HYGROMORPHIC POLYMERS AND COPOLYMERS HAVING HUMIDITY-DRIVEN MOTILITY

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ABSTRACT

New diamine monomers bearing sulfone terminated pendant groups, as well as methods for making the same, are provided. The diamine monomers are useful toward making polyamide, polyimide, and poly(amide-imide) polymers and copolymers, which possess hygromorphic properties and demonstrate driven motility.

7 Claims, 16 Drawing Sheets
References Cited

OTHER PUBLICATIONS


* cited by examiner
FIG. 1
(1-x) \text{H}_2\text{N} \quad \text{NH}_2 \\
\text{O} \quad \text{W} \\
\text{SO}_2\text{R}^2 \\
\text{4a-d} \\
\text{W} = \text{O}, \text{NH}, \text{NMe}, \text{NPh}

\text{+} \\
(x) \text{Ar} \quad \text{CO}_2\text{H} \\
\text{5} \\
\quad \text{Ar} \quad \text{NH}_2 \\
\text{10}

\text{Chemical imidization or Thermal imidization}

\text{W} = \text{O}, \text{NH}, \text{NMe}, \text{NPh}

\text{Ar} \text{ is but not limited to}

\begin{align*}
\text{a. BPADA} \\
\text{b. 6F-BPADA} \\
\text{c. 6FDA} \\
\text{d. DSDA} \\
\text{e. BTDA}
\end{align*}

\text{FIG. 3}
\[
\begin{align*}
H_2N & \quad \text{R} \quad \text{NH}_2 \\
R = \text{H} (9), \text{CO}_2\text{H} (10) & \quad \text{5} \\
\text{(i) NMP, r.t., N}_2 & \\
\text{Solution Thermal Imidization (ST):} & \\
\text{(ii) NMP, 200 °C} & \\
\text{(iii) precipitation in EtOH} & \\
\text{Thermal Imidization (T1):} & \\
\text{(ii) cast film;} & \\
\text{solid-state cure at} & \\
\text{250°C} & \\
\text{Chemical Imidization (SC):} & \\
\text{(ii) Ac}_2\text{O/pyridine, NMP} & \\
\text{(iii) precipitation in EtOH} & \\
\text{R = H (12), CO}_2\text{H (13)} & \\
\text{R = H (14), CO}_2\text{H (15)} & \\
\\frac{\text{Ar}}{= & \\
\mathbf{a. BPADA} & \\
\mathbf{c. 6FDA} & \\
\end{align*}
\]
FIG. 6A
FIG. 6B
FIG. 6C
FIG. 7
FIG. 8
FIGS. 9a and 9b
FIG. 10
FIGS. 14a and 14b
HYGROMORPHIC POLYMERS AND COPOLYMERS HAVING HUMIDITY-DRIVEN MOTILITY

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional Patent Application Ser. No. 62/306,695 entitled “Polymers and Thermally Derived Copolymers with Hygromorphic Effect and Humidity-Driven Motility”, which was filed on Mar. 11, 2016 and is incorporated herein by reference in its entirety.

RIGHTS OF THE GOVERNMENT

The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purposes without the payment of any royalty.

FIELD OF THE INVENTION

The invention generally relates to hygromorphic polymers and copolymers. More particularly, the invention relates to polymide, polyamide, and poly(amide-imide) polymers and copolymers containing ester-sulfone and/or amide-sulfone as pendant chains, which demonstrate hygromorphic- and humidity-driven motility properties, and methods of making the same.

BACKGROUND

An actuator is a mechanical device that is powered by a certain source of energy, such as electric current, pressure and chemical energy, and can transform that energy into motion. According to the energy source utilized for actuation, responsive polymeric materials generally can be divided into three classes: electro-active polymers; light- or heat-responsive elastomers; and pH- or solvent-responsive gels.

Technologically, an actuator with controlled and directed motions upon application of a stimulus is particularly attractive because such a device could mimic organisms, and has numerous applications ranging from sensors, switches, and artificial muscles to nano/micro electromechanical systems. In a specific area, the actuation and power-generation systems that can harvest ambient energy from water gradients have recently attracted a great deal of attention, especially in the development of “dry” or liquid-free polymer actuators based on conducting polymers (CP) such as polypyrroles (PPy), polyanilines, and polythiophenes (PANI) as well as their composite systems. Thus, high hydrophilicity of the doped state, as well as the stress-strain generated from movement of water molecules directed by humidity variation, are being exploited.

For example, the doped PPy film containing perchlorate counter-ions would undergo rapid bending upon asymmetric water-vapor sorption, and would crawl on a wet filter paper, culminating in the design of a soft motor capable of directly transducing chemical potential of water sorption into a continuous circular motion, and origami (folded PPy film) actuators. Furthermore, the doped PPy film would contract in air under an applied voltage, thus generating Joule heating to desorb water molecules and providing an electromechanical control of the device.

In an alternative design in which semi-solid polyelectrolyte had been used, a polymer composite film based on polypyrrole-polyolborate (Ppy-POB) was shown to spontaneously and reversibly capture and release the ambient water vapor to induce film expansion and contraction, resulting in rapid and continuous locomotion on a wet surface. The Ppy-POB machine was strong and powerful enough to lift objects 380 times heavier than itself, and transport cargo 10 times heavier than itself.

Another version of dry CP-actuators based on a polythiophene, viz. commercially available poly(3,4-ethylenedioxythiophene)/poly styrenesulfonate (PEDOT:PSS), has been fabricated, wherein a nontraditional bilayer design with a collective capillarity feature to create the effect of asymmetric water diffusion. This PEDOT:PSS composite material is comprised of doped polyaniline (PANI) nanotubes chemically synthesized in-situ and embedded in a polycarbonate membrane, with one end of the nanotubes attached to a subsequently surface-deposited PANI layer. The so-called “nanotubes embedded membrane” (NEM) showed water diffusion behavior quite similar to those observed for biological ion channels and pumps, and displayed excellent moisture-propelled oscillatory motion, and artificial-muscle capability.

