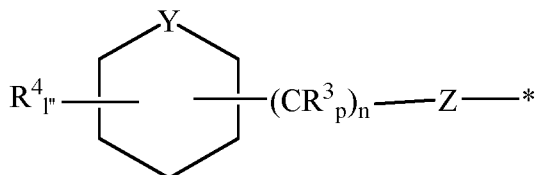
(25A),



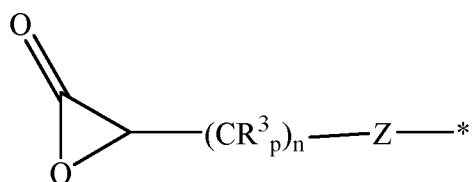
(25B),



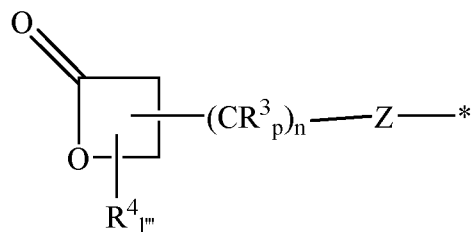
(25C),



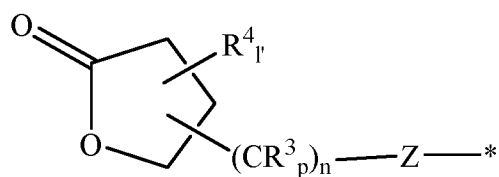
(25D),



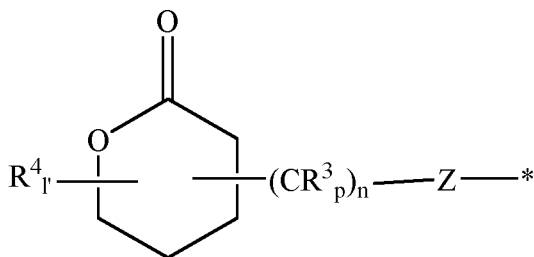
(25E),



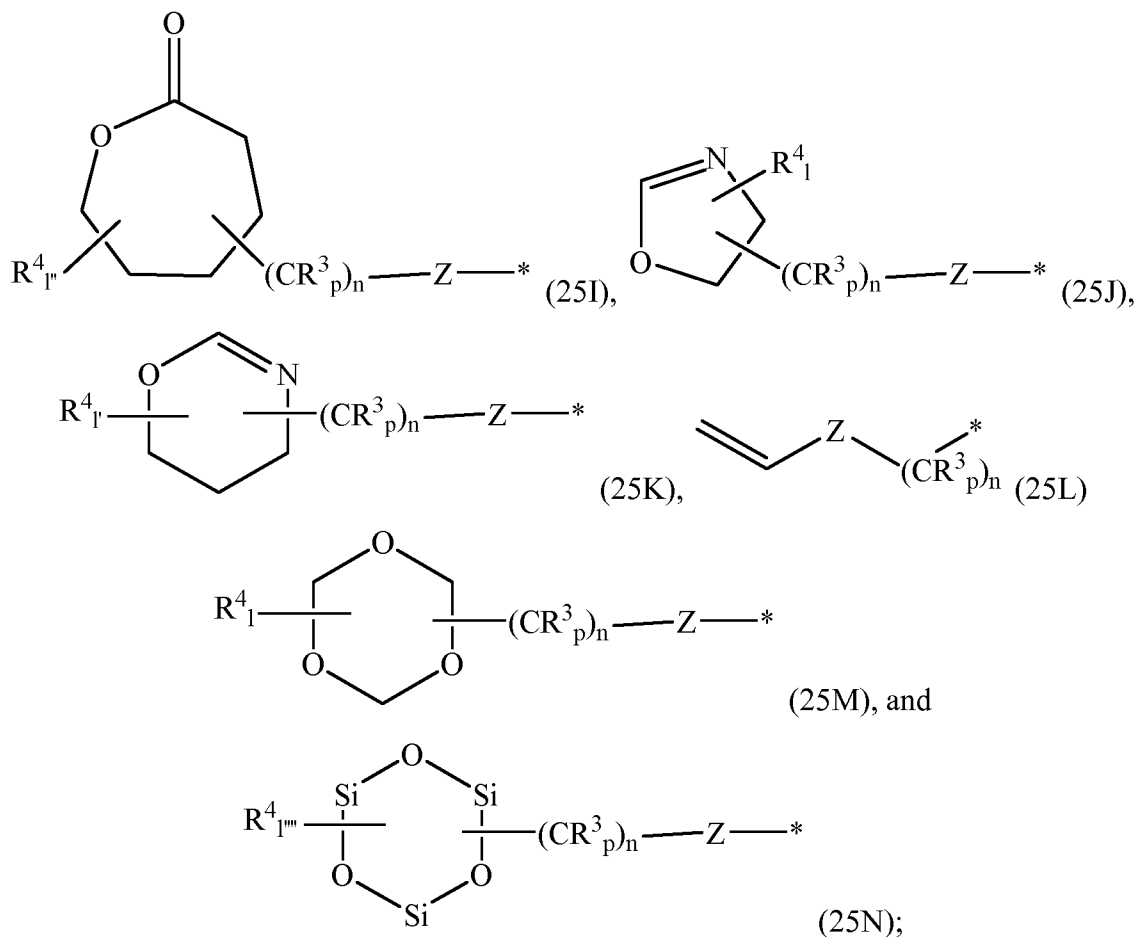
(25F),



(25G),



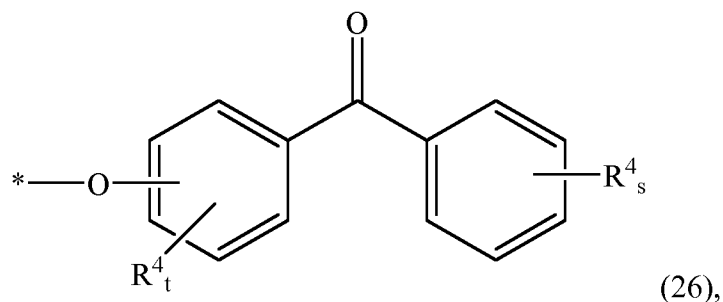
(25H),



5 where Z is a bond or an oxygen; Y is an oxygen or a sulfur; l , l' , l'' , l''' , and l'''' are independently selected integers from 0 to 2, 0 to 3, 0 to 4, 0 to 1 and 0 to 5, respectively. In some embodiments in which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by any one of

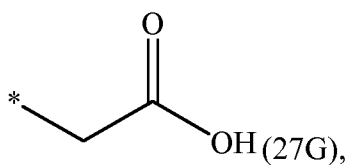
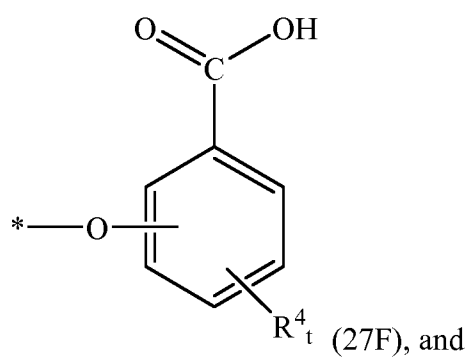
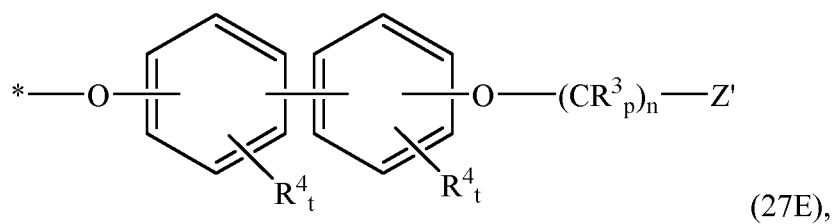
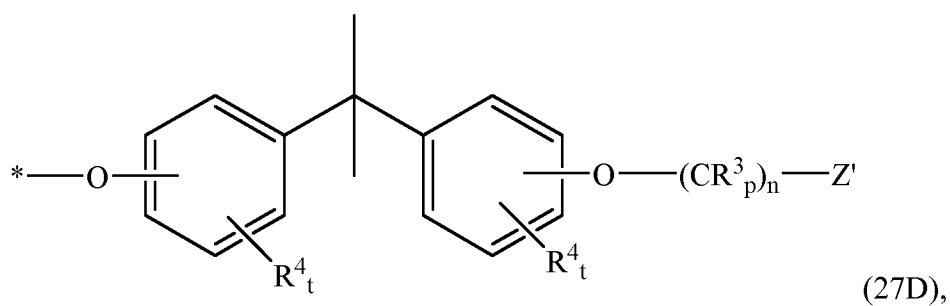
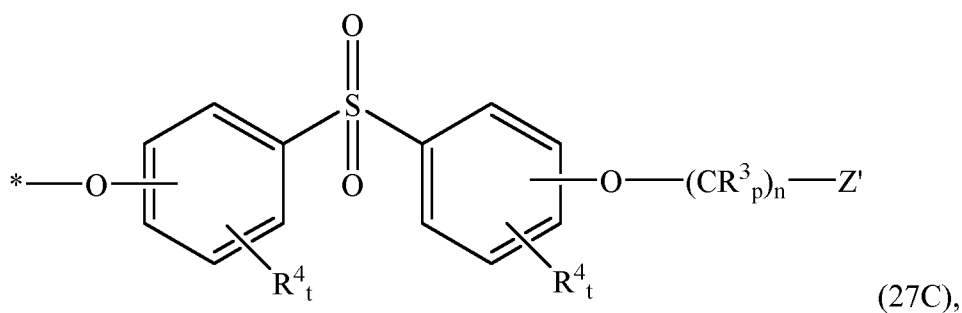
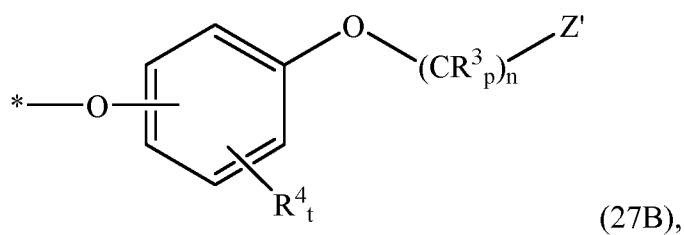
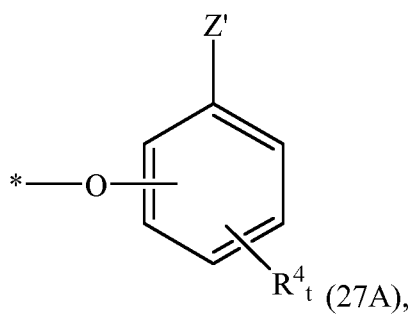
10 Formulas (25A) - (25N). In some such embodiments, each L^1 and L^2 are represented by Formula (25A) and, in further such embodiments, Z is a bond, l and p are 0 and n is 1. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently selected from any one of Formulas (25A) - (25N). In some such embodiments, each L^{1*} and each L^{2*} are represented by Formula (25A) and, in further such embodiments, Z is a bond, l and p are 0 and n is 1.

15 As discussed above, in some embodiments the linking group can be a UV initiator such as a radical photoinitiator group or cationic photoinitiator group. A radical photoinitiator is a compound that decomposes and evolves radical to initiate radical polymerization upon exposure to UV radiation. In some embodiments, the radical photoinitiator group is a benzophenone represented by the following formula:



where s is an integer selected from 0 to 5, t is an integer selected from 0 to 4 and where the $*-O-$ is bonded to the benzyl ring in either the meta or para positions. In some embodiments in which the polymerizable PAE polymer comprises recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by the Formula (26). In some such embodiments, each L^1 and L^2 , s is and t are zero and, in further such embodiments, $*-O-$ is bonded to the benzyl ring the para position. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently represented by a Formula (26). In some such embodiments, each L^1 and L^2 , s is and t are zero and, in further such embodiments, $*-O-$ is bonded to the benzyl ring the para position.

As discussed above, in some embodiments the linking group can be an oxirane reactive group. The oxirane reactive group can be selected from the following group of formulae:



where Z' is a —NH₂ or —OQ and where Q is selected from the group consisting of H, Li, Na, K, Ca, and Mg. In some embodiments in which the polymerizable PAE polymer comprises

recurring unit (R_{PAES}) according to Formula (6) or recurring unit (R_{PAEK}) according to any one of Formulas (14) – (17), each L^1 and each L^2 is independently represented by a formula selected from Formulas (27A) – (27G). In some such embodiments, n is 2 and, in further such embodiments, each t and p are zero. In some Embodiments a) – e) above, L^{1*} and L^{2*} are independently represented by a formula selected from Formulas (27A) – (27G). In some such embodiments, n is 0 or 2, p is 0 and t is 0 and, in further such embodiments.

