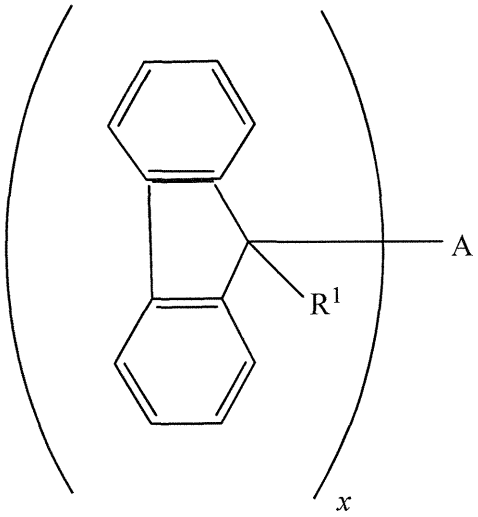
discloses a cross-linking compound as used in the invention described herein, which is blended with an uncrosslinked polymer to achieve a crosslinked organic polymer with a higher glass transition temperature for use in extreme conditions such as in down-hole tool applications.

[0011] While cross-linking agents may be effective, there can be difficulty in controlling the rate and extent of cross-linking. Cross-linked organic polymers having aromatic groups in the backbone such as cross-linked polyarylene ether polymers, including cross-linked polyetherether ketone (PEEK), even when made using agents to control cross-linking as described herein are amorphous polymers that function well at high temperature (having a T_g above about 270°C). The crosslinking provides enhanced chemical resistance to add to the high temperature properties of the base polymers. Cross-linking can be done using techniques as noted in the patents and patent application publications identified above and as described herein using Applicant's techniques. In molding, the controlled cross-linked polymers perform well at about 250°C (or somewhat below the T_g of the materials). However, as molding temperatures rise, the reaction can accelerate such that full cure may be achieved in less than one minute. Cycle times for injection molded articles, such as tubes, rods or electrical connectors, however, are generally three to five minutes or longer. A full cure in less than a minute can impede the usefulness of conventional molding techniques, such as injection molding or extrusion, in forming molded parts.

[0012] Prior art attempts to retard or inhibit and moderate cross-linking reactions using compounds and their reactions are known. *See*, Vanderbilt Rubber Handbook, 13th ed., 1990, p. 281. However, there is still a need in the art to control and inhibit such reactions, and to improve the ability to process such polymers more easily using traditional molding techniques.

BRIEF SUMMARY

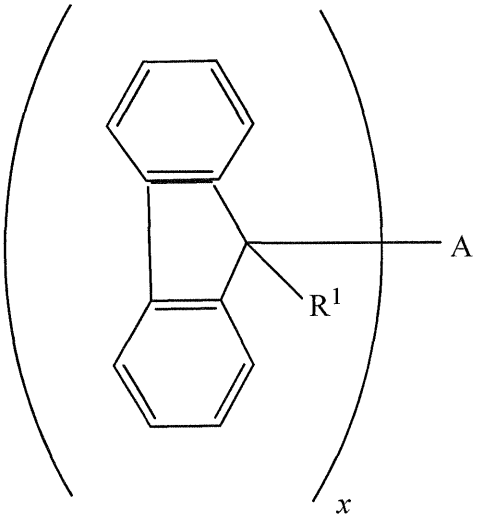
[0013] The present disclosure includes a cross-linking composition comprising a cross-linking compound and a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking compound has a structure according to formula (IV):



(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x = 2.0 to 6.0, wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer, which reactive intermediate oligomer is capable of cross-linking an organic polymer.