From the standpoint of dielectric materials, innovative approaches to humidity-driven actuation take advantage of the stress-strain generated from the orientational change in liquid-crystalline polymers (LCP) and networks (LCN) containing moieties (e.g. OH and COOH) that are sensitive to polar solvent vapors. As hytropic or thermotropic LCP, cellulose derivatives, such as partially hydroxypropylated cellulose (HPC) and partially methylated cellulose stearoyl ester (CSE) may have networks with solid-state properties similar to LCPE and LCN. Their solution-cast films are hygroscopic and have been shown to be promising materials in the development of humidity-powered, soft motors.

Building on a hygroscopic and mechanically robust liquid crystal network (LCN) polymer containing COOH groups that are capable of reversible hydrogen-bonding and become hydrophilic after alkaline treatment, another family of humidity actuators has been created. These new humidity-driven actuators may be in monolithic form or in bilayer configuration with a uniaxially oriented polyamide-6 substrate, and having large responses to humidity change as manifested in bending, folding, and curling motions. Bilayer actuators based on alternating layer-by-layer deposition of polycation/poly(anion) films on hydrophobic polymer substrates and engineered to power devices capable of unidirectional and humidity-controllable locomotion on a ratchet track have also been described.

While the above-mentioned examples for humidity-driven actuators have illustrated several innovative bilayer designs and clever utilization of responsive polymeric and nanocomposite systems, it appears that no simple, wholly covalent polymer in monolithic form with hygromorphic and motile properties has been reported. Accordingly there is a need for new polymers and copolymers with hygromorphic and motile properties, as well as new methods for making them.

SUMMARY OF THE INVENTION

New dianime monomers bearing sulfone-terminated pendant groups, as well as methods for making same, are provided. The dianime monomer is useful toward making polyamide, polyimide, and poly(amide-imide) polymers and copolymers, which possess hygromorphic properties and demonstrate humidity driven motility.
Thus, in accordance with an embodiment of the present invention, an aryl diamine monomer is provided that comprises a sulfone moiety and has a general chemical formula:

\[
\text{H}_2\text{N} \quad \text{NH}_2 \quad \text{O} \quad \text{W} \quad \text{SO}_2\text{R}^2,
\]

wherein W is selected from the group consisting of O, NH, and NR', wherein R' and R'' are independently selected from the group consisting of substituted or unsubstituted C1-C7 alkyl groups, and substituted or unsubstituted phenyl groups, with the proviso that R'' is not methyl when W is O.

In accordance with another embodiment of the present invention, a method of synthesizing the aryl diamine monomer is provided, the method comprises reducing a bis-nitroaryl moiety comprising a sulfone moiety and having a general formula:

\[
\text{O}_2\text{N} \quad \text{NO}_2 \quad \text{O} \quad \text{W} \quad \text{SO}_2\text{R}^2,
\]

The bis-nitro aryl moiety may be obtained directly or indirectly by reacting 3,5-dinitrobenzoic acid or 3,5-dinitrobenzoic acid halide with an ethyl sulfonyl moiety having a general formula:

\[
\text{HW} \quad \text{SO}_2\text{R}^2,
\]

where W and R'' are defined above.

In accordance with yet another embodiment of the present invention, a polymer is provided that comprises a diamine portion derived from the aryl diamine monomer comprising the sulfone moiety, wherein the polymer is selected from the group consisting of a polyamide, a polypimide, and a poly(amide-imide).

In accordance with yet another embodiment of the present invention, a copolymer composition is provided that includes complementary monomer portions of a first monomer portion comprising a sulfone terminated pendant group and having a general formula:

\[
\text{HN} \quad \text{NH} \quad \text{O} \quad \text{W} \quad \text{SO}_2\text{R}^2,
\]

and a second monomer portion comprising a carboxylic acid or carboxamide terminated pendant group and having a general formula:

\[
\text{HN} \quad \text{NH} \quad \text{O} \quad \text{W} \quad \text{SO}_2\text{R}^2,
\]

wherein W is selected from the group consisting of O, NH, and NR', wherein R' and R'' are independently selected from the group consisting of substituted or unsubstituted C1-C7 alkyl groups, and substituted or unsubstituted phenyl groups, and wherein the copolymer is selected from the group consisting of a polyamide copolymer, a polypimide copolymer, and a poly(amide-imide) copolymer.

Advantageously, many of the materials utilized in the syntheses are readily available and cost-effective, allowing for scalability. Moreover, the polymers and copolymers incorporating the hydrophilic sulfone moiety possess hygromorphic properties and demonstrate humidity driven motility. Additional objects, advantages, and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the present invention and, together with a general description of the invention given above, and the detailed description of the embodiments given below, serve to explain the principles of the present invention.

**FIG. 1** is a schematic showing a synthetic route for preparing the aryl diamine monomer comprising a sulfone moiety that is incorporated into the hygromorphic polymers and copolymers, in accordance with an embodiment of the present invention;

**FIG. 2** is a schematic showing a synthetic route for preparing a polyimide and a copolyimide that incorporates the aryl diamine monomer, in accordance with another embodiment of the present invention;
FIG. 3 is a schematic showing copolymerization of the ary1 diamine monomer comprising a sulfone moiety and 3,5-diamino benzoic acid, with various anhydrides to provide copolyamides, in accordance with another embodiment of the present invention;

FIG. 4 is a schematic showing a synthetic route for preparing reference or comparative polyimides for comparison with the inventive polymers and copolymers, in accordance with another embodiment of the present invention;

FIG. 5 is a schematic showing a synthetic route for preparing a polyamide and a copolyamide that incorporate the ary1 diamine monomer, in accordance with another embodiment of the present invention;

FIG. 6A is a schematic showing a first synthetic route for preparing a poly(amine-imide) and copoly(amine-imide) that incorporates the ary1 diamine monomer, in accordance with another embodiment of the present invention;