The Photocurable Polymer Composition

The photocurable polymer compositions described herein are liquid state polymer compositions that contain a functionalized PAE polymer. In some embodiments, photocurable polymer composition can optionally include a polymerization aid or other polymers distinction from the PAE polymer.

The photocurable polymer composition is a liquid at desirable polymerization/crosslinking temperatures (“reaction temperature”). In some embodiments, the reaction temperature is from about 0 °C to about 300 °C, from about 10 °C to about 280 °C or from about 20 °C to about 250 °C.

The photocurable polymer composition includes at least one functionalized PAE polymer. The functionalized PAE polymer can have a concentration of at least about 1 wt.%, at least about 3 wt.%, at least about 5 wt.%, or at least about 10 wt.% and no more than about 60 wt.%, no more than about 55 wt.%, no more than about 50 wt.%, no more than about 45 wt.%, no more than about 40 wt.%, or no more than about 35 wt.%, relative to the total weight of the photocurable polymer composition.

In some embodiments the photocurable polymer composition can include two or more distinct, functionalized PAE polymers. In such embodiments, each functionalized PAE polymer can be as described above, each having distinct recurring units (R_{PAE}). For example, if the photocurable polymer composition includes 2 functionalized PAE polymers, one functionalized PAE polymer can have recurring unit (R_{PAE}) and the other functionalized PAE polymer can have recurring unit (R_{PAE}^*), distinct from recurring unit (R_{PAE}). In embodiments, in which the photocurable polymer composition includes a functionalized PAE polymer, the total functionalized PAE polymer concentration can be as described above. In another embodiments, the concentration of each of the functionalized PAE is independently within the ranges described above.

In some embodiments, the photocurable polymer composition includes a polymerizable compound different from the functionalized PAE polymer. In some such

embodiments, the at least one polymerizable compound polymerizes or crosslinks with the PAE polymer upon excitation with light at a reaction temperature inherent to the photocurable polymer composition. The distinct polymerizable compound is a polymer, an oligomer or a monomer. In general, the at least one polymerizable compound contains a functionality that enables polymerization or crosslinking with the PAE polymer. Based upon the selection of the functionalized PAE polymer, a person of ordinary skill in the art will know how to select the polymerizable compound different from the functionalized PAE polymer such that the polymerizable compound polymerizes or crosslinks with the PAE upon excitation with light.

In embodiments, in which the photocurable polymer compositions includes a polymerizable compound different from the functional PAE polymer, the concentration of the polymerizable compound is at least about 10 wt.%, at least about 15 wt.%, or at least about 20 wt.% and no more than about 95 wt.%, no more than about 90 wt.%, no more than about 85 wt.%, no more than about 80 wt.%, or no more than about 75 wt.%, relative to the total weight of the photocurable polymer composition. In embodiments in which photocurable polymer composition includes two or more distinct polymerizable compounds, the total concentration of the polymerizable compound can be as described above. In other such embodiments, each distinct polymerizable compounds independently has a concentration as described above.

In general, when the functionalized PAE polymers comprises a polymerizable group, the photocurable polymer composition can include a photoinitiator. In some embodiments in which the functionalized PAE polymer includes a radically polymerizable linking group, the polymerizable polymer composition include a radical photoinitiator. Desirable radical photoinitiators include, but are not limited to, acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzophenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphine oxide, benzyl dimethyl ketal, 1-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-

butylperoxycarbonyl)benzophenone (BTTB), combinations of BTTB and dyesensitizers such as xanthene, thioxanthene, cumarin, and ketocumarin.

Similarly, in some embodiments in which the functionalized PAE polymer includes a cationically polymerizable linking group, the polymerizable polymer composition includes a cationic photoinitiator. Desirable cationic photoinitiators include, but are not limited to onium salts with anions of weak nucleophilicity. Examples of onium salts include, but are not limited to, halonium salts, iodosyl salts or sulfonium salts, such as described in published European patent application EP0153904, filed February 4, 1985; sulfoxonium salts, such as described, for example, in published European patent applications EP0035969A1, filed March 2, 1981; EP0044274A2, filed July 6, 1981; EP0054509A2, filed October 29, 1981; and EP0164314A2, filed June 3, 1985; or diazonium salts, such as described, for example, in US. Pat. Nos. 3,708,296, filed August 20, 1968; and 5,002,856, filed August 2, 1989; all of which are incorporated by reference herein. Other cationic photoinitiators are metallocene salts, such as described, for example in published European applications EP0094914A2, filed May 13, 1983; and EP0094915A2, file May 13, 1983, both of which are incorporated by reference herein. Other preferred cationic photoinitiators are mentioned in US. Pat. Nos. 5,972,563 to Steinmann et al., filed on July 28, 1997; and 6,100,007, to Pang et al., filed April 6, 1998; and 6,136,497 to Melisaris et al., filed August 25, 2000; all of which are incorporated by reference herein. Where the polymerizable polymer composition includes a radical or cationic photoinitiator, the photoinitiator is present in a concentration no less than about 0.05 wt.%, no less than about 0.1 wt.%, no less than about 0.3 wt.%, no less than about 0.5 wt.%, no less than about 0.7 wt.%, or no less than about 1 wt.% and no more than about 15 wt.% or no more than about 10 wt.%, relative to the total weight of the polymerizable polymer composition.

In embodiments in which the functionalized PAE polymer includes a radical photoinitiator, the polymerizable polymer composition includes a polymerizable group (*e.g.*, a C=C double bond or an oxirane) containing polymer that can be a PAE polymer or another type of polymer. In some embodiments, desirable polymerizable groups include the radically polymerizable linking groups described above. In some embodiments, in which the photocurable polymer composition includes a polymerizable group containing polymer referred to above, the polymer can be present in concentration of at least about 1 wt.%, at least about 3 wt.%, at least about 5 wt.%, or at least about 10 wt.% and no more than about 60 wt.%, no more than about 55 wt.%, no more than about 50 wt.%, no more than about

45 wt.%, no more than about 40 wt.%, or no more than about 35 wt.%, relative to the total weight of the photocurable polymer composition.

When the functionalized PAE polymer contains an oxirane reactive group, the polymerizable polymer composition can include a cationically polymerizable polymer that can be a functionalized PAE with a cationically photopolymerizable group or a polymer from another type containing a cationically photopolymerizable group and a cationic photoinitiator. In some embodiments, in which the photocurable polymer composition includes a polymerizable group containing polymer referred to above, the polymer can be present in concentration of at least about 10 wt.%, at least about 30 wt.%, at least about 50 wt.%, or at least about 70 wt.% and no more than about 90 wt.%, no more than about 95 wt.%, no more than about 98 wt.%, no more than about 45 wt.%, relative to the total weight of the photocurable polymer composition.

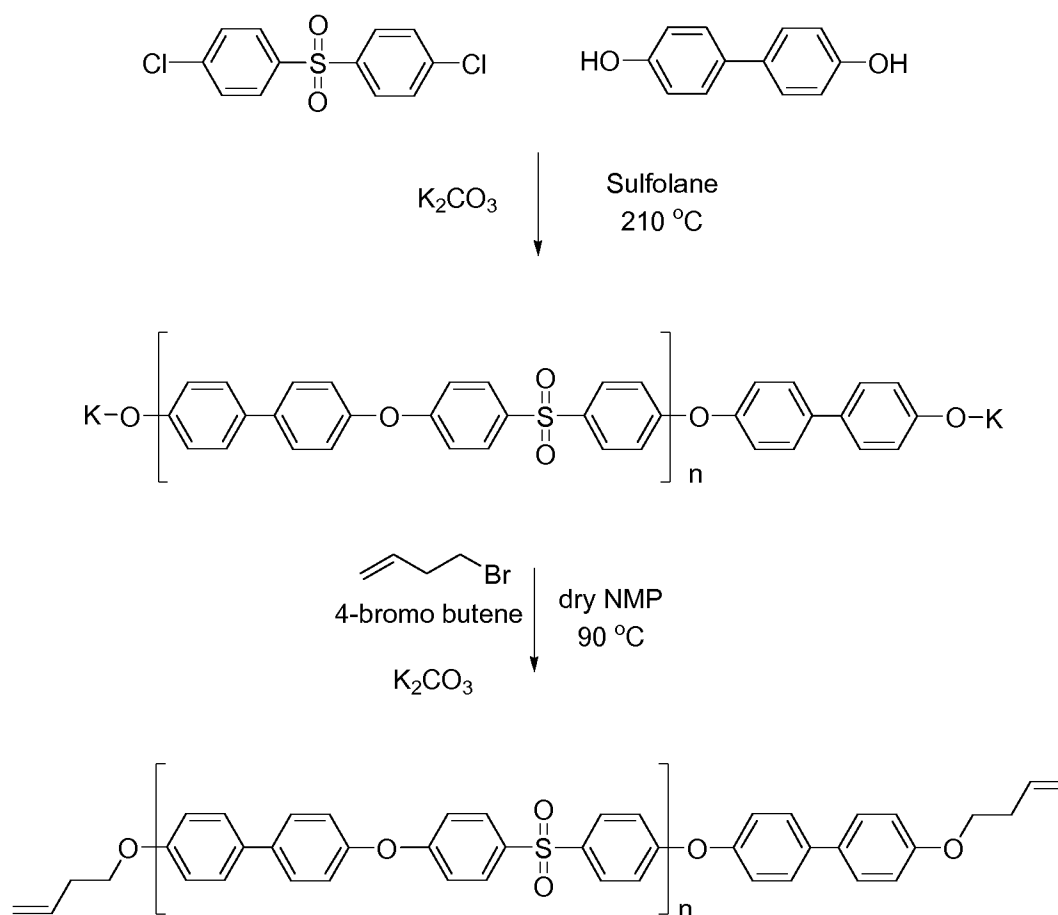
Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

EXAMPLES

The following examples demonstrate the synthesis of functionalized polymers. The examples further demonstrate the thermal stability and flow behavior of the functionalized polymers.

Example 1: Synthesis of PPSU with Olefin Linker Molecules

This example demonstrates the synthesis of a PPSU polymer functionalized with terminal olefin linker molecules according to the following scheme:



This example also demonstrates the thermal stability and flowability of the functionalized PPSU polymer.

5 Synthesis

To demonstrate the synthesis of the functionalized PPSU polymer, 4,4'-dichlorodiphenyl sulfone (82.46g, 0.287 mol), 4,4'-Biphenol (65.37 g, 0.351 mol), K_2CO_3 (50.95 g, 0.369 mol), and sulfolane (345 g) were combined in a 1 L 4-neck reaction vessel equipped with a mechanical stirrer, a Dean-Stark trap (wrapped in insulating cloth), an internal thermometer, and a nitrogen sparge tube. The resulting mixture was then slowly heated with stirring (45 min) to $210\text{ }^\circ\text{C}$ and held at that temperature for 3.5 hours. Following build in molecular weight, the reaction mixture was then cooled to $90\text{ }^\circ\text{C}$ and diluted with anhydrous NMP (about 230 mL) and K_2CO_3 was added (50 g). Following stirring for 15 minutes, 4-bromo-1-butene (112 g, .831 mol) was slowly injected via syringe and the resulting mixture was allowed to stir overnight at $100\text{ }^\circ\text{C}$. To collect the final polymer, the reaction was further diluted with NMP (120 mL) and subsequently filtered via pressure filtration to remove potassium salts followed by coagulation in a blender using a 50:50 mixture of H_2O :Methanol (2.5 L). The precipitated white solid was then collected via

vacuum filtration and repeatedly subjected wash/filtration cycles using water (3 x 2.5 L) and methanol (1 x 2.5 L) in a vacuum oven (110 °C, 36 mmHg) for 16 hours to yield the final polymer as a white solid.

This material was characterized by proton Nuclear Magnetic Resonance, and hydroxyl and chloro end-group titration to confirm the conversion of 97% of the terminal OH groups to the desired olefin terminated PPSU at the desired number average molecular weight ($M_n = 10,900 \text{ g/mol}$ by GPC using a calibration with polystyrene standards).

The Differential Scanning Calorimetry at 20 °C/min demonstrated that the final polymer had a $T_g = 134 \text{ °C}$ and a $T_m = 242 \text{ °C}$ (only seen at the first heat).

Thermal Stability and Flowability

To demonstrate thermal stability, samples of the final polymer obtained were heated above its melting point and isothermally held at 285 °C for periods (“heating periods”) of 0 min, 5 min, 15 min, and 25 minutes in air. Subsequent to each heating period, a GPC analysis was performed on the samples and the resulting data was compared to the un-heat treated samples to check for changes in molecular weight. As shown in Fig. 1, surprisingly, the molecular weight distribution of the heated samples and corresponding curve shape remained constant despite prolonged exposure to high temperatures. The olefin terminated PPSU is stable enough at temperature above 250 °C and has a very low melt viscosity: it is suitable for photo initiated 3D printing processes like SLA or CLIP whatever the temperature.

