



(51) International Patent Classification:

A01N 43/713 (2006.01) C07C 2/42 (2006.01)
C07B 37/12 (2006.01)

(21) International Application Number:

PCT/US2017/025110

(22) International Filing Date:

30 March 2017 (30.03.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/317,050 1 April 2016 (01.04.2016) US

(71) Applicant: **THE ARIZONA BOARD OR REGENTS on behalf of THE UNIVERSITY OF ARIZONA** [US/US];
The University of Arizona, Tech Transfer Arizona, University Services Annex, 4th Floor, P.O. Box 210300A, Tucson, AZ 85721 (US).

(72) Inventors: **LOY, Douglas, A.**; The University of Arizona, 1306 E. University Blvd., P.O. Box 210041, Tucson, AZ 85721 (US). **BAGGE, Robb, E.**; The University of Arizona, 1306 E. University Blvd., P.O. Box 210041, Tucson, AZ 85721 (US).

(74) Agent: **NGUYEN, Quan**; Nguyen & Tarbet, 4199 Campus Drive, Suite 550, Irvine, CA 92612 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CYCLOADDITION POLYMERIZATION OF TETRAZINES TO AFFORD POLYARYLENE DERIVATIVES

(57) Abstract: Polyarylenes are attractive polymers that can exhibit improved mechanical and optical and improved chemical and thermal stability as compared to non-polyarylene organic polymers. Copolymerization of tetrazine monomers with diethynylarene co-monomers via a [4+2] cycloaddition reaction afforded high molecular weight polyphenylenes, polyarylenes or poly(biphenylenes). These materials can be used in fuel cells, batteries, gas separation, water purification, and chemical separation membranes.



CYCLOADDITION POLYMERIZATION OF TETRAZINES TO AFFORD POLYARYLENE DERIVATIVES

CROSS REFERENCE

[0001] This application claims priority to U.S. Patent Application No. 62/317,050, filed April 01, 2016, the specification(s) of which is/are incorporated herein in their entirety by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to methods of preparing polyarylenes, in particular, the cycloaddition polymerization of disubstituted tetrazines with dialkynylarene comonomers.

BACKGROUND OF THE INVENTION

[0003] Polyarylenes are attractive polymers that can exhibit exceptional mechanical and optical and superior chemical and thermal stability as compared to most organic polymers. This greater chemical stability makes these materials attractive for fuel cell, battery, gas separation, water purification, and chemical separation membranes. Unfortunately, preparation of polyarylenes, such as para-polyphenylene, is limited to oligomers due to the insolubility of the polymers from pi stacking and crystallization. Most of these polymers, such as Kevlar® and polybenzimidazole, can only be synthesized as fibers directly from a polymerization vat. This is due to the fact that the same high crystallinity and pi-stacking of the rings that make these materials thermally stable also make them insoluble in any solvent once they have been solidified or precipitated. Currently, it is not possible to thermally process these polymers to make structural materials, molded artifacts, or films.

[0004] To overcome this, substituted polyphenylenes have been prepared using noble metal catalyzed reactions or cycloaddition polymerizations. The presence of substituents permits these materials to be soluble and processable. For example, polyphenylenes, such as PrimoSpire® by Solvay, are commercially available polymers that are the strongest bulk, non-fiber polymers made to date. PrimoSpire® polymers are synthesized via a platinum catalyzed Suzuki polymerization of monomers with bulky substituents designed to keep the polymers soluble and processable by blocking

crystallization and pi-stacking. This route is expensive due to its use of platinum catalysts and complicated monomers.

[0005] Polymerizations involving [4+2] cycloadditions are particularly attractive for making polyarylenes, however, the monomers, such as bis-cyclopentadienone or bis-alpha-pyrones, are often difficult to synthesize. For example, polyarylenes prepared by Diels-Alder cycloaddition polymerization of bis-cyclopentadienone monomers with bis-acetylene comonomers has been widely used in research and is used commercially to make low-k dielectric coatings for computer chips. However, bis-cyclopentadienone monomers are expensive to make and further requires a large number of phenyl groups on each cyclopentadienone ring to prevent the monomer from undergoing cycloaddition with another cyclopentadienone prior to mixing with another co-monomer and forming undesirable materials. Hence, there exist a need for new methods of preparing high molecular weight polyarylenes from relatively inexpensive precursors that allows for control over the type and number of substituents.

SUMMARY OF THE INVENTION

[0006] The present invention features methods of synthesizing polyarylenes by the cycloaddition polymerization of disubstituted tetrazines with dialkynylarene comonomers bearing alkyne and pyridazine groups, as specified in the independent claims. Embodiments of the invention are given in the dependent claims. Embodiments of the present invention can be freely combined with each other if they are not mutually exclusive.