FIG. 6B is a schematic showing a second synthetic route for preparing a poly(amine-imide) and copoly(amine-imide) that incorporates the ary1 diamine monomer, in accordance with another embodiment of the present invention;

FIG. 6C is a schematic showing a third synthetic route for preparing a poly(amine-imide) and copoly(amine-imide) that incorporates the ary1 diamine monomer, in accordance with another embodiment of the present invention;

FIG. 7 shows three 1H-NMR spectra and peak assignments of (a) an exemplary polyimide (i.e., PEI-ES, compound 7a); (b) PEI-ES after heating at 250°C for 2 hrs, resulting in the partial formation of PEI-A (structure shown) and methyl-vinyl sulfone; and (c) a commercial sample of methyl-vinyl sulfone, in accordance with another embodiment of the present invention;

FIG. 8 shows IR spectra comparing four polyimides, i.e., PEI-ES (compound 7a); PEI-ES-A-4 hr (example 24); PEI-A (compound 15); and PEI-N (Ultima® 1000), in accordance with another embodiment of the present invention;

FIGS. 9a and 9b show TGA thermograms of PEI-ES, PEI-A and PEI-N samples in air and in N2, respectively, in accordance with another embodiment of the present invention;

FIG. 10 shows TGA thermograms of PEI-ES (compound 7a) and PEI-ES-A-xhr samples in air (example 24), in accordance with another embodiment of the present invention;

FIG. 11 shows TGA monitoring of retro-Michael reaction by following the ester-sulfonyle to carboxylic-acid conversion after the respective PEI-ES samples had been heated at 250°C for the predetermined durations;

FIG. 12 shows a series of photographs to illustrate a water-gradient actuation and locomotion of a PEI-ES PI film (3 cm x 3 cm x 30 um) on a piece of wet paper towel, in accordance with an embodiment of the present invention;

FIG. 13 shows a series of photographs to illustrate the water-gradient actuation and locomotion of a 6FDI-A PI film on a piece of wet paper towel, in accordance with an embodiment of the present invention;

FIGS. 14a and 14b demonstrate how a humidity gradient drives film curvature, where FIG. 14a is a schematic of the steady state humidity gradient cell where dC/dz is the humidity gradient in the cell and arrows indicate direction of flux; and FIG. 14b shows an effect of side chain and backbone on film curvature, where a trace is added for clarity.

It should be understood that the appended drawings are not necessarily to scale, presenting a somewhat simplified representation of various features illustrative of the basic principles of the invention. The specific design features of the sequence of operations as disclosed herein, including, for example, specific reagents, solvent, catalysts, and/or reaction conditions, will be determined in part by the particular intended application and use environment.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

As part of ongoing research on adaptive polyimide-based systems that have been shown to be mechanically responsive to light, heat and thermal-electrical stimuli, herein new sulfone-containing polyimide, polyamide, and poly(amine-imide) polymers and related thermally-derived copolymers. Further disclosed are the mechanical responsiveness relative to structurally similar polymers containing CO2H-pendants in a humidity gradient, information which may be useful toward developing adaptive structures that are functional in both dry and wet environments.