[0013a] In one aspect of the present disclosure, there is provided a composition comprising a cross-linking compound and a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking compound has a structure according to formula (IV):



(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from the group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0,

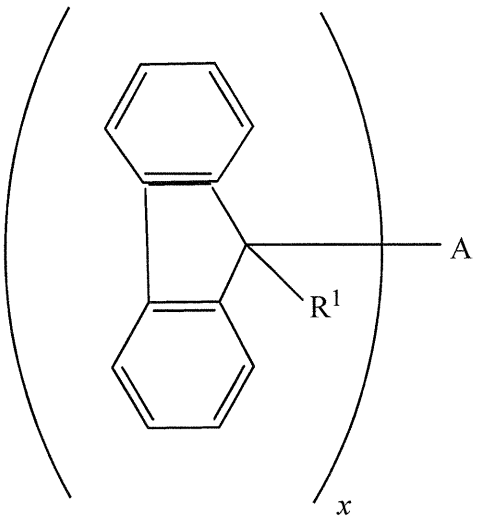
wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer, which reactive intermediate oligomer is capable of cross-linking an organic polymer.

[0013b] In a further aspect of the present disclosure, there is provided an article of manufacture formed from a composition dislosed herein, wherein the article of manufacture is selected from acid-resistant coatings; chemical-casted films; extruded films; solvent-casted films; blown films; encapsulated products; insulation; packaging; composite cells; connectors; sealing assemblies, including O-rings, V-rings, U-cups, gaskets; bearings; valve seats; adapters; wiper rings; chevron back-up rings; and tubing.

[0013c] In another aspect of the present disclosure, there is provided an organic polymer composition for use in forming a cross-linked organic polymer, comprising:

an organic polymer; and

a reactive cross-linking oligomer which is a reaction product of a cross-linking compound having the structure of formula (IV):

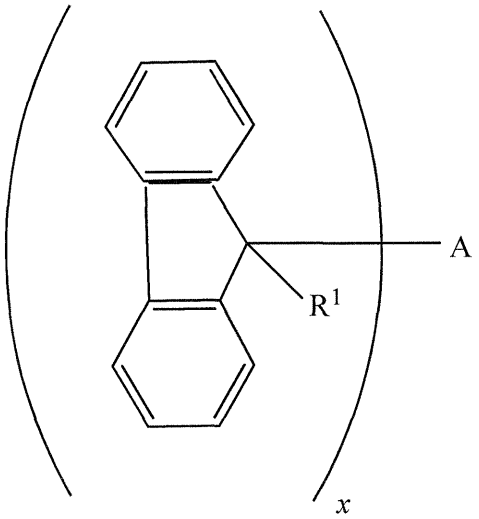


(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0, and a cross-linking reaction additive selected from an organic acid and/or an acetate compound.

[0013d] In a further aspect of the present disclosure, there is provided a method of controlling the cross-linking reaction rate of a cross-linking compound for use in cross-linking an organic polymer, comprising:

a) providing a cross-linking composition comprising a cross-linking compound and a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking compound has the structure according to formula (IV):



(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0, wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer for cross-linking an organic polymer; and

b) heating the cross-linking composition such that oligomerization of the cross-linking compound occurs.

[0013e] In another aspect of the present disclosure, there is provided an organic polymer composition for use in forming a cross-linked organic polymer, comprising:

a dehalogenated organic polymer and

at least one cross-linking compound; wherein the dehalogenated organic polymer is formed by a process comprising reacting an organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break a bond between the organic polymer having the at least one halogen-containing reactive group and a halogen atom in the at least one halogen-containing reactive group to form an intermediate.

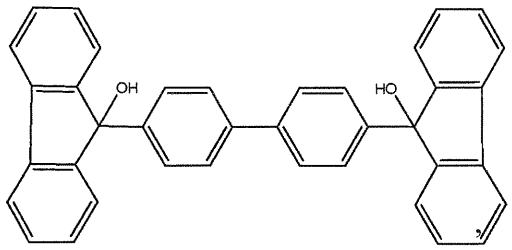
[0013f] In a further aspect of the present disclosure, there is provided a method of controlling the cross-linking reaction rate of an organic polymer having at least one halogen-containing reactive group during a cross-linking reaction, comprising:

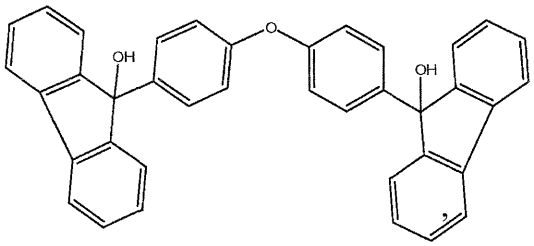
a) reacting the organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break a bond between the organic polymer having the at least one halogen-containing reactive group and a halogen atom in the at least one halogen-containing reactive group, and to form an intermediate having a carbocation;

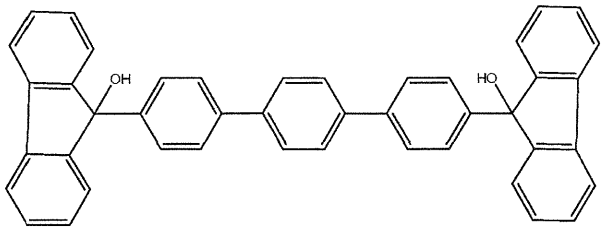
b) reacting the intermediate having the carbocation with acetic acid to form a dehalogenated organic polymer; and

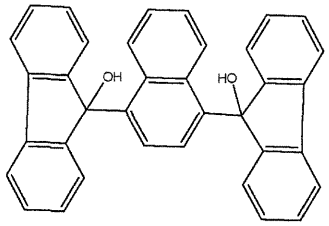
c) crosslinking the dehalogenated organic polymer using a crosslinking reaction.

[0014] **[0013g]** In another aspect of the present disclosure, there is provided a molded article formed from a composition disclosed herein.The cross-linking compound in the composition as noted above may have a structure according to the following:



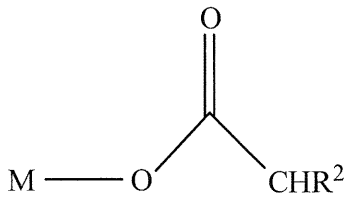






[0017] Thus, in one embodiment, the cross-linking reaction additive is an organic acid which may be glacial acetic acid, formic acid, and/or benzoic acid.

[0018] In another embodiment, the cross-linking reaction additive may be an acetate compound that has a structure according to formula (II):



(II)

wherein M is a Group I or a Group II metal; and R^2 is an alkyl, aryl, or aralkyl group, wherein the alkyl group is a hydrocarbon group of 1 to about 30 carbon atoms, preferably about 1 to about 15 carbon atoms having 0 to about 10 ester or ether groups along or in the chain of the hydrocarbon group, preferably about 0 to about 5 ester or ether groups, wherein R^2 may have 0 to about 10, preferably about 0 to about 5, functional groups that may be one or more of sulfate, phosphate, hydroxyl, carbonyl, ester, halide, mercapto or potassium. More preferably, the acetate compound may be lithium acetate hydrate, sodium acetate and/or potassium acetate, and salts and derivatives thereof.

[0019] The weight percentage ratio of the cross-linking compound to the cross-linking reaction additive may be about 10:1 to about 10,000:1, and more preferably about 20:1 to about 1000:1.

[0020] In another embodiment, the present disclosure includes an organic polymer composition for use in forming a cross-linked organic polymer, comprising a cross-linking compound having a structure as in formula (IV) as described above; a cross-linking reaction additive selected from an organic acid and/or an acetate compound; and at least one organic polymer, wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer, which reactive intermediate oligomer is capable of cross-linking the organic polymer.

[0021] In a further embodiment, the present disclosure includes an organic polymer composition for use in forming a cross-linked organic polymer, comprising an organic polymer and a reactive

crosslinking oligomer which is a reaction product of a cross-linking compound having a structure as in formula (IV) described above and a cross-linking reaction additive selected from an organic acid and/or an acetate compound.