[0007] In one embodiment, the present invention features a method of producing a polyarylene compound. The method may comprise polymerizing a plurality of tetrazine monomers with a plurality of alkynyl comonomers. Without wishing to limit the invention to a particular theory or mechanism, a tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the alkynyl comonomers to undergo a double [4+2] cycloaddition reaction, thereby producing the polyarylene compound.

[0008] In another embodiment, the present invention features a polyarylene compound prepared from a plurality of tetrazine monomers and a plurality of alkynyl comonomers. A tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the

alkynyl comonomers to undergo a double [4+2] cycloaddition reaction to produce the polyarylene compound.

[0009] The inventors have surprisingly discovered that tetrazines can serve as a bis-diene equivalent in cycloaddition polymerizations with bis-dienophiles, such as bis-alkyne comonomers, without concern of self-condensation. This is the first report of successfully polymerizing tetrazines via cycloaddition polymerizations. Without wishing to limit the invention to any theory or mechanism, it is believed that the technical feature of the present invention advantageously provides for a less expensive method for synthesizing substituted polyarylenes. None of the presently known prior references or work has the unique inventive technical feature of the present invention.

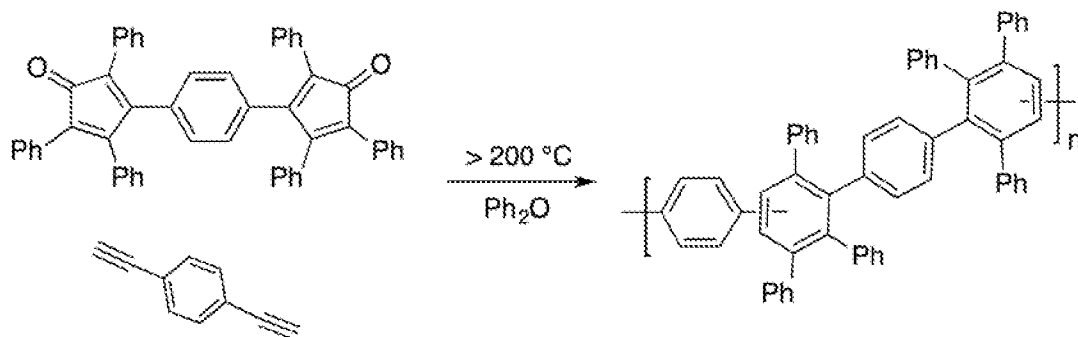
[0010] Any feature or combination of features described herein are included within the scope of the present invention provided that the features included in any such combination are not mutually inconsistent as will be apparent from the context, this specification, and the knowledge of one of ordinary skill in the art. Additional advantages and aspects of the present invention are apparent in the following detailed description and claims.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0011] As known to one of ordinary skill in the art, a polyarylene is a molecule comprising primarily of a plurality of phenyl groups covalently linked together. As used herein, a polyarylene compound or polyarylene polymer is defined as a polymer having a polyarylene backbone. In some embodiments, the polyarylene backbone may have other substituents or functional groups linked thereto.

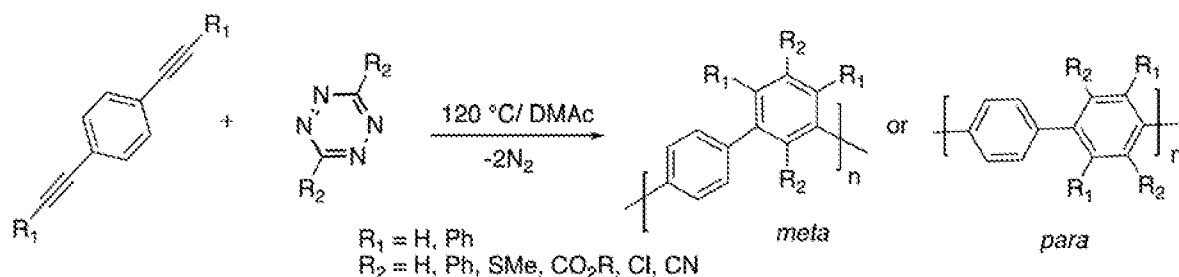
[0012] As previously described, biscyclopentadienone monomers must have a plurality of aryl groups, e.g. four aryl groups, on each cyclopentadienone ring in order to synthesize polyarylenes by Diels Alder cycloaddition polymerization. A reaction schematic thereof is shown in Scheme 1.

[0013] Scheme 1. Cycloaddition polymerization of bis-cyclopentadienones.



[0014] In preferred embodiments of the present invention, the 1,2,4,5-tetrazines can be relatively easy to prepare from organic nitriles or guanidine and hydrazine. Furthermore, the tetrazines may be prepared with substituents at the 3 and 6 positions, such as organic groups (through C-C bonds), halides, amines, thiol ethers, and ethers. The result of these monomers copolymerizing with diethynylbenzene affords 3,6-disubstituted poly(biphenylenes), as shown in Scheme 2. Additional substituents can be incorporated into the second aromatic ring using disubstituted alkynes in the dialkynyl comonomer.