Thus in accordance with an embodiment of the present invention, a new diamine monomer bearing sulfone-terminated pendant groups, as well as methods for making same, are provided. The diamine monomer is useful toward making polyamide, polyimide, and poly(amine-imide) polymers and copolymers, which possess hygromorphic properties and demonstrate humidity driven motility. More specifically, an ary1 diamine monomer is provided that comprises a sulfone moiety and has a general chemical formula:

```
H2N               H2N
\   /             \   /
 O=S=O             O=S=O
 /     \           /     \\
 NH2               NH2
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wherein W is selected from the group consisting of O, NH, and NR2, wherein R1 and R2 are independently selected from the group consisting of substituted or unsubstituted C1-C7 alkyl groups, and substituted or unsubstituted phenyl groups, with the proviso that R2 is not a methyl when W is O.

In FIG. 1, exemplary synthetic routes to preparing the ary1 diamine monomer are provided. In an embodiment, esterification of 3,5-dinitrobenzoyl chloride (1) with a suitable sulfone-substituted ethyl alcohol derivative (FIG. 1, W=O, compound 2a) provides the corresponding 3,5-dinitrobenzoate ester (3a), which is followed by reduction of the nitro groups to provide the corresponding 3,5-diamino benzoate ester (4a). For example, esterification of 3,5-dinitrobenzoyl chloride (1) with 2-(methylsulfonyl)ethanol (FIG. 1, compound 2a, where W=O, R2=Me) affords 2-(methylsulfonyl)ethyl-3,5-dinitrobenzoate, which can be subsequently converted to the desired diamine monomer 2-methylsulfonyl-ethyl-3,5-diaminobenzoate, which is a known compound, by catalytic hydrogenation. However, its synthesis and utility as a monomer in polymerization have not been reported in literature. Other sulfone-substituted ethyl alcohol derivatives (R2 may be substituted or unsubstituted C1-C7 alkyl groups, or substituted or unsubstituted phenyl groups) may be reacted with 3,5-dinitrobenzoyl
chloride (1) or 3,5-dinitrobenzoic acid to prepare the Ester-Sulfonyl diamines (ES-diamines) (4a), as depicted in Scheme 1.

Analogous Amide-Sulfonyl diamine (AS-diamines) (FIG. 1, W=NH or NR₂, e.g., compounds 4b-d) may be readily synthesized by reacting sulfone-substituted ethyl amine derivatives (e.g., compounds 2b-d). An exemplary synthetic route to prepare the requisite sulfone-substituted ethylamine derivatives (2b-d) can be realized by exploiting a Michael Addition reaction of R₃NH₂ to a vinylsulfone (R[S=O]CH₂—CH₃), or a Michael Addition reaction of R₃BuNH₂ (where R₃Bn represents benzyl) to a vinyl sulfone (R[S=O]CH₂—CH₃), followed by de-benzylation via transfer-hydration with ammonium formate. Because of higher reactivity of primary alkyl amines, benzyl (CH₃Ph) is preferably used as a masking group to preclude double Michael addition with two vinyl sulfones. The resulting sulfone-substituted ethyl amines (2b-d) can then be fed into the similar two-step synthesis to obtain AS-diamine monomers (4b-d).

It should be appreciated that the resultant hygroscopic properties and humidity driven motility of any polymer incorporating aryl diamine monomer 4 can be influenced by modification of the polarity of the monomer. Accordingly, increasing the carbon chain lengths of R¹ and R² may reduce the hydropathicity of the monomer, which thereby reduces the hygroscopic properties (and/or its associated kinetics) of the polymer or copolymer. Conversely, decreasing the chain length of R¹ and R² may increase the hydrophilicity of the monomer, which thereby increases the hygroscopic properties (and/or its associated kinetics) of the polymer or copolymer. Exemplary groups suitable for R¹ and R² include but are not limited to methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, benzyl, phenyl. In accordance with another embodiment of the present invention, R¹ and R² may be substituted with functional groups such as halide, hydroxyl, alkoxyl, acyl, or amido. For example, R² may be CF₃.

The ary1 diamine monomer 4 may be incorporated into a variety of polymers and copolymers, including random, block, and tapered polymers. In accordance with an embodiment of the present invention, the ary1 diamine monomer 4 is used to provide polycyamide, polyamide, and poly(amicide-imide) polymers and copolymers, as further described herein.

POLYIMIDE: Synthesis of a polyamide is typically accomplished by polymerization of a diamine and a dianhydride in a 1:1 molar ratio to generate a poly(amic acid) precursor, which is then converted to the corresponding polyamide typically by either thermal cure (e.g., by heating to an elevated temperature in solution or solid state) or chemical imidization (e.g., using a dehydrating agent or promoter such as acetic anhydride/triethylamine or acetic anhydride/pyridine). With reference to FIG. 2, an exemplary polyamide synthesis is provided that shows the ester-sulfon yl diamine (ES-diamine) 4a (where W=O) reacted with a dianhydride 5 to form a polyamic acid (PAA) 6, which is converted to a polyimide 7 under suitable imidization conditions.