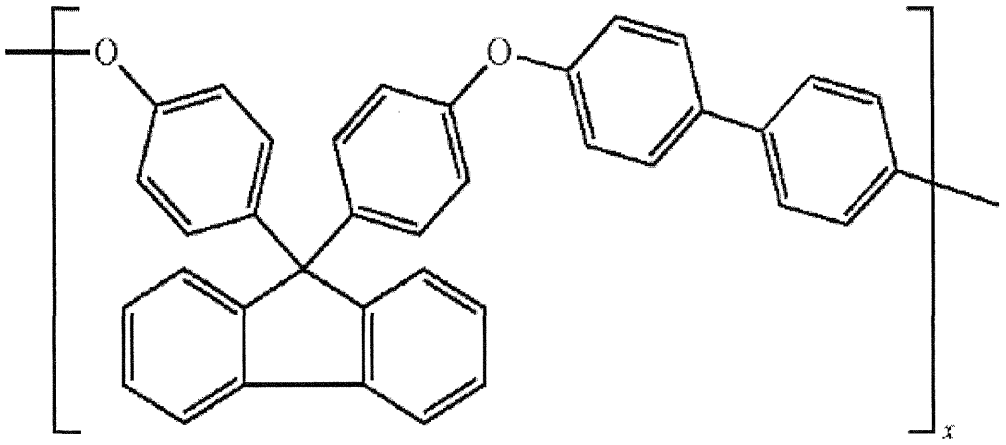
[0022] The organic polymer is preferably a polymer selected from poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, poly(benzimidazole)s and polyaramids.

[0023] The organic polymer may also be a polymer in one embodiment herein that is a poly(arylene ether) including polymer repeating units along its backbone having the following structure:

$$-(O-Ar^1-O-Ar^2-)_m\ (-O-Ar^3-O-Ar^4-)_n-$$

wherein Ar^1, Ar^2, Ar^3 and Ar^4 are identical or different aryl radicals, m = 0 to 1.0, and n = 1-m.

[0024] In a further preferred embodiment, the organic polymer is a polymer having an aromatic group in the backbone, preferably a poly(arylene ether), m is 1 and n is 0 and the polymer has repeating units along its backbone having the structure of formula (V):



(V)

[0025] The cross-linking compound in this embodiment may have the various structures noted above and the arene moiety may also have the characteristics as noted above.

[0026] In one embodiment of the present disclosure, the cross-linking reaction additive is an organic acid such as glacial acetic acid, formic acid and/or benzoic acid. In an alternative embodiment of the present disclosure, the cross-linking reaction additive is an acetate compound such as those noted

[0030] In one embodiment, the method further comprises heating the cross-linking composition before heat molding. In an alternative embodiment, the method further comprises heating the cross-linking composition during heat molding.

[0031] The cross-linking compound used in the method may have any of the various structures as noted above. In one embodiment, the cross-linking reaction additive is an organic acid and/or acetate as described above.

[0032] In one embodiment, the method further comprises combining the cross-linking compound and the cross-linking reaction additive in a solvent and reacting the cross-linking compound and the cross-linking reaction additive to form a reactive oligomerized cross-linking compound. In an alternative embodiment, the method further comprises combining the cross-linking compound and the cross-linking reaction additive in solid form.

[0033] The method of forming an organic polymer composition may also include the steps of adding the reactive oligomerized cross-linking compound to an organic polymer to form a cross-linkable composition, cross-linking the organic polymer composition to form a cross-linked organic polymer. The organic polymer of the method can one of the various polymers noted above, including the preferred polyarylene polymers having a repeating unit as in formula (V).