Example 2: Synthesis of PPSU with Benzophenone Linker Molecules

This example demonstrates the synthesis of a PPSU polymer functionalized with terminal benzophenone linker molecules according to the following scheme:

To demonstrate synthesis of the PPSU polymer, 4,4'-dichlorodiphenyl sulfone (7.17 g, 0.0250 mol), 4,4'-Biphenol (4.92 g, 0.0264 mol), K_2CO_3 (4.02 g, 0.029 mol), and sulfolane (28.2 g) were combined in a 200 mL 3-neck round bottom flask equipped with a mechanical stirrer, a Dean-Stark trap (wrapped in heat tape set at 150 °C), and a nitrogen sparge tube. The resultant mixture was then heated to 210 °C with stirring under low nitrogen flow for 4 hours at which point a pre-dissolved solution of 4-chlorobenzophenone (0.883 g, 0.00441 mol) dissolved in sulfolane (9.2189 g) was added via syringe. Upon complete addition, the reaction was stirred for an additional 1.5 hours, allowed to cool to 100 °C,

diluted with NMP (60 mL), pressure filtered to remove potassium salts, and coagulated in a 50:50 solution of ethanol: hot water (~60 °C). The white solid polymer collected via filtration was further purified via several wash/filtration cycles using boiling water (3 x 500 mL) and ethanol (2 x 500 mL) and the final polymer was dried in a vacuum oven
5 (120 °C, 36 mmHg) for 16 hours to produce 8 g of benzophenone terminated PPSU.

This material was characterized by NMR and hydroxyl and chloro end-group titration to confirm 99% conversion of terminal OH groups to the desired benzophenone terminated PPSU at the desired molecular weight ($M_n = 10,160 \text{ g/mol}$ by GPC).

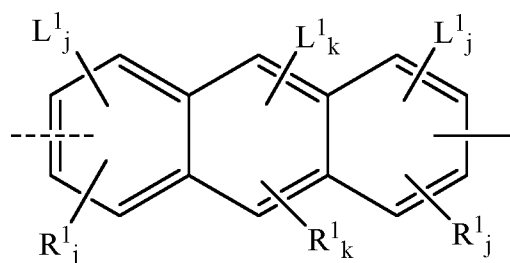
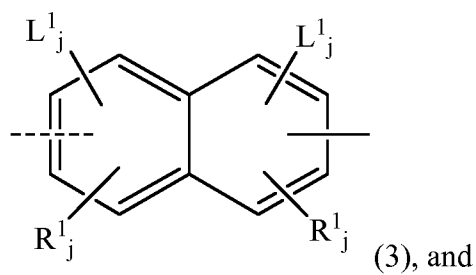
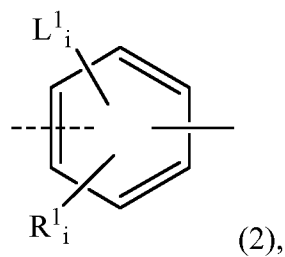
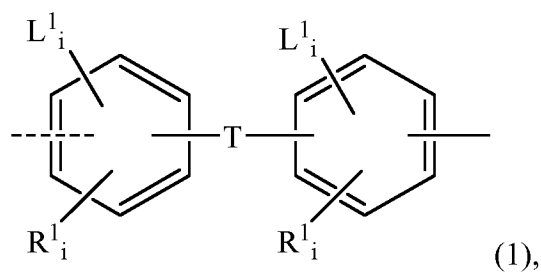
The embodiments above are intended to be illustrative and not limiting. Additional
10 embodiments are within the inventive concepts. In addition, although the present invention is described with reference to particular embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention. Any incorporation by reference of documents above is limited such that no subject matter is incorporated that is contrary to the explicit disclosure herein.

What is claimed is:

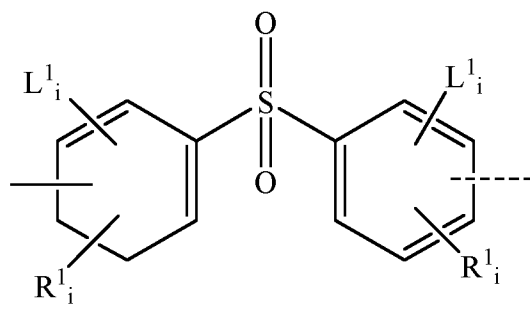
1. A functionalized poly(aryl ether) ("PAE") polymer comprising:
recurring unit (R_{PAES}) represented by the formula $--[M_A-O-M_S-O]--$

5 where

- M_A is represented by a formula selected from the following group of formulae:

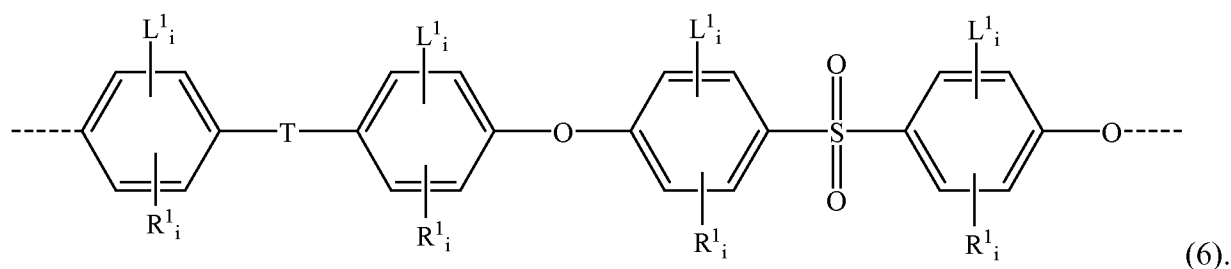


- M_S is represented by the following formula:



- each R^1 is independently selected from the group consisting of a halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium;
- each L^1 is a linker molecule independently selected from the group consisting of a radically polarizable group, a cationically polarizable group, a radical initiator group, and a oxirane reactive group;
- each i is an independently selected integer from 0 to 4;
- each j is an independently selected integer from 0 to 3;
- each k is an independently selected integer from 0 to 2; and
- T is selected from the group consisting of a bond, $-\text{CH}_2-$; $-\text{O}-$; $-\text{SO}_2-$; $-\text{S}-$; $-\text{C}(\text{O})-$; $-\text{C}(\text{CH}_3)_2-$; $-\text{C}(\text{CF}_3)_2-$; $-\text{C}(\text{=CCl}_2)-$; $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{COOH})-$; $-\text{N}=\text{N}-$; $-\text{R}^a\text{C}=\text{CR}^b-$, where each R^a and R^b , independently of one another, is a hydrogen or a C_1 - C_{12} -alkyl, C_1 - C_{12} -alkoxy, or C_6 - C_{18} -aryl group; $-(\text{CH}_2)_n-$ and $-(\text{CF}_2)_n-$ with n being an integer from 1 to 6; an aliphatic divalent group, linear or branched, of up to 6 carbon atoms; and combinations thereof.

2. The PAE polymer of claim 1, wherein recurring unit (R_{PAES}) is represented by the following formula:



3. The PAE polymer of claim 2, wherein T is selected from a bond, $-\text{SO}_2-$ and $-\text{C}(\text{CH}_3)_2-$.

4. The PAE polymer of any of claims 1 to 3, wherein the PAE polymer is represented by one of the following formulae:

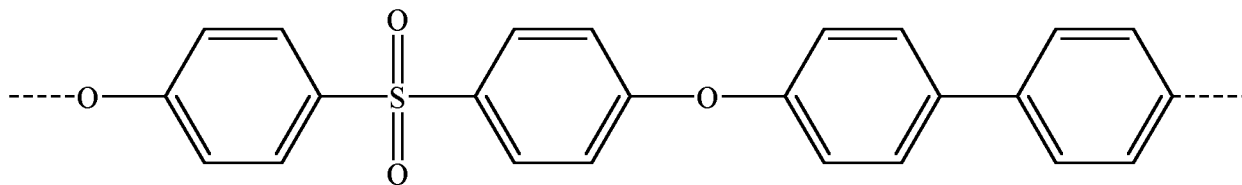


5 where

- M_A^* and M_S^* are identical to M_A and M_S , respectively, with the exception that L^1 , i , j , and k are replaced by L^{1*} , i^* , j^* , and k^* respectively;
- each L^{1*} is a linking group independently selected from the group consisting of a polarizable group, a UV initiating group, and a oxirane reactive group; and
- each i^* is an independently selected integer from 0 to 4; each j^* is an independently selected integer from 0 to 3; and each k^* is an independently selected integer from 0 to 2.

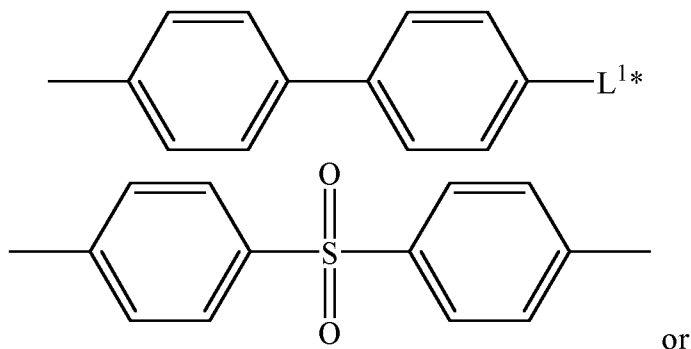
5. The PAE polymer of claim 4, wherein

f) R_{PAES} is represented by

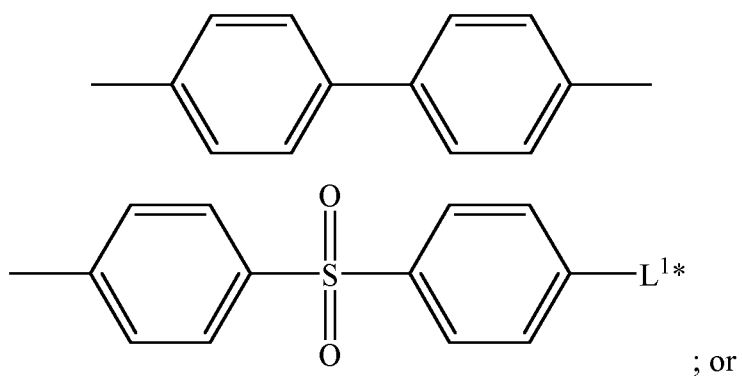


and

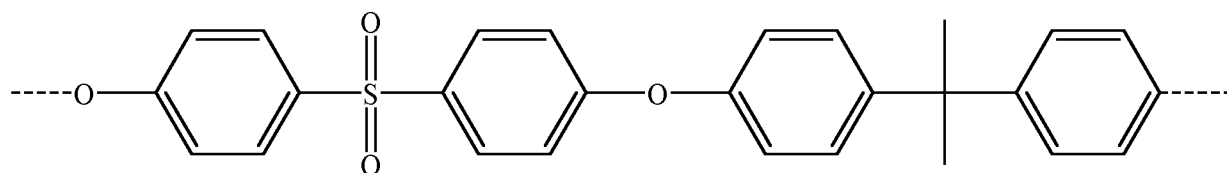
iii. the PAES polymer is represented by Formula (18A) with M_A^* and M_S^* respectively represented by



iv. the PAES polymer is represented by Formula (18B) with M_A^* and M_S^* respectively represented by