For example, the ES-diamine 4a can be polymerized with a dianhydride, such as 2,2'-[bis(4-phenylphthalimide)]-1,1',3,3',3',3'-hexafluoroisopropane (6f-PDA); 4,4'-oxybis(phthalimide anhydride) (ODPA); 3,3',4,4'-diphenyldisulfone tetracarboxylic dianhydride (SDSA); 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA); biphenyl/tetracarboxylic acid dianhydride (BPDA); 4,4'-1,2,2-trifluoro-1-phenylethylidenephthalic anhydride; 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPDA); 4,4'-1,4'-Hexafluoroisopropylidenephenoxyoxybis(phthalic anhydride) (6f-PBADA); 4,4'-(p-phenyleneoxy)bis [phthalic anhydride]; 4,4'-(m-phenyleneoxy)bis[phthalic anhydride]; 4,4'-(o-phenyleneoxy)bis[phthalic anhydride]; pyromellitic dianhydride (PMDA); or mixtures thereof. In an embodiment, BPADA, 6f-PBADA, 6f-DQA, DSDA and BTDA are reacted with the ES-diamine monomer 4a. The ES-diamine 4a and the dianhydride 5 may be reacted in a suitable solvent, such as NMP, to yield a series of polyamic acids (PAA) 6 at room temperature. The PAA’s were either thermally imidized at about 175°C. (conditions labelled as “11” in FIG. 2) or chemically imidized by acetic anhydride and pyridine (conditions labelled as “SC” in FIG. 2) to afford polypyrimides 7 containing ester-sulfon yl (ES) groups, PI-ES’s (7a-e). The IR spectra of polypyrimides prepared by both methods were observed to be almost identical.

Typically, PAA cast films are thermally imidized at temperatures above about 200°C. However, during the early stage of this work, it was observed that when the PAA 6a cast film was heat-treated at temperatures above 200°C, the corresponding copolymer containing ester-sulfon yl and carboxylic acid pendant (PEI-ESA, 8a; Scheme 3) was obtained cleanly from a retro-Michael reaction of the ES pendant group (i.e. —COO—CH₂CH₂ SO₃Me), resulting in the formation of COOH pendant and liberation of methylvinylsulfone molecule. These retro-Michael products were easily detected by ¹H-NMR experiments after a piece of PEI-ES film had been heated at 250°C. For 2 hr in an NMR tube, followed by adding DMSO-d₆ at room temperature (see FIG. 7). Based on the NMR analysis and area-integration results, about 42 mol % of ES groups were found to have converted into carboxylic acids. The new byproduct peaks in spectrum 7b is identical to that of the authentic methylvinylsulfone sample (spectrum 7c). Although ~50% of methylvinylsulfone generated had escaped into air during the heat treatment at 250°C, the other half remained in the polymer film because of the relatively nonvolatile nature of methylvinylsulfone (b.p. 115-120°C/19 torrs).

Ostensibly, the series of PI-ES: A copolymers can also be prepared by copolymerization with appropriate stoichiometric ratio of the methysulfonylethyl ester-containing diamine (4a), 3,5-diaminobenzoic acid and dianhydride monomer following conventional methods of synthesizing polyimides, i.e. via polyamic acid precursor and chemical or thermal imidization. As depicted in FIG. 3, the scope of such copolymerization can be broadened to include diamines 4b-c, from which the corresponding amide-sulfon yl pendant could be incorporated as well.

As shown in FIG. 4, comparative materials comprising non-functionalized polyimides (PI-N) (e.g., compounds 14a, c) and polyimides bearing COOH-pendant groups (PI-A) (e.g., compounds 15a-c) were also prepared for comparison purposes by polycondensation of m-phenylenediamine (9, m-PDA) and 3,5-diaminobenzoic acid (10, DABA) with BPADA; and 6f-DQA, respectively to form the respective poly(amic acid)s. Two sets of imidization conditions were used for these less temperature-sensitive polyimides: (ST) solvent imidization at 190-200°C; and (T2) imidization of cast PAA film up to 250°C.

POLYIMIDE: The synthesis of a polyamide is typically accomplished by two general methods. The first method involves polymerization of a diamine and a diacid chloride in a 1:1 molar ratio in an amide solvent such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), N-methylpyrrolidone (NMP), etc. The second method of synthesizing a polyamide involves polymerization of a diamine and a dicarboxylic acid with the aid of a
promoter/catalyst combination such as triethylphosphite/pyridine (via Yamazaki-Higashi reaction) in an amide solvent such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), etc. The preparation of polyamides containing ester-sulfone or amide-sulfone in every repeat unit is depicted in Fig. 5. Also depicted in this figure is the feasibility of converting the resulting amide homopolymers to the corresponding amide copolymers containing in complementary portions of COOH and COWCH_{2}CH_{2}SO_{2}R\textsuperscript{3} pendants (e.g., where W=O, NH, NMe or NPh) via similar solid-state retro-Michael reaction of the methylsulfonyl ethyl moieties.

In accordance with an embodiment of the present invention, the dicarboxylic acid monomer may include an aliphatic dicarboxylic acid or an aromatic dicarboxylic acid, or its corresponding acid halide. Exemplary aliphatic dicarboxylic acids may include, but are not limited to, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, dicarboxylic acid compounds or sebacic acid. Aromatic dicarboxylic acids may include, but are not limited to, isophthalic acid; terephthalic acid; 4,4'-dicarboxy diphenyl; 3,3'-dicarboxy diphenyl; 3,3'-dicarboxy diphenyl ether; 4,4'-dicarboxy diphenyl ether; 3,3'-dicarboxy diphenyl alkane; 3,3'-dicarboxy diphenyl methylene; 4,4'-dicarboxy diphenyl methylene; 4,4'-dicarboxy diphenylalkane; 3,3'-dicarboxy diphenyl sulfone; 4,4'-dicarboxy diphenyl sulfone; 3,3'-dicarboxy diphenyl sulfide; 4,4'-dicarboxy diphenyl sulfide; 3,3'-dicarboxy diphenyl ketone; 4,4'-dicarboxy