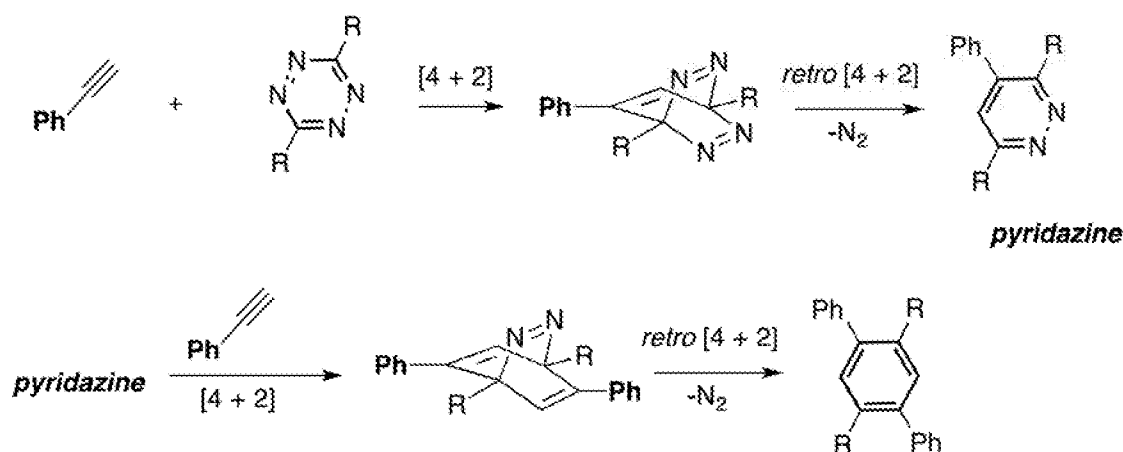
[0015] Scheme 2. Cycloaddition polymerization of tetrazine with bis-alkynyl comonomers.



[0016] Without wishing to limit the invention to a particular theory or mechanism, the polymerizations involve a cycloaddition reaction of the tetrazine to afford a bicyclic cycloadduct that subsequently loses a molecule of nitrogen gas in a retro [4+2] cycloaddition reaction, also called a cheletropic elimination. The result is a pyridazine group with two nitrogen atoms in the aromatic ring and a pendant aryl group with another ethynyl group. The pyridazine group can also undergo a cycloaddition reaction with an ethynyl group to afford a bicyclic cycloadduct that loses a second equivalent of nitrogen via the cheletropic elimination. Scheme 3 illustrates this reaction mechanism. In reactions of tetrazines with diethynyl arenes, these cycloadditions lead to the

formation of linear macromolecules. To the inventor's knowledge, this is the first time that the cycloaddition polymerization of tetrazines has been observed and used to afford polyarylenes of any sort.

[0017] Scheme 3. A non-limiting example of the cycloaddition mechanism of the present invention.

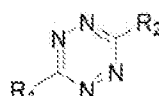


[0018] Without wishing to limit the invention to a particular theory or mechanism, the variety of different functional groups that can be incorporated at the 3 and 6 positions allows an unprecedented range of new polyarylenes or polybiphenylenes to be prepared. In contrast to the bis-pyrone and bis-cyclopentadienone monomer, many more tetrazines can also be prepared. For example, 3,6-dichlorotetrazine can be converted into amine, ether, or thioether derivatives. Many of these functional groups allow the polymers to be further modified to afford polyphenylene electrolytes, water soluble polymers, fluorescent polymers, or UV absorbing polymers with the strength and stability of the aromatic backbone. In some embodiments, these materials may be used in light emitting diodes or photovoltaic applications. Modifications to the nature of the dialkynylarene can also allow for tuning of the level of substitution, substitution geometry, and backbone configuration. For example, 4,4'-diethynylbiphenyl can result in 3,6-disubstituted polyterphenylenes.

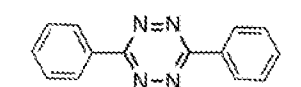
[0019] According to some embodiments, the present invention features a method of producing a polyarylene compound. The method may comprise polymerizing a plurality of tetrazine monomers with a plurality of alkynyl comonomers. In one embodiment, a tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the

alkynyl comonomers to undergo a double [4+2] cycloaddition reaction, thereby producing the polyarylene compound. Without wishing to limit the invention to a particular theory or mechanism, the method is effective for producing the polyarylene compound that exhibits improved mechanical and optical properties, and improved chemical and thermal stability, as compared to non-polyarylene polymers.