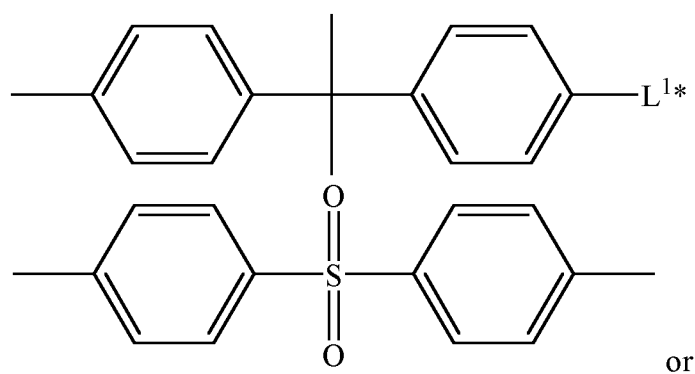


g) R_{PAES} is represented by

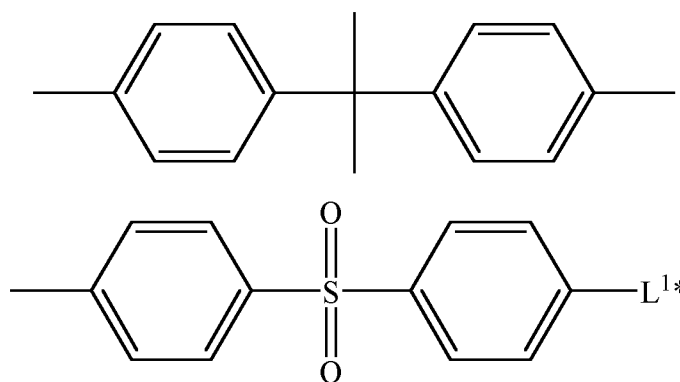


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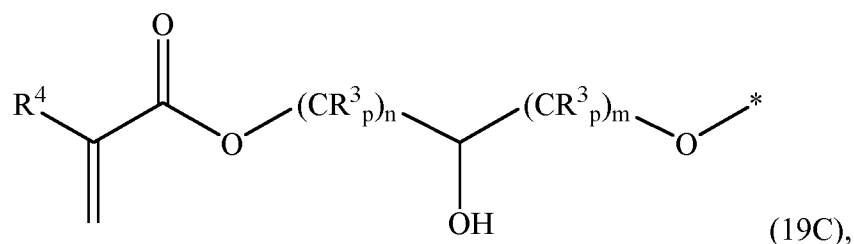
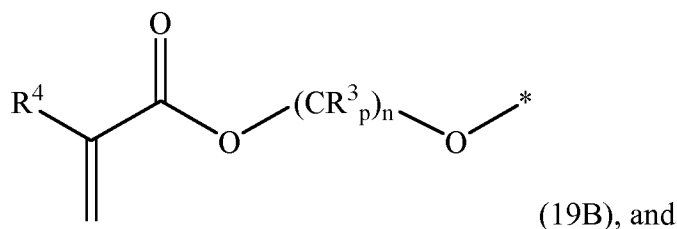
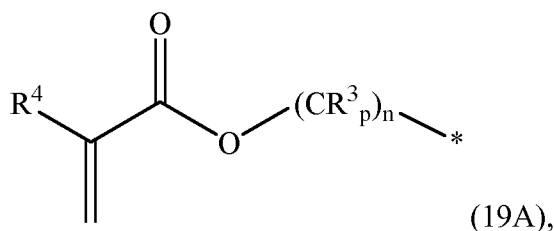
iii. the PAES polymer is represented by Formula (18A) with M_A^* and M_S^* respectively represented by



10 iv. the PAES polymer is represented by Formula (18B) with M_A^* and M_S^* respectively represented by



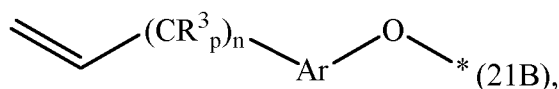
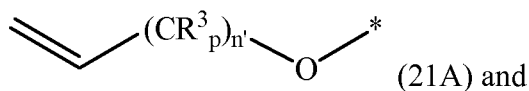
6. The PAE polymer of any of claims 1 to 5 where each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:



where

- each R^4 and each R^3 are independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2; and
- n and m are independently selected integers from 0 to 15.

7. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:

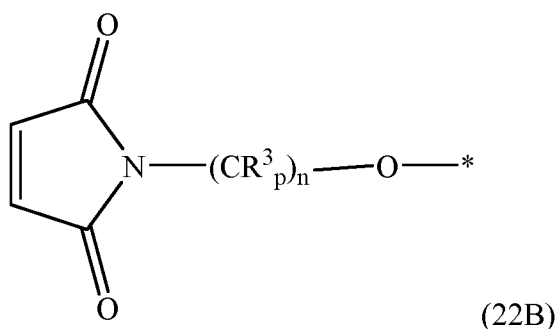
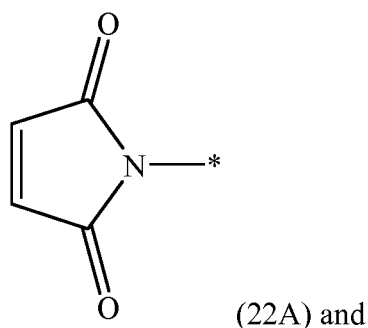


where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;

- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- n' is an integer from 1 to 15.

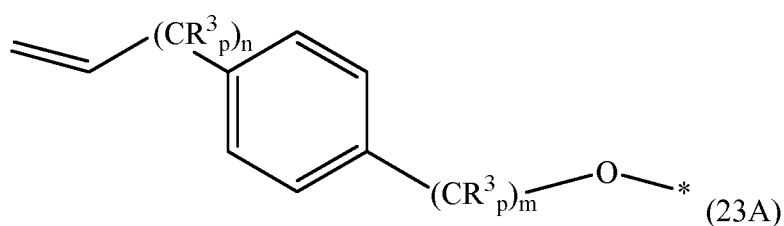
5 8. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:

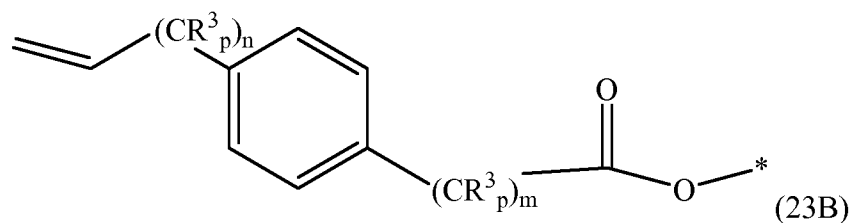


where

- 10
- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
 - p is an independently selected integer from 0 to 2; and
 - n is an integer from 0 to 15.

15 9. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:

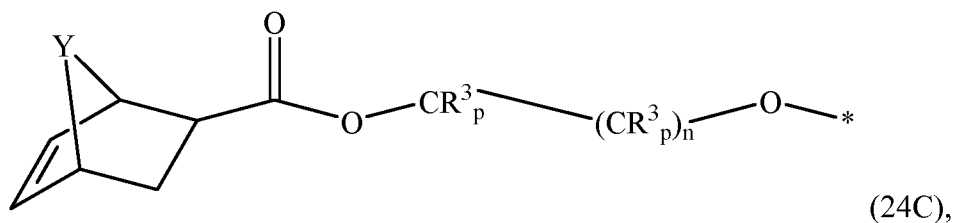
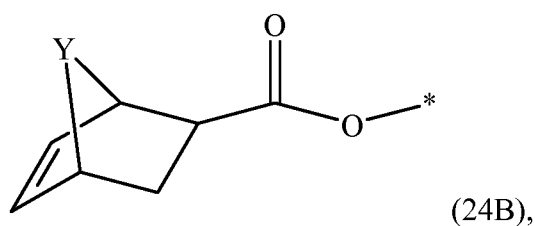
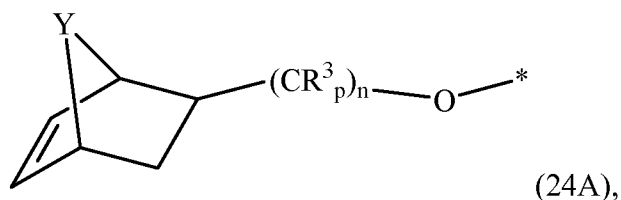


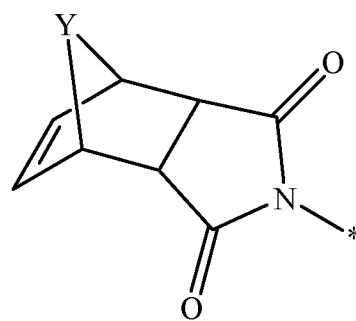


where

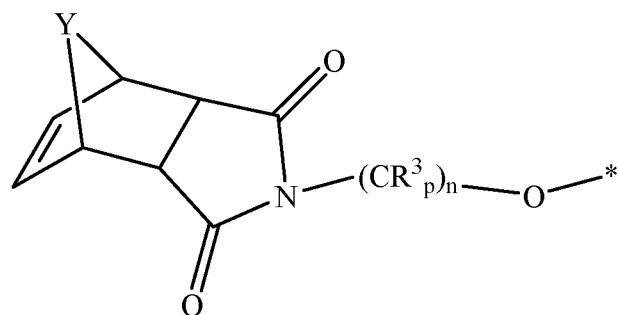
- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- n' is an integer from 1 to 15.

10. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:





(24D), and

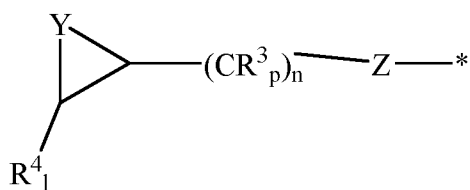


(24E),

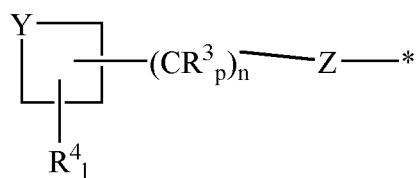
where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- Y is and oxygen or a $-CH_2-$ group.

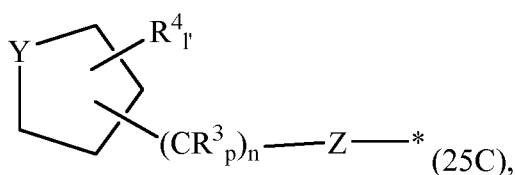
11. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae:



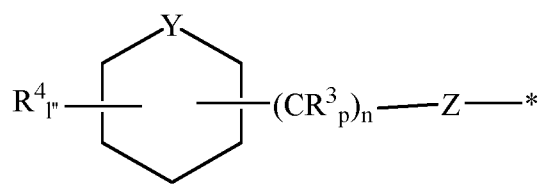
(25A),



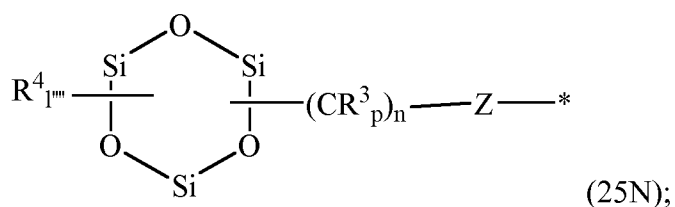
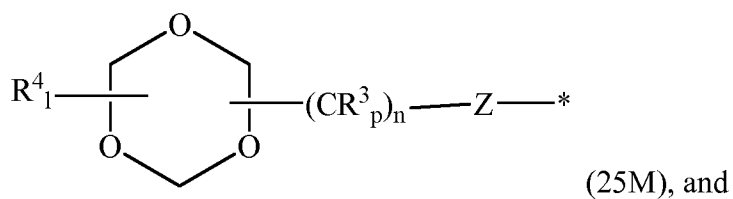
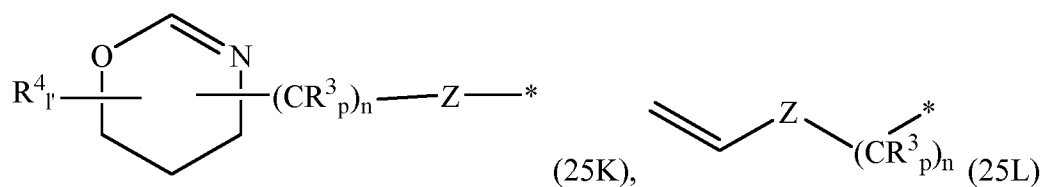
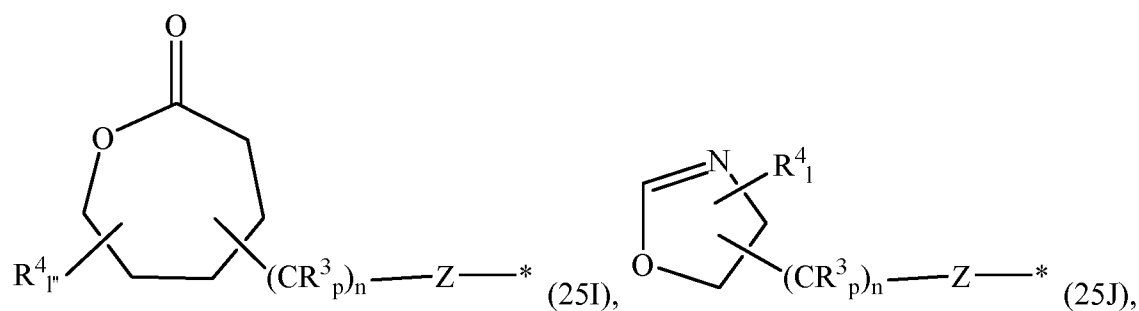
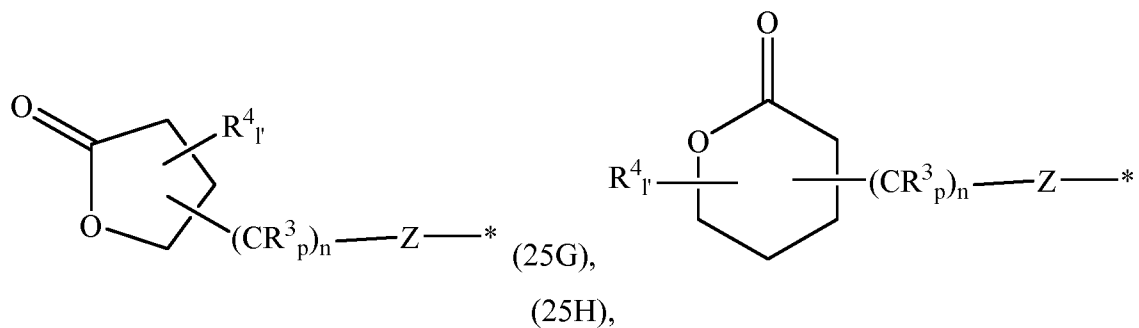
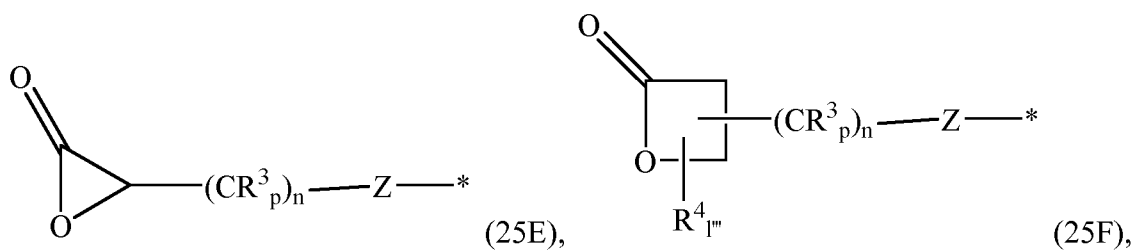
(25B),