diphenyl ketone; 2,2-bis(3-carboxyphenyl) propane; 2,2-bis(3,4-dicarboxyphenyl) propane; 2,2-bis(3-carboxyphenyl) hexafluoropropane; 2,2-bis(4-carboxyphenyl) hexafluoropropane; 1,3-bis(3-carboxy-phenoxo) benzene; 1,4-bis(3-carboxy-phenoxo) benzene; 1,4-bis(4-carboxy-phenoxo) benzene; 3,3'-1,4-phenylene bis(1-methyl-ethylidene) bis-benzoic acid; 3,4-(1,4-phenylene bis(1-methyl-ethylidene)) bis-benzoic acid; 4,4-(1,4-phenylenebis(1-methyl-ethylidene)) bis-benzoic acid; 2,2-bis(4-(3-carboxy-phenoxo) phenyl) propane; 2,2-bis(4-(4-carboxyphenoxy)phenyl) propane; 2,2-bis(4-(3-carboxy-phenoxo)phenyl) hexafluoropropane; 4,4-bis(4-(4-carboxy-phenoxo)phenyl) sulfoxide; bis(4-(4-carboxy-phenoxo)phenyl)sulfone; bis(4-(3-carboxy-phenoxo)phenyl) sulfoxide; or bis (4-(4-carboxy-phenoxo)phenyl)sulfone). In addition, combinations of two or more may be used.

POLY(AMIDEMID): There are three common method for the synthesis of a polyamide-imide by polymerization of a diamine and: (A) trimellitic anhydride (TMA) with poly(amide-imide) as isolable polymer precursor, which can be subsequently either chemically or thermally imidized (see Fig. 6A:); (B) a dicarboxylic acid monomer derived from trimellitic anhydride, and assisted by triethylphosphate/pyridine (Yamazaki-Higashi reagent) in a 1:1 molar ratio in an amide solvent such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP) etc (see Fig. 6B:); (C) a biphthalic anhydride monomer that can be prepared from low-temperature reaction of 2 equivalents of TMA's and a diamine, followed by treatment with acetic anhydride/trimethylamine. Similar to method A, it involves an isolable poly(amide-imide) precursor, which can be subsequently either chemically or thermally imidized (see Fig. 6C).

The application of these methods to the aryl diamine monomers 4a-d is depicted in FIGS. 6A, 6B, and 6C. Also depicted in FIGS. 6A-6C is the feasibility of converting the resulting amide homopolymers to the corresponding amide copolymers containing in complementary portions of COOH and COWCH_{2}CH_{2}SO_{2}R\textsuperscript{3} pendants (e.g., where W=O, NH, NMe or NPh) via similar solid-state retro-Michael reaction of the methylsulfonyl ethyl moieties.

The following examples are presented as illustrative of the present invention or methods of carrying out the invention, and are not restrictive or limiting of the scope of the invention in any manner.

EXAMPLE 1

2-(Methylsulfonyl)ethyl 3,5-dinitrobenzoate (3a)

Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stir bar and nitrogen inlet and outlet were placed 3,5-dinitrobenzoyl chloride (1; 8.48 g, 40.0 mmol), 2-(methylsulfonyl)ethanol (2a; 4.96 g, 40 mmol), pyridine (10.0 g), and CH_{2}Cl_{2} (100 mL). The homogeneous mixture was stirred at room temperature for 24 h. The resulting white precipitates were collected by filtration, and recrystallized from ethanol/toluene (1:1) to yield 10.6 g (61%) of white crystals; m.p. 138.5-140.3°C. NMR (DMSO-d_{6}; δ in ppm): 3.11 (s, 3H, CH_{3}); 3.73-3.76 (t, 2H, SO_{2}CH_{2}); 4.76-4.79 (t, 2H, COOCH_{3}); 8.95-8.96 (d, 2H, Ar=H); 9.04-9.06 (t, 1H, Ar=H). MS (m/z): 318 (M+). Anal. Calcd. for C_{13}H_{10}O_{5}P:S: C, 37.74%; H, 3.17%; N, 8.80%. Found: C, 37.74%; H, 3.12%; N, 8.90%. ATR-IR (Bulk powder; cm\textsuperscript{-1}): 3103, 3027, 3012, 2930, 1730 (C=O), 1632, 1539 (sym.NO_{2}), 1464, 1349 (sym.NO_{2}), 1298 (asym.NO_{2}), 1281, 1195, 1171, 1145, 1131 (sym.NO_{2}), 1079, 1005, 984, 949, 919, 761, 719, 665, 548, 486, 410.

Example 2

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (ES-Diamine, 4a)

2-(Methylsulfonyl)ethyl 3,5-dinitrobenzoate (3; 3.18 g, 10.60 mmol) dissolved in THF (50 mL) and palladium on activated carbon (0.20 g) was placed in a hydrogenation bottle. The bottle was tightly secured on a Parr hydrogenation apparatus, flushed four times with hydrogen gas, and pressurized to 55 psi. After the mixture had been agitated at room temperature for 6 h under the hydrogen pressure of 55 psi, it was filtered through Celite. The filter cake was washed with THF, and then the filtrate was concentrated on a rotovap to a volume of ~25 mL. The resulting mixture was heated to refluxing, until all the solid dissolved, and allowed to cool to room temperature to afford, after filtration and drying, 2.10 g (81.4%) of white needle crystals; m.p. 113.2-115.5°C. 1H NMR (DMSO-d_{6}; δ in ppm): 3.05 (s, 3H, CH_{3}); 3.55-3.67 (t, 2H, SO_{2}CH_{2}); 4.50-4.53 (t, 2H, COOCH_{3}); 5.00 (s, 4H, NH_{2}), 6.02-6.03 (t, 1H, Ar=H), 6.41-6.42 (d, 2H, Ar=H). MS (m/z): 258 (M+). Anal. Calcd. for C_{13}H_{10}O_{5}N_{2}S: C, 46.50%; H, 5.46%; N, 10.85%. Found: C, 46.65%; H, 5.39%; N, 10.89%. ATR-IR (Bulk Powder; cm\textsuperscript{-1}): 3438, 3416, 3345 (NH_{2}), 3217, 3009, 2955, 2920, 1771 (C=O), 1695 (sym., sym.)
Example 3

4,4′-(4,4′-Hexamethylenedioxybis(phthalic anhydride) (6f-BPADA, 5b)

Potassium hydroxide (25 g) was dissolved in 40 g of water in a 250 mL round-bottomed flask fitted with a reflux condenser. Then 2.2-bis[4-(3-dicyano-phenoxy)phenyl](II; 18.6 g, 30.0 mmol) was added to the solution, followed by 100 mL of methanol. The mixture was refluxed at 105°C for 40 h by which time evolution of ammonia had ceased. The mixture was then diluted with water (300 mL). The acidity was adjusted, by addition of concentrated hydrochloric acid solution, to pH 1.5-2. The resulting precipitate was filtered, washed three times with water and dried to yield 20.0 g (100%) of white powder-4,4′-(4,4′-Hexamethylenedioxybis(phthalic anhydride) (IV), which was used in next reaction step without further purification. ATR-IR (Bulk powder, cm⁻¹): 3100, 2500-3500 (br, COOH), 1849, 1780, 1620, 1592, 1508, 1480, 1277, 1265, 1229, 1213, 1179, 1170, 1158, 1071, 1023, 966, 935, 890, 875, 857, 738, 724, 674, 526, 483.