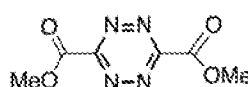
[0020] In one embodiment, each tetrazine monomer may be according to the following:



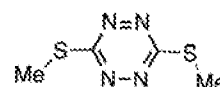
where R_1 and R_2 are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, or alkene ether. In another embodiment, the tetrazine monomers are selected from a group consisting of the following:



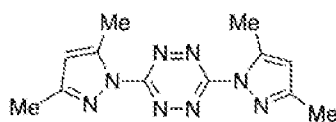
3,6-diphenyl-1,2,4,5-tetrazine



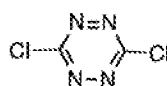
dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate



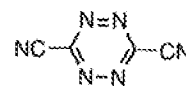
3,6-bis(methylthio)-1,2,4,5-tetrazine



3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine

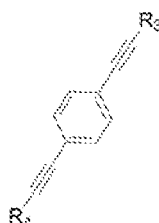


3,6-dichloro-1,2,4,5-tetrazine



1,2,4,5-tetrazine-3,6-dicarbonitrile

[0021] In one embodiment, each alkynyl comonomer may comprise one alkynyl moiety, and each tetrazine monomer can react with two alkynyl comonomers to undergo the double [4+2] cycloaddition reaction. In another embodiment, each alkynyl comonomer may be a bis-alkyne comonomer, and each tetrazine monomer can react with the bis-alkyne comonomer to undergo the double [4+2] cycloaddition reaction. In yet another embodiment, the alkynyl comonomers may be alkynylarene comonomers or dialkynylarene comonomers. Examples of the alkynylarene comonomers include, but are not limited to, phenylacetylene comonomers. In a further embodiment, the dialkynylarene comonomers are according to the following structure:

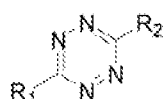


where R_3 and R_4 are each a hydrogen, trimethylsilyl, or phenyl. Examples of the dialkynylarene comonomers include, but are not limited to, 1,4-diethynylbenzene, 1,3-diethynylbenzene, 1,4-bis(trimethylsilyl ethynyl)benzene, or 1,4-di(phenylethynyl)-benzene comonomers.

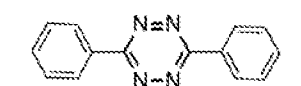
[0022] In some embodiments, the method of making a polyarylene compound may comprise adding a tetrazine monomer as a diene of a Diels-Alder reaction in a reaction vessel, and adding an alkynyl comonomer as a dienophile of the Diels-Alder reaction in the same reaction vessel. The mixture is then mixed to generate the polyarylene compound.

[0023] According to another embodiment, the present invention features a polyarylene compound prepared from a plurality of tetrazine monomers and a plurality of alkynyl comonomers. Without wishing to limit the invention to a particular theory or mechanism, a tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the alkynyl comonomers to undergo a double [4+2] cycloaddition reaction to produce the polyarylene compound. In preferred embodiments, the polyarylene compound exhibits improved mechanical and optical properties, and improved chemical and thermal stability, as compared to non-polyarylene polymers.

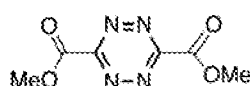
[0024] In some embodiments, each tetrazine monomer may be according to the following:



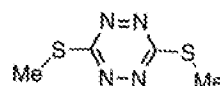
where R_1 and R_2 are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, nitrile, or alkene ether. In other embodiments, the tetrazine monomers are selected from a group consisting of the following:



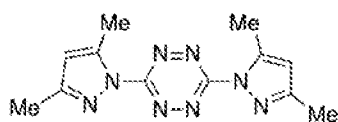
3,6-diphenyl-1,2,4,5-tetrazine



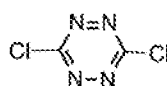
dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate



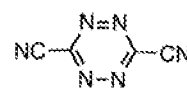
3,6-bis(methylthio)-1,2,4,5-tetrazine



3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine

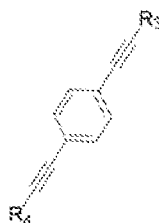


3,6-dichloro-1,2,4,5-tetrazine



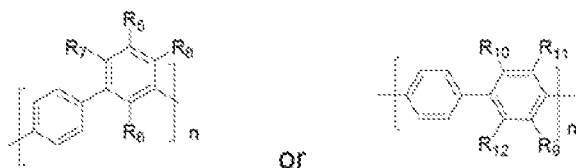
1,2,4,5-tetrazine-3,6-dicarbonitrile

[0025] In some embodiments, each alkynyl comonomer may comprise one alkynyl moiety, and each tetrazine monomer can react with two alkynyl comonomers to undergo the double [4+2] cycloaddition reaction. In other embodiments, each alkynyl comonomer may be a bis-alkyne comonomer, and each tetrazine monomer can react with the bis-alkyne comonomer to undergo the double [4+2] cycloaddition reaction. In still other embodiments, the alkynyl comonomers may be alkynylarene comonomers or dialkynylarene comonomers. Examples of the alkynylarene comonomers include, but are not limited to, phenylacetylene comonomers. In further embodiments, the dialkynylarene comonomers are according to the following structure:



where R_3 and R_4 are each a hydrogen, trimethylsilyl, or phenyl. Examples of the dialkynylarene comonomers include, but are not limited to, 1,4-diethynylbenzene, 1,3-diethynylbenzene, 1,4 bis(trimethylsilyl ethynyl)benzene, or 1,4-di(phenylethynyl)-benzene comonomers.