(25C),



(25D),



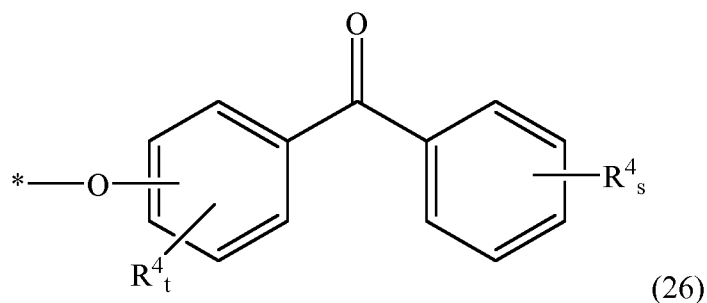
where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and

- Z is a bond or an oxygen;
- Y is an oxygen or a sulfur; and
- l , l' , l'' , l''' , and l'''' are independently selected integers from 0 to 2, 0 to 3, 0 to 4, 0 to 1 and 0 to 5, respectively.

5

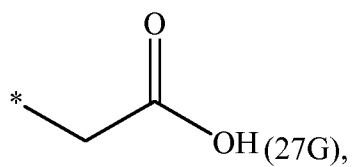
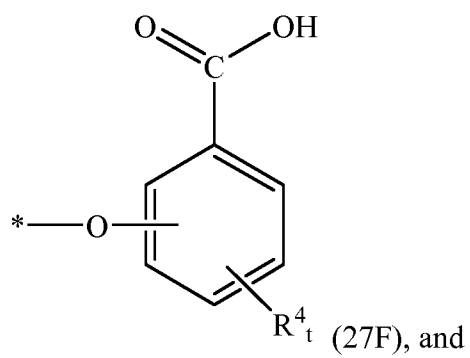
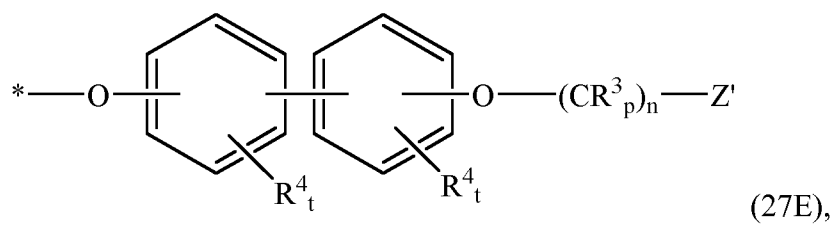
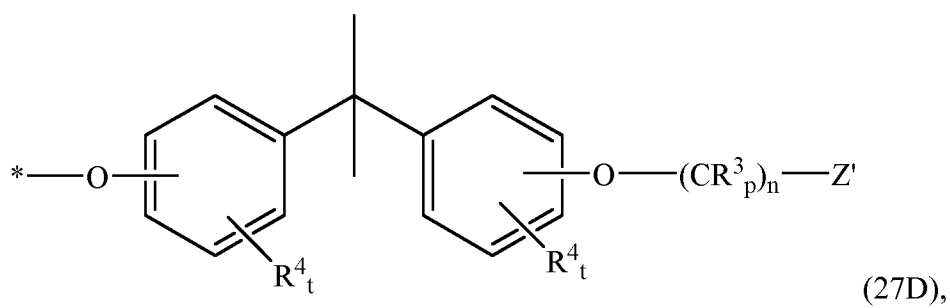
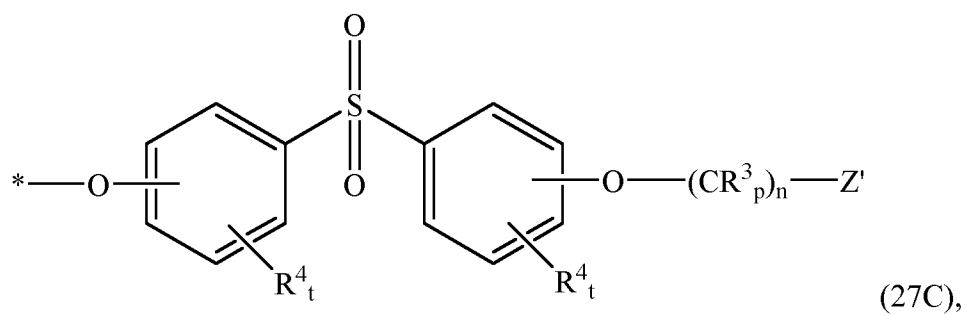
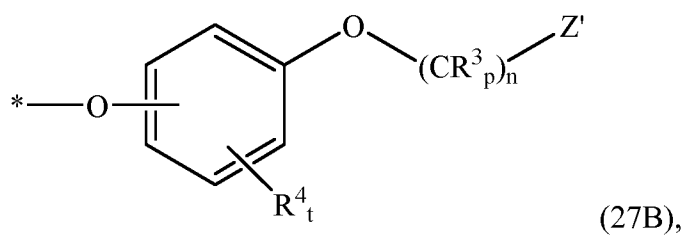
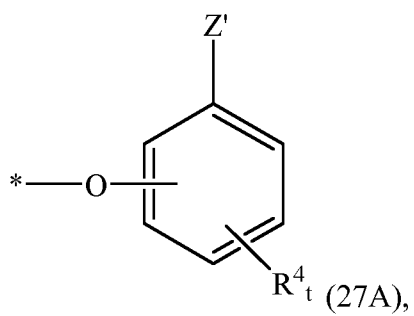
12. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae



wherein

- 10
- each R^4 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
 - s is an integer from 0 to 5; and
 - t is an integer from 0 to 4.

- 15
13. The PAE polymer of any of claims 1 to 5, wherein each L^1 and L^{1*} are independently represented by a formula selected from the following group of formulae



wherein

- each R^4 and each R^3 are independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- each p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15,
- t is an integer from 0 to 4
- Z' is a $-NH_2$ or $-OQ$, where Q is selected from the group consisting of H, Li, Na, K, Ca, and Mg.

14. The PAE polymer of any of claims 1 to 13, wherein the PAE polymer comprises 1 to 50 recurring units (R_{PAES}).

15. The PAE polymer of any of claims 1 to 14, wherein the PAE polymer comprises about 50 mol%, at least 60 mol%, at least 70 mol%, at least 80 mol%, at least 90 mol%, at least 95 mol%, or at least 99 mol% recurring unit (R_{PAES}).

16. The PAE polymer of any of claims 1 to 15, wherein the PAE polymer has a number average molecular weight of less than about 20,000 g/mol, less than about 15,000 g/mol, or less than about 10,000 g/mol.

17. The PAE polymer of claim 16, wherein the PAE polymer has a number average molecular weight of no less than about 1,000 g/mol or no less than about 2,000 g/mol.

18. A curable polymer composition comprising,

the functionalized PAE polymer of any of claims 1 to 17 and

- if the linking group is a radically polymerizable group, a radical photoinitiator selected from the group consisting of: acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzophenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphine oxide, benzyl dimethyl ketal, 1-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one,

fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone (BTTB), combinations of BTTB and dyesensitizers such as xanthene, thioxanthene, cumarin, and ketocumarin.

- 5 - If the linking group is a cationically polymerizable group, a salt selected from the group consisting of halonium salts, iodosyl salts, sulfonium salts, sulfoxonium salts, dizaonium salts, metallocene salts.
- If the linking group is a radical photoinitiator, a polymer distinct from the functionalize polymer that contains a C=C double bond or oxirane. and
- 10 - If the linking a oxirane reactive group, a polymer having a cationically polarizable group distinct from or the same as the functionalized PAE polymer.

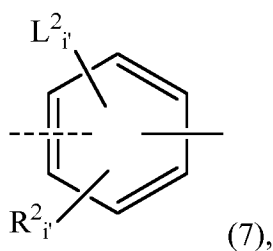
19. A method of curing the functionalized PAE polymer of any of claims 1 to 18, the method comprising irradiating the PAE polymer in a liquid state with UV light, wherein the
15 curing comprises polymerizing or cross-linking.

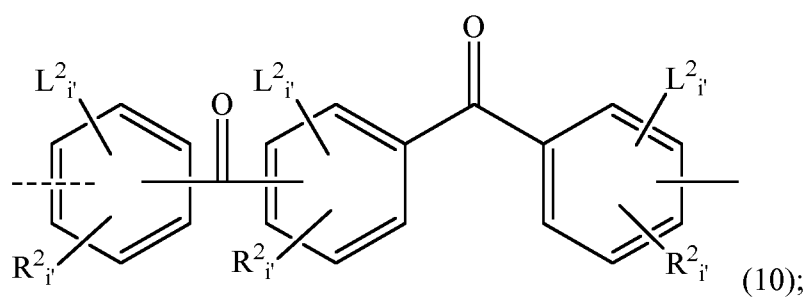
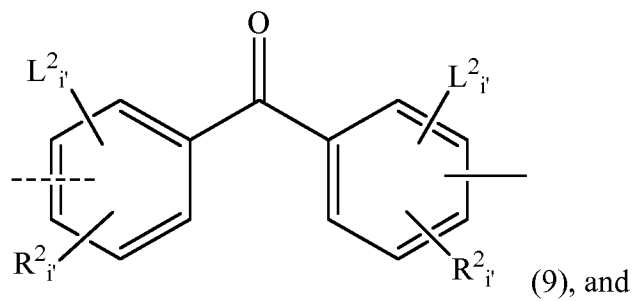
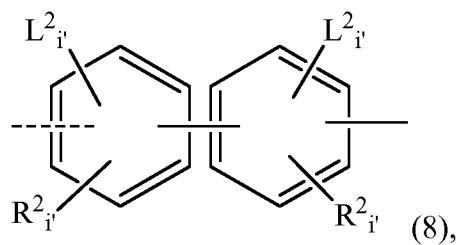
20. The method of claim 19, wherein the UV light is laser light.