Then, 4,4′-(4,4′-Hexamethylenedioxybis(phthalic anhydride) (pH solution was added to 200 mL of acetic anhydride (150 mL). The mixture was refluxed for 2 h until all the solid disappeared. The resulting white needle product, which crystallized on cooling, was filtered to give a 17.8 g (94.4%) of pH: m.p. 233.0-235.0°C (ref. 2 233-235°C). NMR (DMSO-d₆, δ in ppm): 7.30-7.32 (d, 4H, Ar–H), 7.50-7.52 (d, 4H, Ar–H), 7.61-7.64 (m, 4H, Ar–H), 8.10-8.12 (d, 2H, Ar–H). ATR-IR (Bulk powder, cm⁻¹): 3100, 1848, 1771, 1620, 1591, 1507, 1479, 1277, 1258, 1228, 1170, 1178, 1147 (conjugated asx(SO₂), 1287, 1223, 1178, 1147 (conjugated asx(SO₂), 1127 (aliphatic asx(SO₂), 1100, 1069, 965, 917, 762, 739, 671, 638, 562.

Example 4

SC: Representative procedure for preparation of PEI-ES via solution chemical imidization: (7a-SC)

2-(Methylylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol) and NMP (8.0 mL) were added to a 25 mL 3-necked flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30 min. BPADA (5a; 1.041 g, 2.000 mmol) was then charged. The light yellow solution was agitated at room temperature for 24 h to afford a viscous poly(anic) solution. A mixture of pyridine (0.5 mL) and acetic anhydride (0.5 mL) was added to the solution. Stirring was continued for an additional 24 hours, and the solution was poured into ethanol to precipitate the polymer product. Fibrous polynimide was collected by filtration, followed by Soxhlet extraction with ethanol for 48 hours. The polynimide was then dried overnight in vacuum oven at 100°C. ATR-IR (Fibers, cm⁻¹): 3065, 2965, 2930, 1777, 1716, 1620, 1598, 1504, 1477, 1456, 1395, 1350 (asx(SO₂)), 1265, 1232, 1125 (asx(SO₂)), 1077, 1013, 846, 764, 742, 626.

Example 5

6FPEI-ES (7b-SC)

2-(Methylylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), 6F-BPADA (5b; 1.257 g, 2.000 mmol)

Example 6

6FDI-ES (7c-SC)

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), 6FDI (5c; 0.889 g, 2.000 mmol), and NMP (8.0 mL) were used. H NMR (Fibers, DMSO-d₆, δ in ppm): 3.06 (s, 3H, CH₃), 3.31 (s, 2H, SO₂CH₃), 4.70 (s, 2H, COOCH₃), 7.78 (s, 2H, Ar–H), 7.92 (s, 1H, Ar=H), 7.97 (s, 2H, Ar–H), 8.20 (s, 4H, Ar–H). ATR-IR (Fibers, cm⁻¹): 3082, 2932, 1785, 1720, 1600, 1459, 1398, 1355 (asx(SO₂), 1297, 1241, 1207, 1190, 1127 (asx(SO₂), 1095, 990, 962, 847.

Example 7

DSDI-ES (7d-SC)

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), DSIA (5d; 0.7165 g, 2.000 mmol) and NMP (8.0 mL) were used. ATR-IR (Fibers, cm⁻¹): 3099, 2930, 1784, 1722, 1600, 1554, 1458, 1399, 1360 (conjugated asx(SO₂)), 1313 (aliphatic asx(SO₂)), 1287, 1223, 1178, 1147 (conjugated asx(SO₂), 1127 (aliphatic asx(SO₂)), 1100, 1069, 965, 917, 762, 739, 671, 638, 562.

Example 8

BTDI-ES (7e-SC)

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), BTDIA (5e; 0.6444 g, 2.000 mmol) and NMP (8.0 mL) were used. The polymer precipitated from solution in 2 h after addition of acetic anhydride and trimethylamine due to poor solubility.

Example 9

ST: Representative Procedure for Preparation of PEI-A Via Solution Thermal Imidization: (15a-ST)

3,5-Diaminobenzoic acid (10; 0.761 g, 5.000 mmol) and NMP (12.6 mL) and toluene (5 mL) were added to a 50 mL 3-necked flask equipped with a magnetic stirrer, Dean-Stark trap, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30 min. BPADA (5a; 2.602 g, 5.000 mmol) was then charged. The light yellow solution was agitated at room temperature for 24 h to afford a viscous poly(anic) solution. The light yellow solution was agitated and heated to 150°C/1 h, 160°C/1 h, 170°C/1 h, 180°C/1 h and 190°C/1 h to afford a very viscous, gel-like solution. It was diluted by adding NMP (5 mL), allowed to cool to room temperature. The final mixture was poured into ethanol to precipitate a white fibrous solid, which was collected and dried in the oven at 50°C overnight. The film was prepared by dissolving the dried polymer in DMAc with 10 wt % solid content, cast onto glass slides followed by vacuum evaporation of DMAc at 50°C, and heat-treated at 105°C/2 h, 150°C/2 h, 175°C/1 h, 200°C/1 h and 250°C/1 h. The film thickness was approximately 20-50 μm. ATR-IR (film, cm⁻¹): 3067, 2966, 2927, 2500-3500 (br, COOH), 1778,
Example 10

6FDI-A (15c-ST)

Following the procedure described for Example 9, 3,5-Diaminobenzoic acid (10; 0.5087 g, 4.000 mmol), 6FDA (5c; 1.777 g, 4.000 mmol), NMP (12.0 mL) and toluene (5 mL) were used. 1H NMR (Fibers, DMSO-d6, δ in ppm): 7.77 (s, 2H, Ar—H), 7.846 (s, 1H, Ar—H), 7.93-7.95 (d, 2H, Ar—H), 8.08 (s, 2H, Ar—H), 8.18-8.20 (d, 2H, Ar—H), 13.43 (br. s. 1H, COOH). ATR-IR (Fibers, cm⁻¹): 3091, 2500-3500 (br., COOH), 1784, 1718, 1596, 1452, 1399, 1350, 1298, 1240, 1206, 1188, 1086, 990, 964, 846, 717, 631.

Example 11

T1: Representative Procedure for Preparation of PEI-ES (7a-T1)