[0034] The present disclosure also includes heat-molded articles useful for down-hole and other extreme condition end applications which are formed from the organic polymer compositions and methods as described above. The articles may be formed by various methods or techniques including extrusion, injection molding, blow molding, blown film molding, compression molding and/or injection/compression molding. Preferably, the articles include, for example, but are not limited to acid-resistant coatings, chemical-casted films, extruded films, solvent-casted films, blown films, encapsulated products, insulation, packaging, composite cells, connectors, and sealing assemblies in the shape of O-rings, V-rings, U-cups, gaskets, bearings, valve seats, adapters, wiper rings, chevron back-up rings, and tubing.

[0035] In addition to use of the compounds noted above, the applicants herein have observed that as viscosity increases in such aromatic group-containing organic polymers, the degree of inhibition which can be achieved from using such cross-linking reaction additives for rate control may not always be sufficient such that in some embodiments herein, additional modification is desirable to improve end effects be reducing and/or controlling the curing and cross-linking rate.

[0036] Thus, Applicant has also developed a solution to the need in the art for easier, smooth processing and heat molding of cross-linked organic polymers, either formed using techniques described herein or formed using prior art techniques, allowing for use of traditional molding techniques which require a window of curing which can be longer than what may be achieved using a direct cross-linking process as in the prior art techniques noted above and/or even over and above the inhibition effects achieved using Applicant's enhanced cross-linking reaction additives as described above and elsewhere herein.

[0037] Thus, the present disclosure further provides debrominated organic polymers for cross-linking, particularly useful for those organic polymers having an aromatic group in the backbone and/or that are in the category of high glass transition temperature polymers, as well as compositions including such dehalogenated organic polymers and methods for preparing and cross-linking the same. The resulting articles are formed using controlled cross-linking reaction rates enabling use of traditional molding techniques during crosslinking of such polymers due to the enhanced processability of the dehalogenated organic polymers. The present disclosure opens an avenue for creating a variety of unique and readily moldable cross-linked organic polymer articles of manufacture providing the beneficial properties of such materials, including chemical resistance, high-temperature and high-pressure performance and strength for a variety of end applications.

[0038] Included herein is an organic polymer composition for use in forming a cross-linked aromatic polymer, comprising a dehalogenated organic polymer and at least one cross-linking compound. In one embodiment, the dehalogenated organic polymer is a debrominated organic polymer.

[0039] In one embodiment, the cross-linking compound has a structure according to formula (IV):

[0056] The present disclosure also includes molded articles formed from the compositions noted above and described further herein.

[0057] The present disclosure also includes a method of controlling the cross-linking reaction rate of an organic polymer having at least one halogen-containing reactive group during a cross-linking reaction, preferably organic polymers having an aromatic group in the backbone chain of the polymer. The method comprises: (a) reacting the organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break the bond between the organic polymer having the at least one halogen-containing reactive group and the halogen atom in the at least one halogen-containing reactive group and thereby forming an intermediate having a carbocation; (b) reacting the intermediate having the carbocation with acetic acid to form a dehalogenated organic polymer; and (c) crosslinking the dehalogenated organic polymer using a crosslinking reaction.

[0058] The at least one halogen-containing reactive group is generally a terminal group and the organic polymer may be any of those noted above, such as poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, poly(benzimidazole)s and polyaramids, and is preferably one having an aromatic group in the backbone chain of the polymer. In one embodiment, the organic polymer having the halogen-containing reactive group is poly(arylene ether) including polymer repeating units along its backbone having the following structure:

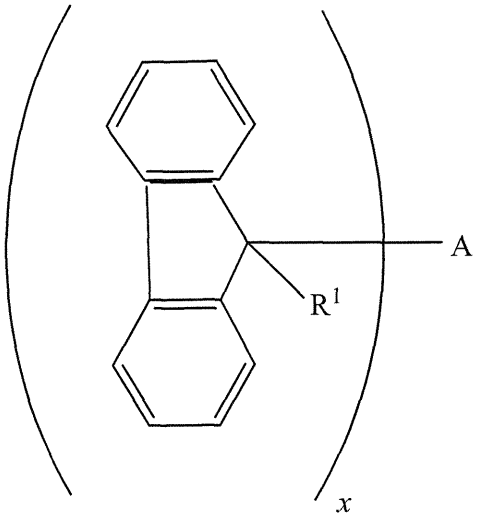
$$-(O-Ar^{1}-O-Ar^{2}-)_{m}\ (-O-Ar^{3}-O-Ar^{4}-)_{n}-$$