21. A method of forming a 3-dimensional article, the method comprising the method of
20 claim 19 or 20.

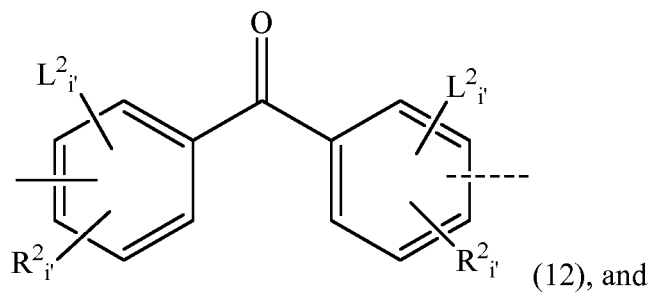
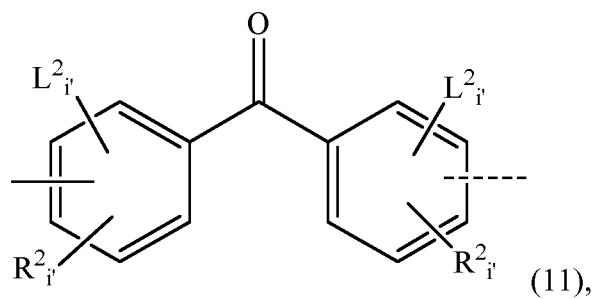
22. A functionalized poly(aryl ether) ("PAE") polymer comprising:
recurring unit (R_{PAEK}) represented by the formula $--[M_B-O-M_K-O]--$
where

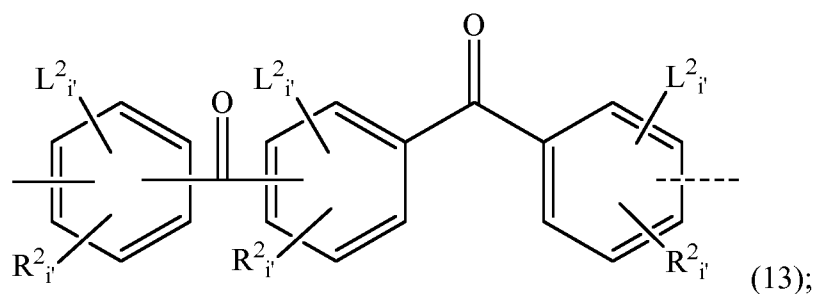
- 25 - M_B is represented by a formula selected from the following group of formulae





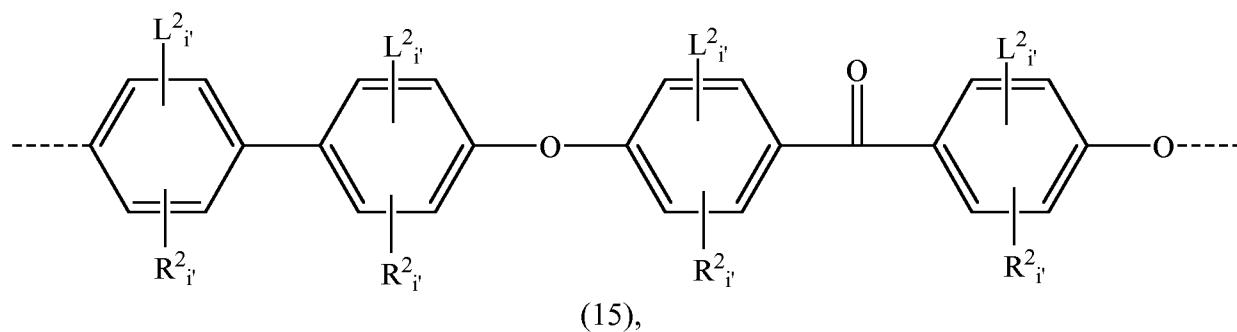
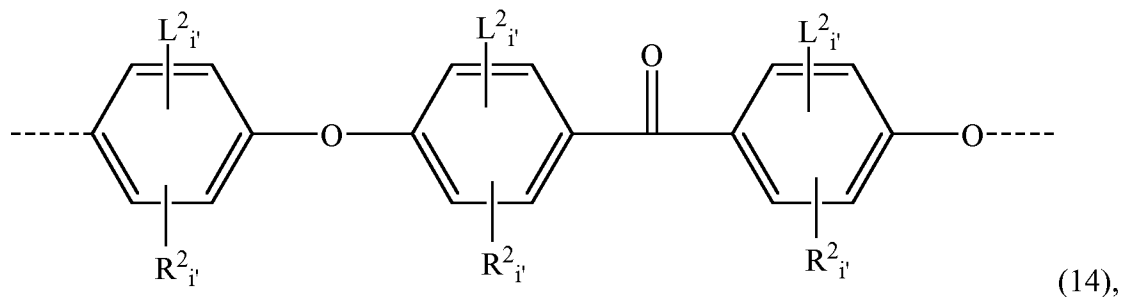
- M_K is represented by a formula selected from the following group of formulae:

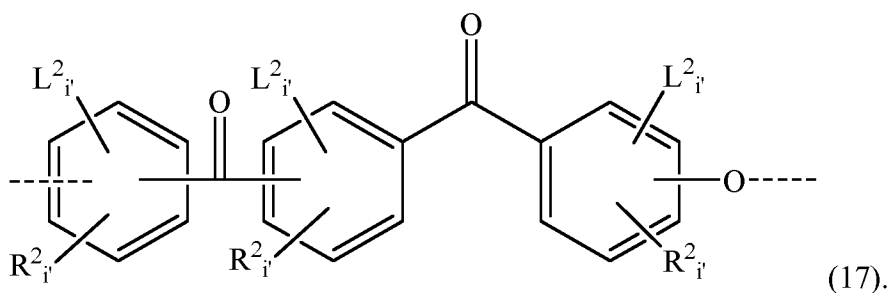
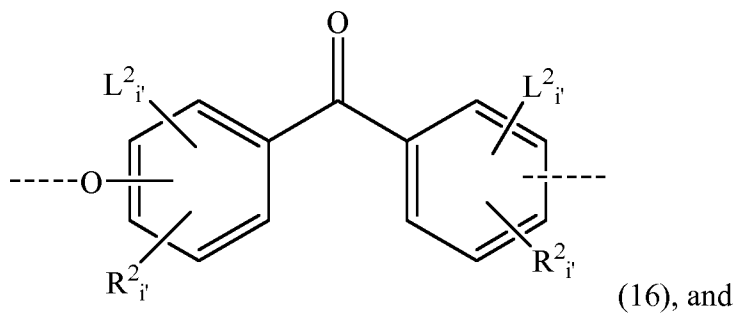




- each R^2 is independently selected from the group consisting of a halogen, alkyl, alkenyl, alkynyl, aryl, ether, thioether, carboxylic acid, ester, amide, imide, alkali or alkaline earth metal sulfonate, alkyl sulfonate, alkali or alkaline earth metal phosphonate, alkyl phosphonate, amine and quaternary ammonium;
- each L^2 is a linker molecule independently selected from the group consisting of radically polarizable group, a cationically polarizable group, a radical initiator group, and a oxirane reactive group; and
- each i' is an independently selected integer from 0 to 4.

23. The PAE polymer of claim 22, wherein recurring unit (R_{PAEK}) is represented by a formula selected from the following group of formula:





24. The PAE polymer of either claim 22 or 23, wherein the PAE polymer is represented
5 by one of the following formulae:

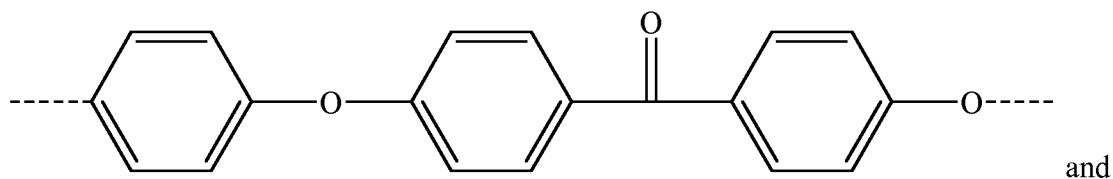


wherein

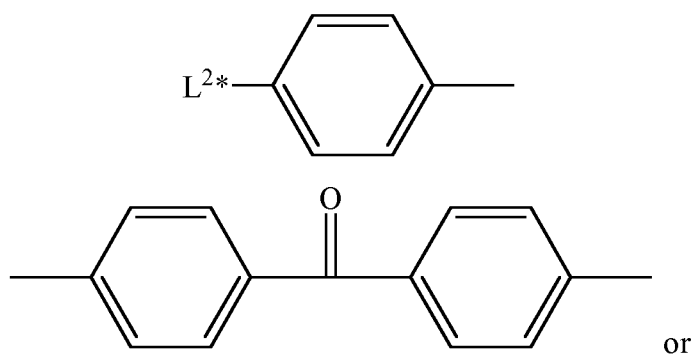
- M_B^* and M_K^* are identical to M_B and M_K , respectively, with the exception that L^2
10 and i' are replaced by L^{2*} and i'^* respectively;
- each L^{2*} is a linking group independently selected from the group consisting of a polarizable group, a UV initiating group, and a oxirane reactive group; and
- each i'^* is an independently selected integer from 0 to 4.

25. The PAE polymer of claim 24, wherein

a) R_{PAEK} is represented by

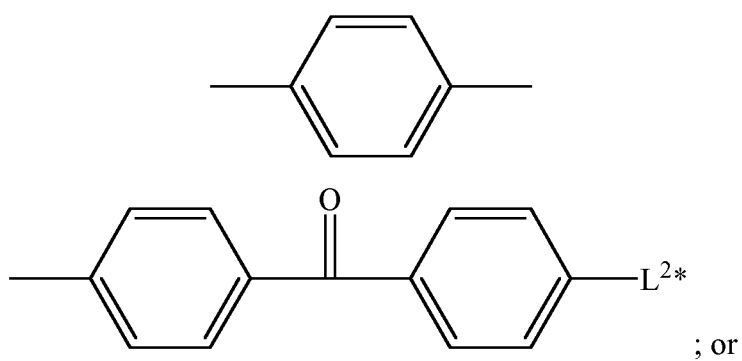


- i. the PAEK polymer is represented by Formula (18C) with M_B^* and M_K^*
20 respectively represented by

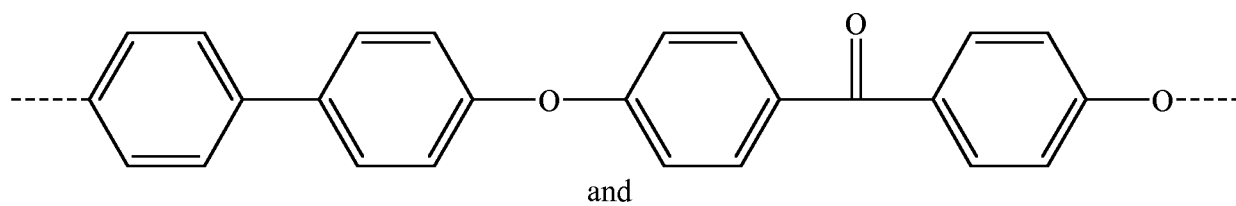


- ii. the PAEK polymer is represented by Formula (18D) with M_B^* and M_K^* respectively represented by

5

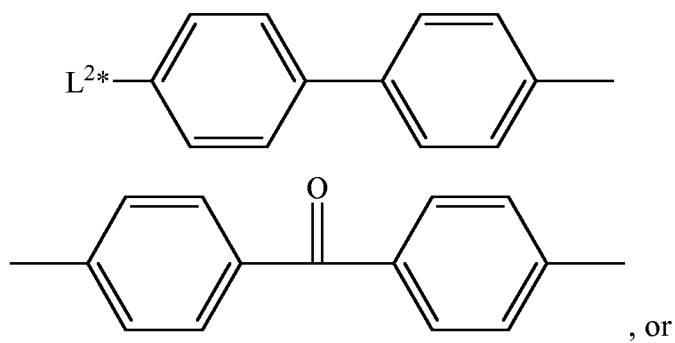


- b) R_{PAES} is represented by



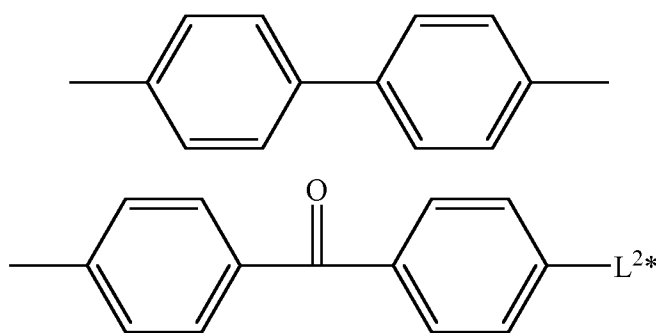
10

- i. the PAEK polymer is represented by Formula (18C) with M_B^* and M_K^* respectively represented by

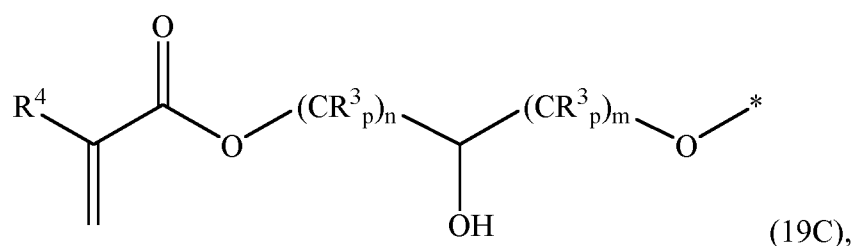
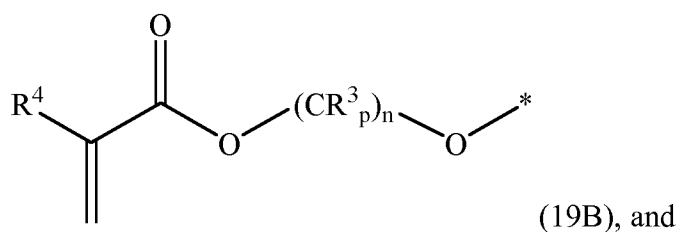
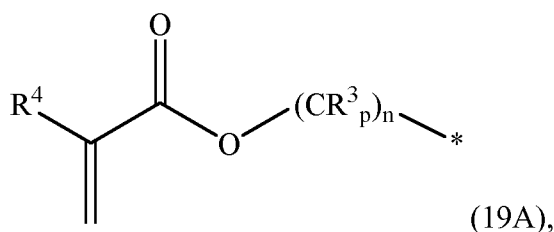


15

- ii. the PAEK polymer is represented by Formula (18D) with M_B^* and M_K^* respectively represented by



- 5 26. The PAE polymer of any of claims 22 to 25 where each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:

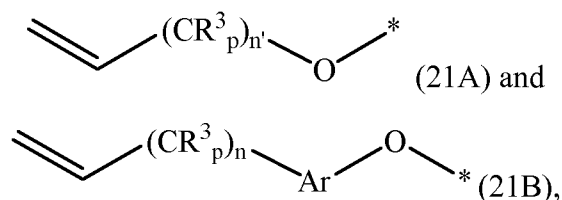


10 where

- each R^4 and each R^3 are independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2; and
- n and m are independently selected integers from 0 to 15.