[0026] According to another embodiment, the present invention features a mixture of regioisomers of a polyarylene compound. In some embodiments, the regioisomers are according to the following structures:



where R_5 , R_6 , R_9 , and R_{10} are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, nitrile, or alkene ether, where R_7 , R_8 , R_{11} , and R_{12} are each a hydrogen or aryl, and where $m = 5-10,000$ and $n = 5-10,000$. In preferred embodiments, the mixture of regioisomers is effective for increasing a solubility of the polyarylene compound.

[0027] In one embodiment, at least two equivalent of nitrogen gas is produced during the reaction of a tetrazine component and a bisalkynyl component for every equivalent of tetrazine used. In the present invention, a carbon dioxide gas is not produced during the

reaction of a tetrazine component and a bisalkynyl component. Therefore, the polymer material formed by the reaction of a tetrazine component and a bisalkynyl component can be considered a greener material.

[0028] In some embodiments, the regiochemistry of the cycloaddition polymerization may nominally give a mixture of para and meta isomeric linkages in the polymer backbone. This can undoubtedly make these materials more soluble than a strictly para regiopolymer. In preferred embodiments, a mixture of two regioisomers of the polyarylene backbone is produced. For example, the mixture may comprise a meta-polyarylene backbone and a para-polyarylene backbone, which increase the solubility of the polyarylene polymers. In further embodiments, the present invention allows for the ability control the cycloadditions to allow block, triblock, star polymers, branched and thermoset polyarylenes to be prepared.

[0029] In some embodiments, the cycloaddition reaction to synthesize the polyarylenes may be conducted in polar aprotic or organic solvents. In other embodiments, the reaction may be performed at a wide range of temperatures. For example, the temperature can be as low as 120°C or as high as 240°C.

[0030] In one embodiment, the cycloaddition reaction is performed at ambient pressures. In another embodiment, the reaction is performed at higher pressures, such as, for example, about 0.7 to 2 GPa. Without wishing to limit the invention to a particular theory or mechanism, the cycloaddition reaction may be accelerated by orders of magnitude with the application of high pressure (> 0.7 GPa). In one embodiment, the synthesis of the polyarylene material may be conducted in a high pressure reactor.

[0031] In a preferred embodiment, the polyarenes can be prepared to have molecular weights greater than 1 MegaDalton (10^6 g/mole). In more preferred embodiments, the resulting polymers may be soluble and processable into films and fibers. In still other embodiments, the polyarylene polymer may be a foam. For example, the polymer may be a thermoset foam where molten precursors are mixed and the reaction increases the molecular weight and generates nitrogen to foam the growing and hardening polymer. Small amounts of tri-ethynyl precursors may also be used to crosslink the foam. Without wishing to limit the invention to a particular theory or mechanism, the polyarylene

material can have improved mechanical and optical properties and improved chemical and thermal stability, as compared to non-polyarylene organic polymers.

[0032] According to some embodiment, the present invention may be utilized as an inexpensive material in applications including, but not limited to, high strength fibers, self-reinforced structural polymers, membranes for chemical, gas and water purification, OLED, and photovoltaics.

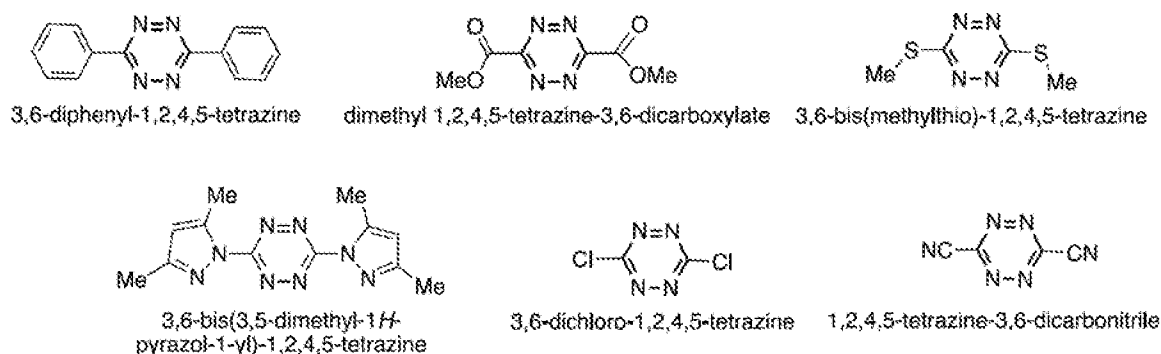
[0033] EXAMPLES

[0034] The following are non-limiting examples of preparing the polymer material of the present invention. Equivalents or substitutes are within the scope of the invention

[0035] EXAMPLE 1

[0036] In one embodiment, 1,2,4,5-tetrazines were prepared from benzonitrile and hydrazine for 3,6-diphenyl-1,2,4,5-tetrazine. In another embodiment, dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate was prepared from glycine ethyl ester hydrochloride. In still another embodiment, 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine was prepared from guanidine and hydrazine. In yet another embodiment, dichlorotetrazine was prepared from 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine. In a further embodiment, 3,6-bis(methylthio)-1,2,4,5-tetrazine was prepared from 3,6-dichloro-1,2,4,5-tetrazine. In yet a further embodiment, the 1,2,4,5-tetrazine-3,6-dicarbonitrile was prepared in two steps from dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate.