wherein Ar^{1}, Ar^{2}, Ar^{3} and Ar^{4} are identical or different aryl radicals, m = 0 to 1.0, and n = 1-m. In one embodiment, such an organic polymer is a poly(arylene ether), m is 1 and n is 0 and the polymer has repeating units along its backbone having the structure of formula (V):

CLAIMS

We claim:

1. A composition comprising a cross-linking compound and a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking compound has a structure according to formula (IV):

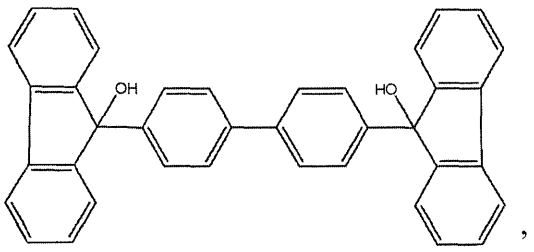


(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from the group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0,

wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer, which reactive intermediate oligomer is capable of cross-linking an organic polymer.

2. The composition according to claim 1, wherein the cross-linking compound has a structure selected from a group consisting of



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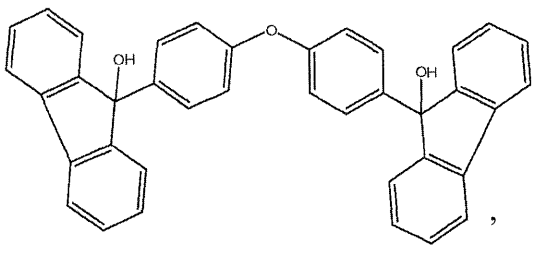

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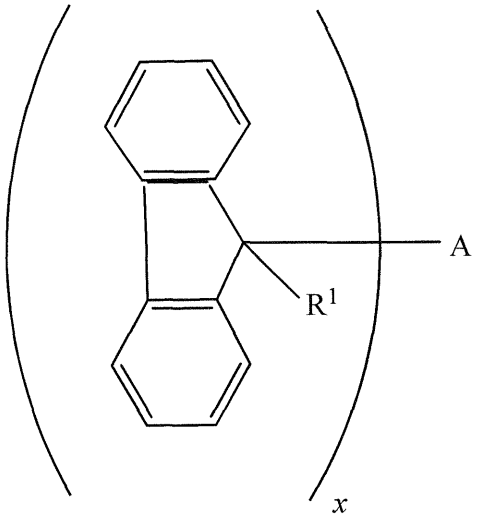


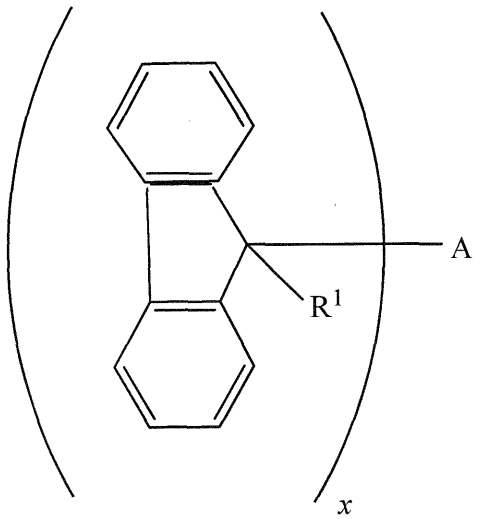
(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0, and a cross-linking reaction additive selected from an organic acid and/or an acetate compound.