15

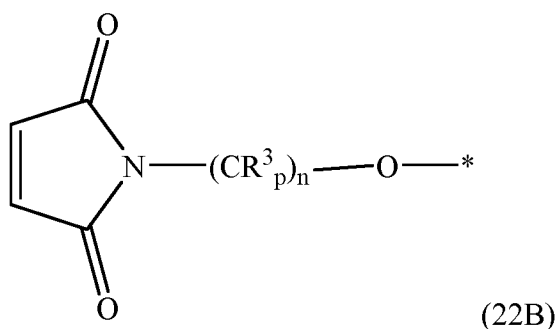
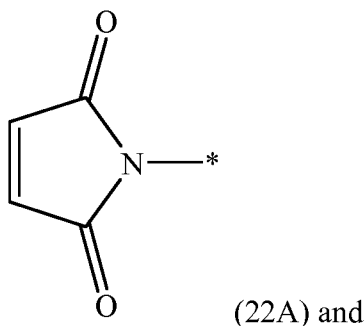
27. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:



where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- n' is an integer from 1 to 15.

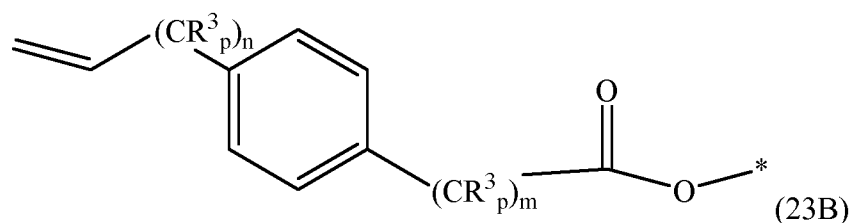
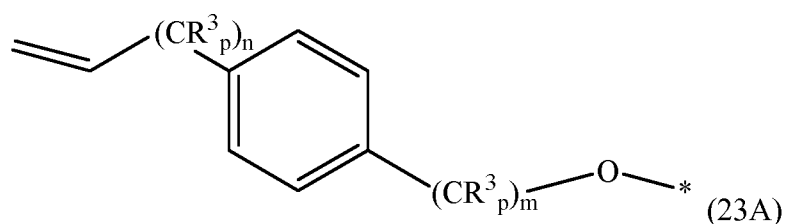
28. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:



where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2; and
- n is an integer from 0 to 15.

29. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:



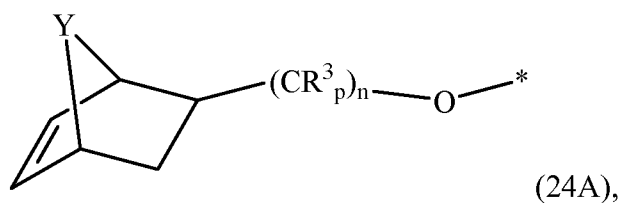
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where

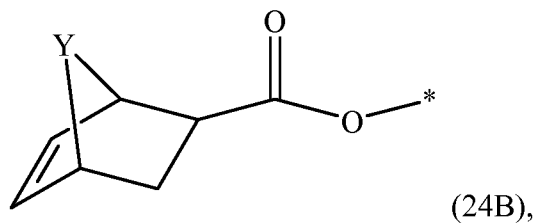
- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- n' is an integer from 1 to 15.

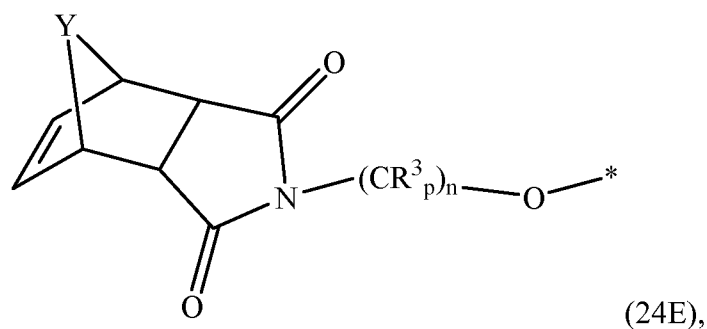
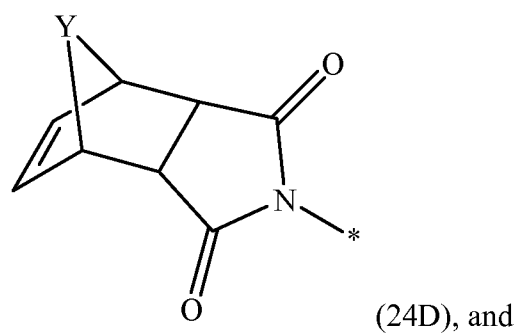
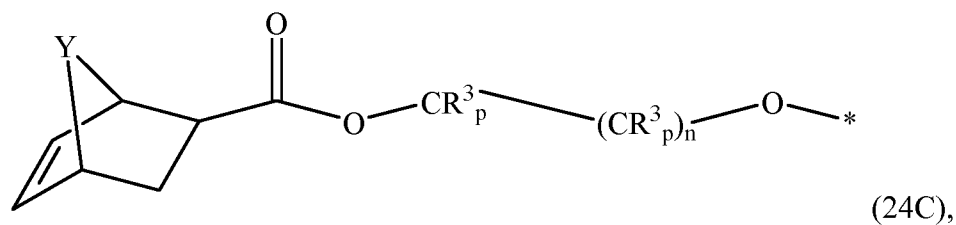
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30. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:



15



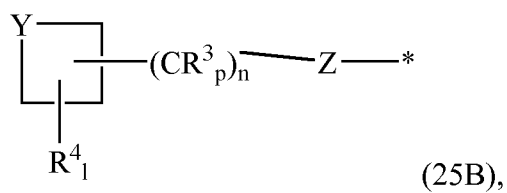
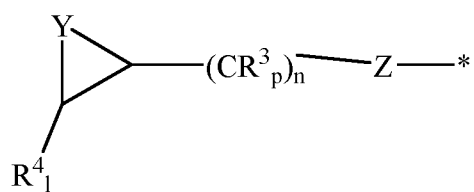


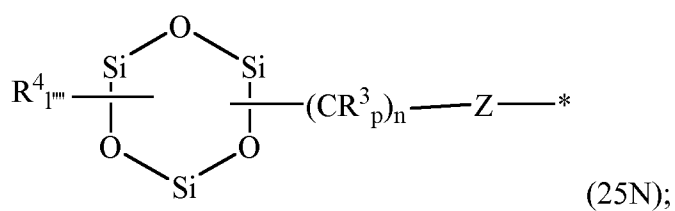
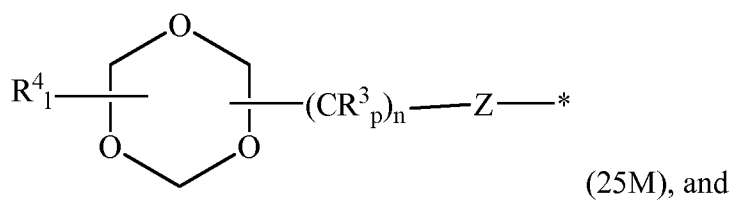
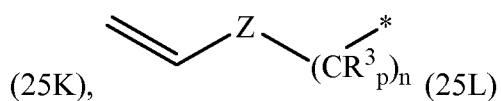
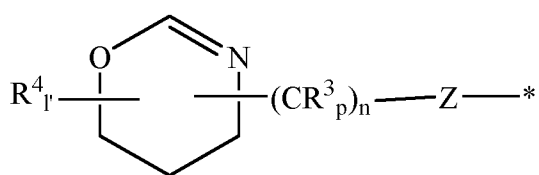
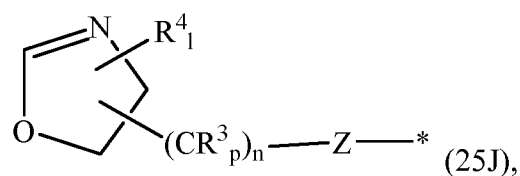
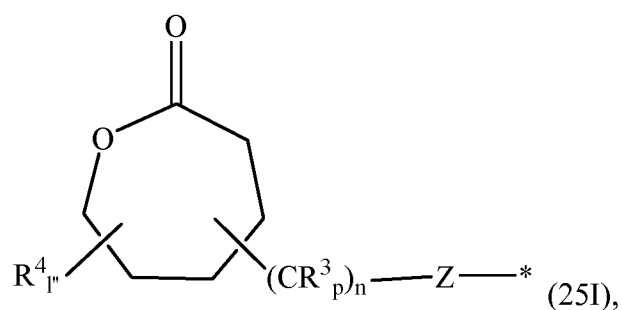
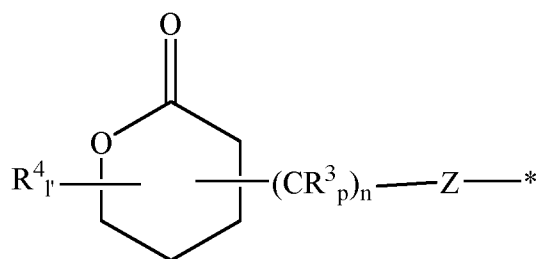
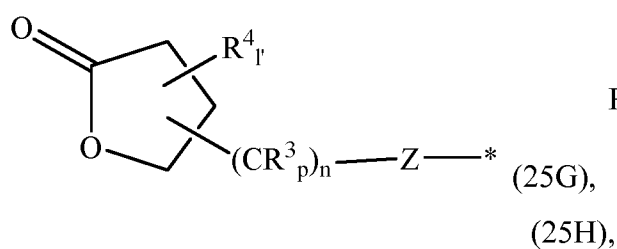
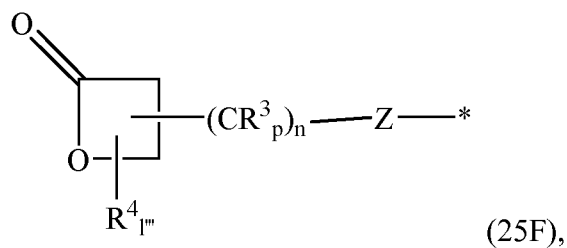
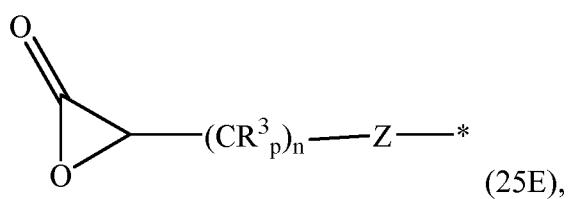
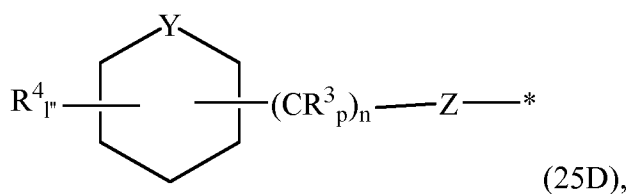
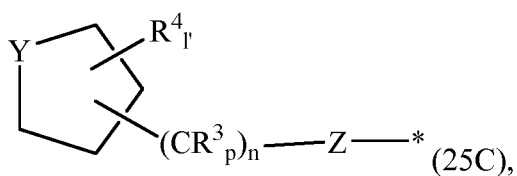
where

- 5 - each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- Y is and oxygen or a $-CH_2-$ group.