[0037] Scheme 4. Non-limiting examples of 1,2,4,5-tetrazines



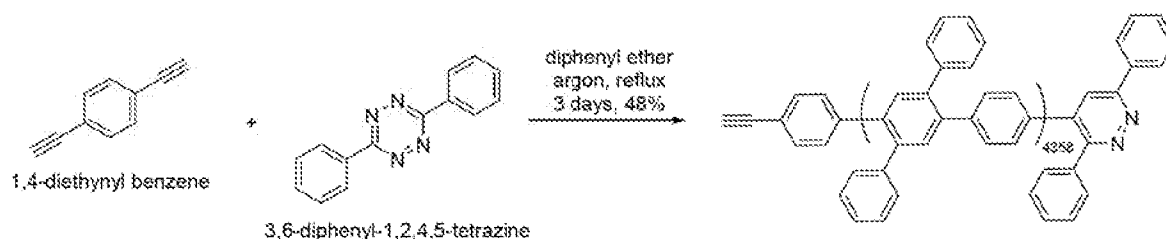
[0038] EXAMPLE 2

[0039] Commercial 1,4-diethynylbenzene, 1,3-diethynylbenzene, 1,4 bis(trimethylsilyl ethynyl)benzene, and 1,4-di(phenylethynyl)benzene were purified by sublimation before

polymerizing. The polymerizations are carried out under inert atmosphere in polar aprotic or aryl ether solvents.

[0040] Referring to Scheme 5, a 10 mL 14/20 one-neck round bottom flask was equipped with a magnetic stir before the addition of diethynyl benzene (0.126 g, 9.99×10^{-4} mol), 3,6-diphenyl-1,2,4,5-tetrazine (0.234 g, 9.99×10^{-4} mol), and diphenyl ether (3 mL). The system was set up for reflux then degassed and placed under positive pressure with argon before being heated to reflux. At this point the solution was dark purple and contained undissolved white particles of diethynyl benzene. As the reaction was heated to reflux, the diethynyl benzene dissolved creating a dark purple homogenous solution. The reaction was refluxed for 3 days after which the solution had changed to a transparent light yellow color, and a brown precipitate had formed. The reaction was cooled, and then the solution was poured into 30 mL of 1:1 acetone and hexanes to precipitate any remaining polymer. The brown precipitate was collected with vacuum filtration and rinsed with acetone before being dried under high vacuum giving a final yield of 0.145 g, 47.7% conversion. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.60-8.00 (s br, 4 H), 8.00-6.60 (s br, 14 H), **FT-IR** (KBr): cm^{-1} = 3426.22, 3055.67, 3029.84, 2919.99, 2850.82, 1677.54, 1634.83, 1601.79, 1583.28, 1569.16, 1487.98, 1442.99, 1389.07, 1311.16, 1234.45, 1178.97, 1156.73, 1107.52, 1074.80, 1021.46, 909.35, 837.91, 800.56, 766.92, 694.78, 631.95, 586.68, 521.94, 459.49 **GPC (polystyrene standards):** M_n 657,000 (Da), M_w 1,327,000 (Da), PDI = 2.0.

[0041] Scheme 5. Polymerization of diethynylbenzene with 3,6-diphenyltetrazine.



[0042] As used herein, the term "about" refers to plus or minus 10% of the referenced number.

[0043] Various modifications of the invention, in addition to those described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims. Each reference cited

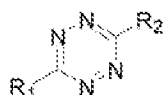
in the present application is incorporated herein by reference in its entirety.

[0044] Although there has been shown and described the preferred embodiment of the present invention, it will be readily apparent to those skilled in the art that modifications may be made thereto which do not exceed the scope of the appended claims. Therefore, the scope of the invention is only to be limited by the following claims. Reference numbers recited in the claims are exemplary and for ease of review by the patent office only, and are not limiting in any way. In some embodiments, the figures presented in this patent application are drawn to scale, including the angles, ratios of dimensions, etc. In some embodiments, the figures are representative only and the claims are not limited by the dimensions of the figures. In some embodiments, descriptions of the inventions described herein using the phrase "comprising" includes embodiments that could be described as "consisting of", and as such the written description requirement for claiming one or more embodiments of the present invention using the phrase "consisting of" is met.