25. A molded article formed from the composition of claim 24.

26. A method of controlling the cross-linking reaction rate of a cross-linking compound for use in cross-linking an organic polymer, comprising:

a) providing a cross-linking composition comprising a cross-linking compound and a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking compound has the structure according to formula (IV):



(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine ($-NH_2$), halide, ether, ester, or amide, and x is about 2.0 to about 6.0, wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer for cross-linking an organic polymer; and

b) heating the cross-linking composition such that oligomerization of the cross-linking compound occurs.

27. The method according to claim 26, wherein step (b) further comprises heating the cross-linking composition before heat molding.

28. The method according to claim 26, wherein the cross-linking reaction additive is an organic acid selected from glacial acetic acid, formic acid and/or benzoic acid, and/or an acetate compound selected from lithium acetate hydrate, sodium acetate, and/or potassium acetate, and salts and derivatives thereof.

29. The method according to claim 26, further comprising combining the cross-linking compound and the cross-linking reaction additive in solid form in step (a).

30. The method according to claim 26, further comprising combining the cross-linking compound and the cross-linking reaction additive in a solvent in step (a) and reacting the cross-linking compound and the cross-linking reaction additive to form a reactive oligomerized cross-linking compound.

31. The method according to claim 30, further comprising

(c) adding the reactive oligomerized cross-linking compound to an organic polymer to form a cross-linkable composition and

(d) cross-linking the organic polymer composition to form a cross-linked organic polymer.

32. The method according to claim 31, further comprising adding at least one additive in step (c).

33. The method according to claim 26, wherein the organic polymer is selected from poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, poly(benzimidazole)s and/or polyaramids.

34. The method according to claim 33, wherein the organic polymer is a poly(arylene ether) including polymer repeating units having the following structure:

$$(— O — Ar^1 — O — Ar^2 —)_m \ (— O — Ar^3 — O — Ar^4 —)_n$$

wherein Ar^1, Ar^2, Ar^3 and Ar^4 are identical or different aryl radicals, m = 0 to 1.0, n = 1-m.

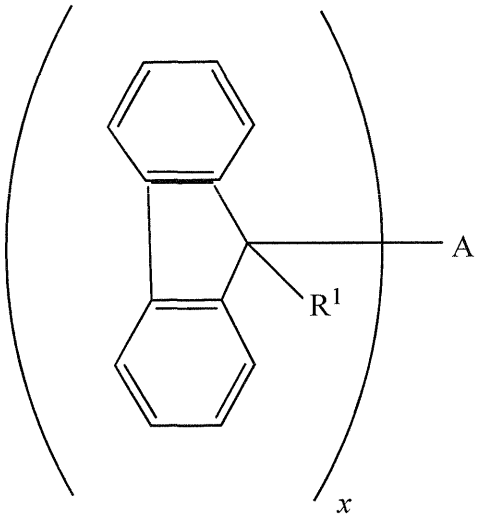
35. An organic polymer composition for use in forming a cross-linked organic polymer, comprising:

a dehalogenated organic polymer and

at least one cross-linking compound; wherein the dehalogenated organic polymer is formed by a process comprising reacting an organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break a bond between the organic polymer having the at least one halogen-containing reactive group and a halogen atom in the at least one halogen-containing reactive group to form an intermediate.

36. The organic polymer composition according to claim 35, wherein the dehalogenated organic polymer is a debrominated organic polymer.

37. The organic polymer composition according to claim 35, wherein the cross-linking compound has a structure according to formula (IV):



(IV)

wherein A is an arene moiety having a molecular weight of less than 10,000 g/mol, R^1 is selected from a group consisting of hydroxide (-OH), amine (-NH_2), halide, ether, ester, or amide, and x is about 2.0 to about 6.0.

38. The organic polymer composition according to claim 35, further comprising a cross-linking reaction additive selected from an organic acid and/or an acetate compound, wherein the cross-linking reaction additive is capable of reacting with the cross-linking compound to form a reactive intermediate in the form of an oligomer, which reactive intermediate oligomer is capable of cross-linking the dehalogenated organic polymer.