10

31. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae:

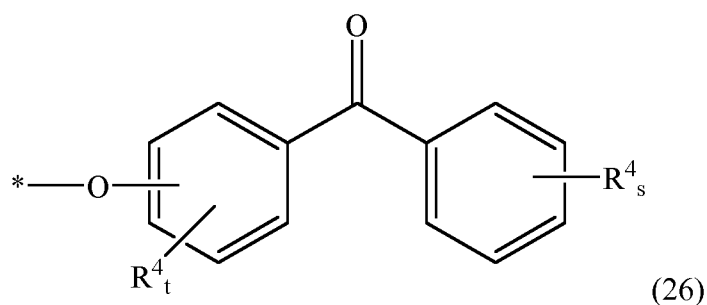




where

- each R^3 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15; and
- Z is a bond or an oxygen;
- Y is an oxygen or a sulfur; and
- l, l', l'', l''' , and l'''' are independently selected integers from 0 to 2, 0 to 3, 0 to 4, 0 to 1 and 0 to 5, respectively.

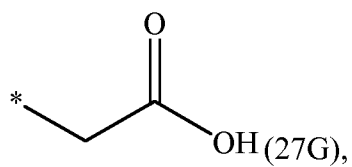
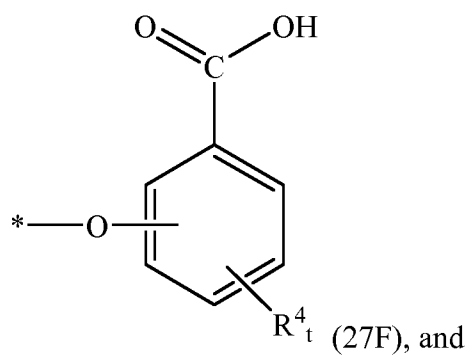
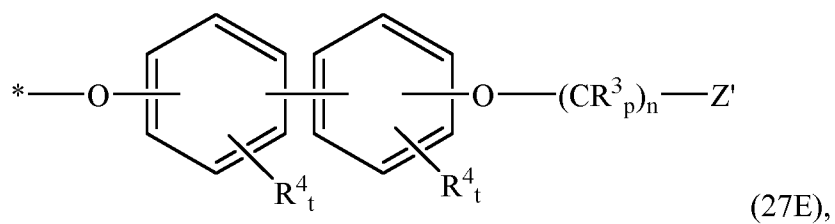
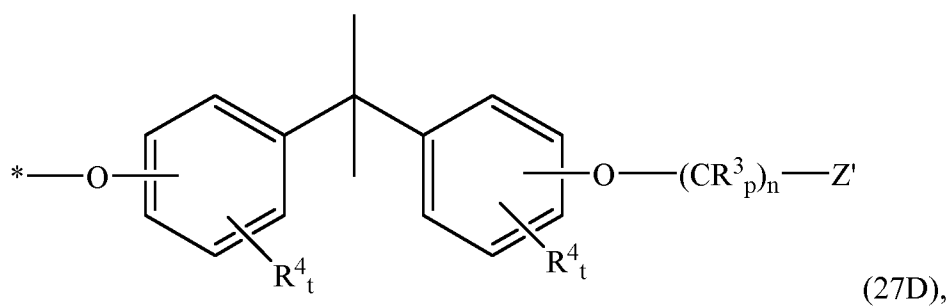
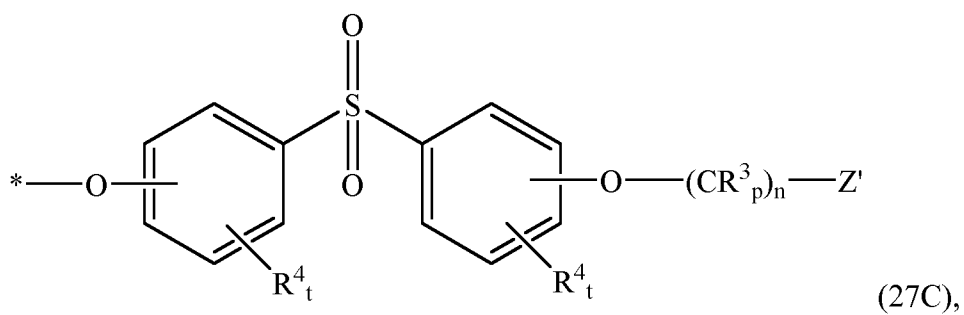
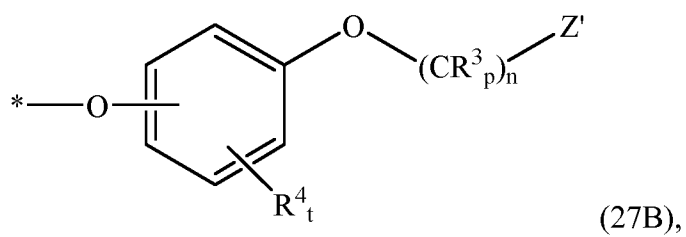
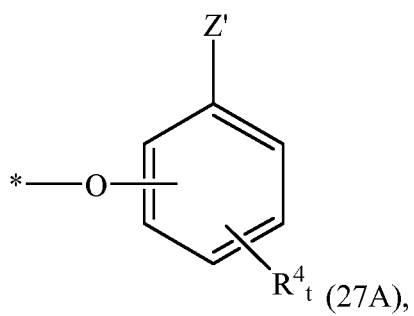
32. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae



wherein

- each R^4 is independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- s is an integer from 0 to 5; and
- t is an integer from 0 to 4.

33. The PAE polymer of any of claims 22 to 25, wherein each L^2 and L^{2*} are independently represented by a formula selected from the following group of formulae



wherein

- each R^4 and each R^3 are independently selected from the group consisting of a hydrogen and a linear or branched a C_1 - C_{12} -alkyl group;
- each p is an independently selected integer from 0 to 2;
- n is an integer from 0 to 15,
- t is an integer from 0 to 4
- Z' is a $-NH_2$ or $-OQ$, where Q is selected from the group consisting of H, Li, Na, K, Ca, and Mg.

34. The PAE polymer of any of claims 1 to 33, wherein the PAE polymer comprises 1 to 50 recurring units (R_{PAEK}).

35. The PAE polymer of any of claims 1 to 34, wherein the PAE polymer comprises about 50 mol%, at least 60 mol%, at least 70 mol%, at least 80 mol%, at least 90 mol%, at least 95 mol%, or at least 99 mol% recurring unit (R_{PAES}).

36. The PAE polymer of any of claims 1 to 35, wherein the PAE polymer has a number average molecular weight of less than about 20,000 g/mol, less than about 15,000 g/mol, or less than about 10,000 g/mol.

37. The PAE polymer of claim 36, wherein the PAE polymer has a number average molecular weight of no less than about 1,000 g/mol or no less than about 2,000 g/mol.

38. A curable polymer composition comprising,
the functionalized PAE polymer of any of claims 22 to 37 and

- if the linking group is a radically polymerizable group, a radical photoinitiator selected from the group consisting of: acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzophenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphine oxide, benzyl dimethyl ketal, 1-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one,

fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone (BTTB), combinations of BTTB and dyesensitizers such as xanthene, thioxanthene, cumarin, and ketocumarin.

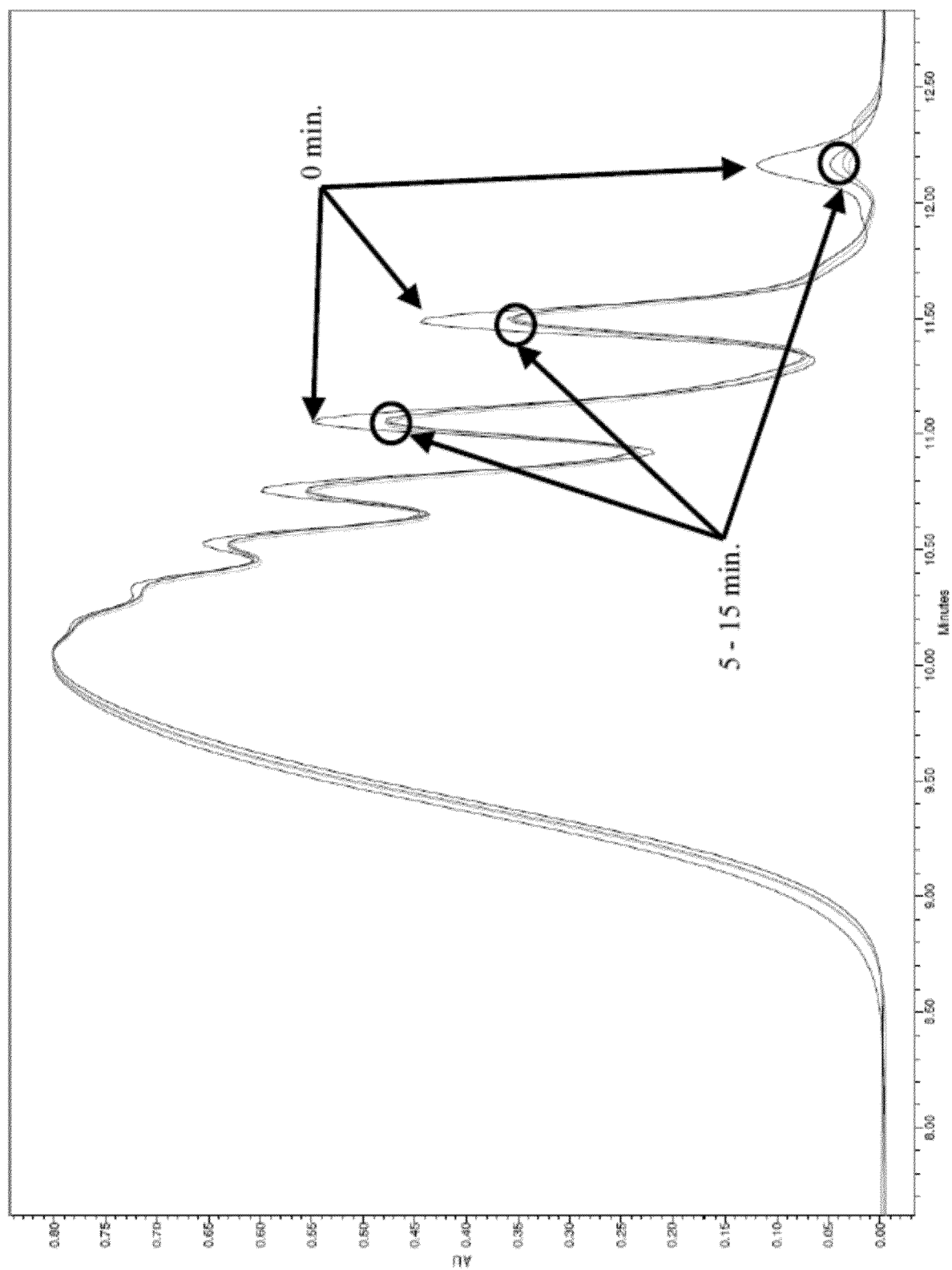
- 5 - If the linking group is a cationically polymerizable group, a salt selected from the group consisting of halonium salts, iodosyl salts, sulfonium salts, sulfoxonium salts, dizaonium salts, metallocene salts.
- If the linking group is a radical photoinitiator, a polymer distinct from the functionalize polymer that contains a C=C double bond or oxirane. and
- 10 - If the linking a oxirane reactive group, a polymer having a cationically polarizable group distinct from or the same as the functionalized PAE polymer.

39. A method of curing the functionalized PAE polymer of any of claims 22 to 38, the method comprising irradiating the PAE polymer in a liquid state with UV light, wherein the
15 curing comprises polymerizing or cross-linking.

40. The method of claim 39, wherein the UV light is laser light.

41. A method of forming a 3-dimensional article, the method comprising the method of
20 claim 39 or 40.

FIG 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/057924

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G75/23 B29C67/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VIRGIL PERCEC ET AL: "Functional polymers and sequential copolymers by phase transfer catalysis, 3.+ Syntheses and characterization of aromatic poly(ether sulfone)s and poly(oxy-2,6-dimethyl-1,4-phenylene) containing pendant vinyl groups", MAKROMOLEKULARE CHEMIE, MACROMOLECULAR CHEMISTRY AND PHYSICS., vol. 185, no. 11, 1 November 1984 (1984-11-01), pages 2319-2336, XP055378716, CH ISSN: 0025-116X, DOI: 10.1002/macp.1984.021851110 schemes 1, 2; figures 1-12; table 1 ----- -/-	1-18, 34-37



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 June 2017

Date of mailing of the international search report

21/06/2017

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/057924

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	----- EP 2 791 200 A2 (SOLVAY SPECIALTY POLYMERS USA [US]) 22 October 2014 (2014-10-22) paragraph [0082]; examples 1-5	22-38
Y	----- US 2009/243156 A1 (MOROHOSHI KIMITAKA [JP] ET AL) 1 October 2009 (2009-10-01) paragraphs [0049] - [0060] -----	19-21, 39-41

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Information on patent family members

International application No

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