WHAT IS CLAIMED IS:

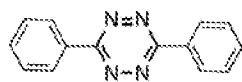
1. A method of producing a polyarylene compound, the method comprising polymerizing a plurality of tetrazine monomers with a plurality of alkynyl comonomers, wherein a tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the alkynyl comonomers to undergo a double [4+2] cycloaddition reaction, thereby producing the polyarylene compound.

2. The method of claim 1, wherein each tetrazine monomer is according to the following:

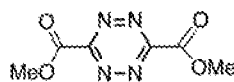


wherein R_1 and R_2 are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, nitrile, or alkene ether.

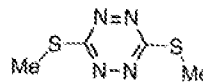
3. The method of claim 1, wherein the tetrazine monomers are selected from a group consisting of the following:



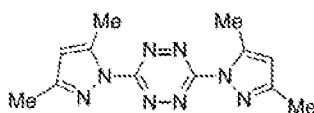
3,6-diphenyl-1,2,4,5-tetrazine



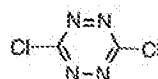
dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate



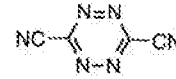
3,6-bis(methylthio)-1,2,4,5-tetrazine



3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine



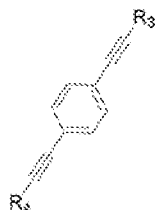
3,6-dichloro-1,2,4,5-tetrazine



1,2,4,5-tetrazine-3,6-dicarbonitrile

4. The method of claim 1, wherein each alkynyl comonomer comprises one alkynyl moiety.
5. The method of claim 4, wherein each tetrazine monomer reacts with two alkynyl comonomers to undergo the double [4+2] cycloaddition reaction.
6. The method of claim 1, wherein each alkynyl comonomer is a bis-alkyne comonomer.
7. The method of claim 6, wherein each tetrazine monomer reacts with the bis-alkyne comonomer to undergo the double [4+2] cycloaddition reaction.

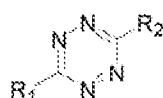
8. The method of claim 1, wherein the alkynyl comonomers are alkynylarene comonomers or dialkynylarene comonomers.
9. The method of claim 8, wherein the alkynylarene comonomers are phenylacetylene comonomers.
10. The method of claim 8, wherein the dialkynylarene comonomers are according to the following structure:



wherein R₃ and R₄ are each a hydrogen, trimethylsilyl, or phenyl.

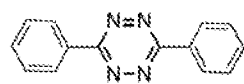
11. The method of claim 8, wherein the dialkynylarene comonomers are 1,4-diethynylbenzene, 1,3-diethynylbenzene, 1,4 bis(trimethylsilyl ethynyl)benzene, or 1,4-di(phenylethynyl)benzene comonomers.
12. The method of claim 1, wherein the method is effective for producing the polyarylene compound that exhibits improved mechanical and optical properties, and improved chemical and thermal stability, as compared to non-polyarylene polymers.
13. The method of claim 1, wherein the cycloaddition reaction produces a mixture of regioisomers of the polyarylene compound.
14. The method of claim 13, wherein the mixture of regioisomers comprises a meta-polyarylene backbone and a para-polyarylene backbone.
15. The method of claim 13, wherein the mixture of regioisomers increases a solubility of the polyarylene compound.
16. The method of claim 1, wherein the polyarylene compound is formed into a foam, film, or fiber.

17. The method of claim 1, wherein the method is performed at a temperature ranging from about 120°C to 240°C.
18. The method of claim 1, wherein the method is performed at ambient pressure.
19. The method of claim 1, wherein the method is performed at a pressure greater than about 0.7 GPa.
20. The method of claim 1, wherein the method is performed at a pressure ranging from about 104 kPa to 2 GPa.
21. The method of claim 1, wherein the polyarylene compound has molecular weight greater than about 1 MegaDalton.
22. A polyarylene compound prepared from a plurality of tetrazine monomers and a plurality of alkynyl comonomers, wherein a tetrazine moiety of each tetrazine monomer reacts with two alkynyl moieties of the alkynyl comonomers to undergo a double [4+2] cycloaddition reaction to produce the polyarylene compound.
23. The polyarylene compound of claim 22, wherein each tetrazine monomer is according to the following:

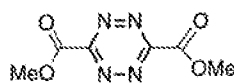


wherein R_1 and R_2 are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, nitrile, or alkene ether.