39. The organic polymer composition according to claim 35, wherein the dehalogenated organic polymer is a polymer selected from poly(arylene ether)s, polysulfones,

43. The organic polymer composition according to claim 35, wherein the dehalogenated organic polymer is formed by

reacting an organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break a bond between the organic polymer having the at least one halogen-containing reactive group and a halogen atom in the at least one halogen-containing reactive group, and to form an intermediate; and

reacting the intermediate with acetic acid to form the dehalogenated organic polymer.

44. The organic polymer composition according to claim 43, wherein the alkali metal compound is selected from the group consisting of R^3—M', wherein M' is an alkali metal and R^3 is H or a branched or straight chain organic group selected from alkyl, alkenyl, aryl and aralkyl groups of from 1 to about 30 carbon atoms having from 0 to about 10 ester or ether groups along or in a chain or structure of the group, and wherein R^3 may be substituted or unsubstituted.

45. The organic polymer composition according to claim 44, wherein the alkali metal compound is *t*-butyllithium.

46. The organic polymer composition according to claim 43, wherein the halogen-containing reactive group is a bromine-containing reactive group.

47. The organic polymer composition according to claim 43, wherein the organic polymer having at least one halogen-containing end group is reacted with the alkali metal compound in a solvent and the organic polymer having the at least one halogen-containing end group is dried prior to reacting in the solvent.

48. A molded article formed from the composition according to claim 35.

49. A method of controlling the cross-linking reaction rate of an organic polymer having at least one halogen-containing reactive group during a cross-linking reaction, comprising:

a) reacting the organic polymer having at least one halogen-containing reactive group with an alkali metal compound to break a bond between the organic polymer having the at least one halogen-containing reactive group and a halogen atom in the at least one halogen-containing reactive group, and to form an intermediate having a carbocation;

b) reacting the intermediate having the carbocation with acetic acid to form a dehalogenated organic polymer; and

c) crosslinking the dehalogenated organic polymer using a crosslinking reaction.

50. The method according to claim 49, wherein the at least one halogen-containing reactive group is a terminal group and the organic polymer having the at least one halogen-containing reactive group is a polymer selected from poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, poly(benzimidazole)s, and polyaramids.

51. The method according to claim 49, wherein the at least one halogen-containing reactive group is represented by $—R^4—(X)_p$, wherein R^4 is carbon or a branched or straight chain organic group selected from alkyl, alkenyl, aryl and aralkyl groups of from 1 to about 30 carbon atoms having from 0 to about 10 ester or ether groups along or in a chain or structure of the group, and wherein R^4 may be substituted or unsubstituted; and X is a halogen atom and p is an integer that is 1 or 2.

52. The method according to claim 49, wherein the alkali metal compound is selected from the group consisting of $R^3—M'$, wherein M' is an alkali metal and R^3 is H or a branched or straight chain organic group selected from alkyl, alkenyl, aryl and aralkyl groups of from 1 to about 30 carbon atoms having from 0 to about 10 ester or ether groups along or in a chain or structure of the group, and wherein R^3 may be substituted or unsubstituted.

53. The method according to claim 52, wherein the alkali metal compound is *t*-butyllithium.

54. The method according to claim 49, wherein the organic polymer having the at least one halogen-containing end group is reacted with the alkali metal compound in a solvent.

55. The method according to claim 54, wherein the solvent is capable of dissolving the organic polymer having the at least one halogen-containing reactive group and is free of functional groups that react with the halogen in the halogen-containing reactive group under reaction conditions for step (a).

56. The method according to claim 55, wherein the solvent is selected from a heptane, a hexane, tetrahydrofuran, and a diphenyl ether.

57. The method according to claim 54, wherein the organic polymer having the at least one halogen-containing end group is dried prior to reacting with the alkali metal compound in the solvent.