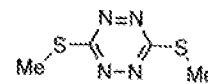
24. The polyarylene compound of claim 22, wherein the tetrazine monomers are selected from a group consisting of the following:



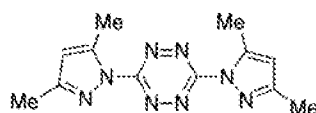
3,6-diphenyl-1,2,4,5-tetrazine



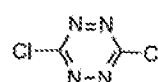
dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate



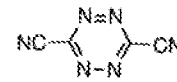
3,6-bis(methylthio)-1,2,4,5-tetrazine



3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine

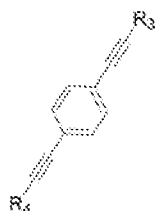


3,6-dichloro-1,2,4,5-tetrazine



1,2,4,5-tetrazine-3,6-dicarbonitrile

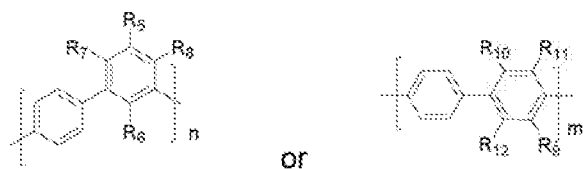
25. The polyarylene compound of claim 22, wherein each alkynyl comonomer comprises one alkynyl moiety.
26. The polyarylene compound of claim 25, wherein each tetrazine monomer reacts with two alkynyl comonomers to undergo the double [4+2] cycloaddition reaction.
27. The polyarylene compound of claim 22, wherein each alkynyl comonomer is a bis-alkyne comonomer.
28. The polyarylene compound of claim 27, wherein each tetrazine monomer reacts with the bis-alkyne comonomer to undergo the double [4+2] cycloaddition reaction.
29. The polyarylene compound of claim 22, wherein the alkynyl comonomers are alkynylarene comonomers or dialkynylarene comonomers.
30. The polyarylene compound of claim 29, wherein the alkynylarene comonomers are phenylacetylene comonomers.
31. The polyarylene compound of claim 29, wherein the dialkynylarene comonomers are according to the following structure:



wherein R₃ and R₄ are each a hydrogen, trimethylsilyl, or phenyl.

32. The polyarylene compound of claim 29, wherein the dialkynylarene comonomers are 1,4-diethynylbenzene, 1,3-diethynylbenzene, 1,4 bis(trimethylsilyl ethynyl)benzene, or 1,4-di(phenylethynyl)benzene comonomers.
33. The polyarylene compound of claim 22, wherein the polyarylene compound exhibits improved mechanical and optical properties, and improved chemical and thermal stability, as compared to non-polyarylene polymers.

34. The polyarylene compound of claim 22, wherein the cycloaddition reaction produces a mixture of regioisomers of the polyarylene compound.
35. The polyarylene compound of claim 34, wherein the mixture of regioisomers comprises a meta-polyarylene backbone and a para-polyarylene backbone.
36. The polyarylene compound of claim 34, wherein the mixture of regioisomers increases a solubility of the polyarylene compound.
37. The polyarylene compound of claim 22, wherein the polyarylene compound is formed into a foam, film, or fiber.
38. The polyarylene compound of claim 22, wherein the polyarylene compound has a molecular weight greater than about 1 MegaDalton.
39. A method of making a polyarylene compound, said method comprising:
- adding, to a reaction vessel, a plurality of tetrazine monomers as a diene of a Diels-Alder reaction;
 - adding a plurality of alkynyl comonomers as a dienophile of the Diels-Alder reaction to the same reaction vessel; and
 - mixing the tetrazine monomers and the alkynyl comonomers, thereby generating the polyarylene compound.
40. A mixture of regioisomers of a polyarylene compound, wherein the regioisomers are according to the following structures:



wherein R_5 , R_6 , R_9 , and R_{10} are each a halide, thiol, ester, carboxylate, amine, ether, thioether, heteroaromatic, phenyl, alkyl, nitrile, or alkene ether,

wherein R_7 , R_8 , R_{11} , and R_{12} are each a hydrogen or aryl, and

wherein $m = 5-10,000$ and $n = 5-10,000$.

41. The mixture of claim 41, wherein the mixture of regioisomers is effective for increasing a solubility of the polyarylene compound.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/25110

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A01N 43/713; C07B 37/12; C07C 2/42 (2017.01)

CPC - A01N 43/713; C07B 37/12; C07C 2/42

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0264544 A1 (LOY, DA) 22 October 2009; abstract; paragraphs [0022], [0027], [0030]-[0031], [0034], [0032], [0043], [0051], [0055], [0060], [0062], [0064]; claim 7	1-11, 13-18, 20, 22-32, 34-37, 39-41
---		---
Y		12, 19, 21, 33, 38
Y	KANG, JW et al. Low-Loss Fluorinated Poly(Arylene Ether Sulfide) Waveguides with High Thermal Stability. Journal of Lightwave Technology, Vol. 19, No. 6, June 2001, pp. 872-875; abstract; page 872, column 1, paragraph 2	12, 33
Y	WO 2015/121336 A1 (ETH ZURICH) 20 August 2015; abstract; page 15, lines 5-10	19
Y	US 2009/0253015 A1 (ONODERA, T et al) 8 October 2009; paragraph [0053]	21, 38

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

26 May 2017 (26.05.2017)

Date of mailing of the international search report

22 JUN 2017

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774