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol) and NMP (8.0 mL) were added to a 25 mL 3-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30 min. BPADA (5a; 1.041 g, 2.000 mmol) was then charged. The light yellow solution was agitated at room temperature for 24 hr to afford a viscous poly(amic acid) solution. This solution was poured into a glass dish, followed by vacuum evaporation of NMP at 50°C, and heat-treated at: 100°C/2 hr, 150°C/2 hr and 175°C/1 hr to form imidized polymers. The film thickness was approximately 20-50 μm. ATR-IR (Film, cm⁻¹): 3065, 2967, 2930, 1777 νas(amide CO), 1715 νs(amide CO), 1597, 1503, 1477, 1444, 1396, 1350, 1265, 1231, 1119, 1076, 1013, 838, 741.

Example 12

6FEPI-ES (7b-T1)

Following the procedure described for Example 11, 2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), 6-FBADA (5b; 1.257 g, 2.000 mmol) and NMP (8.0 mL) were used. ATR-IR (Film, cm⁻¹): 3070, 2934, 1780, 1724, 1603, 1510, 1478, 1459, 1398, 1355, 1261, 1236, 1208, 1175, 1136, 1067, 968, 956, 929, 849, 784, 744, 628.

Example 13

6FDI-ES (7c-T1)

Following the procedure described for Example 11, 2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), 6FDA (5c; 0.889 g, 2.000 mmol) and NMP (8.0 mL) were used. 1H NMR (Fibers, DMSO-d6, δ in ppm): 3.06 (s, 3H, CH3), 3.64 (s, 2H, SO2CH2), 4.69 (s, 2H, COOCH2), 7.28-7.31 (d, 4H, Ar—H), 7.48-7.59 (m, 8H, Ar—H), 7.90 (s, 1H, Ar—H), 8.02-8.04 (d, 2H, Ar—H), 8.17 (s, 2H, Ar—H). ATR-IR (Film, cm⁻¹): 3082, 2932, 1785, 1720, 1600, 1459, 1398, 1353, 1297, 1241, 1207, 1190, 1127, 1095, 990, 962, 847. 

Example 14

DSI-ES (7d-T1)

Following the procedure described for Example 11, 2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), DSDA (5 d; 0.7165 g, 2.000 mmol), and NMP (8.0 mL) were used. ATR-IR (Film, cm⁻¹): 3094, 2930, 1783, 1716, 1597, 1456, 1396, 1366, 1311, 1283, 1221, 1176, 1176, 1124, 1095, 1057, 1006, 963, 914, 855, 761, 737, 669, 635, 557.

Example 15

BTDI-ES (7e-T1)

Following the procedure described for Example 11, 2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol), BTADA (5e; 0.6444 g, 2.000 mmol), and NMP (8.0 mL) were used. ATR-IR (Film, cm⁻¹): 3093, 2930, 1779, 1713, 1595, 1455, 1396, 1354, 1288, 1248, 1195, 1125, 1090, 959, 921, 853, 768, 714, 631.

Example 16

PEI-ES; A Copolymers Via Solid-State Thermal Imidization and Retro-Michael Reaction

2-(Methylsulfonyl)ethyl 3,5-diaminobenzoate (4a; 0.5166 g, 2.000 mmol) and NMP (8.0 mL) were added to a 25 mL 3-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and stirred under dry nitrogen at room temperature for 30 min. BPADA (5a; 1.041 g, 2.000 mmol) was then charged. The light yellow solution was agitated at room temperature for 24 hr to afford a viscous poly(amic acid) solution. This solution was poured into a glass dish, followed by vacuum evaporation of NMP at 50°C, and heat-treated at: 100°C/2 hr, 150°C/2 hr, 175°C/1 hr, 200°C/1 hr and 250°C/1-16 hr to form a series of imidized copolymers of PEI-ES and PEI-A. Retro-Michael reaction of the methylsulfonyl/ethyl ester pendant and late-stage of imidization of amic acid moiety occurred concurrently at temperatures >175°C. The resulting copolyimides are designated as PEI-ES:A-x hr, where x corresponds to number of hours at 250°C C, and qualitatively correlated to the amount of CO₂ pendants generated. The film thickness was approximately 20-50 μm. ATR-IR (Film, cm⁻¹) for PEI-ES:A-4 hr: 3086, 2500-3500 (br., COOH), 1785, 1718, 1600, 1458, 1399, 1361 (asym SO₂), 1298, 1240, 1206, 1189 (sym SO₂), 1148, 1090, 989, 963, 846, 741, 718, 631, 568.

With reference to FIG. 7, 1H NMR spectra and peak assignments of PEI-ES are provided showing: (a), PEI-ES after heated at 250°C C/N₂ for 2 hr (b), and commercial sample of methylvinylsulfone (c) for authentication. All spectra were taken in DMSO-de, which has proto residues with signals at 3.38 ppm (H₂O) and 2.50 ppm (DMSO). Based on area integration (A) of the pertinent peaks numerically or alphabetically labeled in spectrum 2(b), -42 mol % of PEI-ES was found to have decomposed into PEI-A as calculated form the following equation, [Aox/(Aox+Amx)]×100%; and -50 mol % loss of methylvinylsulfone formed as calculated form the following equation, (1–Aox/Aox)×100%; where Aox is the area of the corresponding peak i.
Following the polymerization procedure and imidization conditions described for PEI-ES-A (Example 16), 3,5-Di-aminobenzoic acid (10: 0.761 g, 5.000 mmol), BPADA (5a; 2.602 g, 5.000 mmol) and NMP (12.6 mL) were used. ATR-IR (film, cm⁻¹): 3099, 2966, 2927, 2500-3500 (br, COOH), 1778, 1715, 1597, 1503, 1476, 1444, 1397, 1348, 1266, 1230, 1172, 1013, 930, 837, 744, 625, 541.

Example 18

6FPI-A (15c-T2)

Following the polymerization procedure and imidization conditions described for PEI-ES-A (Example 16), 3,5-Di-aminobenzoic acid (10: 0.6087 g, 4.000 mmol), 6FDA (5c; 1.777 g, 4.000 mmol) and NMP (12.0 mL) were used. ATR-IR (fibers, cm⁻¹): 3091, 2500-3500 (br, COOH), 1784, 1718, 1596, 1498, 1399, 1350, 1298, 1240, 1206, 1188, 1140, 1086, 990, 964, 844, 744, 717, 645.

Example 19

PEI-N (Ultrem®-1000, 14a-T2)

Following the polymerization procedure and imidization conditions described for PEI-ES-A (Example 16), 3,5-Di-aminobenzene (9: 0.2162 g, 2.000 mmol), BPADA (5a; 0.889 g, 2.000 mmol), and NMP (10.0 mL) were used. ATR-IR (film, cm⁻¹): 3081, 1784, 1719, 1625, 1605, 1495, 1456, 1437, 1353, 1297, 1240, 1206, 1189, 1140, 1100, 1005, 985, 891, 846, 786, 755, 717, 679, 629, 569, 545.

Example 20

6FDI-N (14c-T2)

Following the polymerization procedure and imidization conditions described for PEI-ES-A (Example 16), 3,5-Di-aminobenzene (9: 0.2162 g, 2.000 mmol), 6FDA (5c; 1.041 g, 2.000 mmol) and NMP (10.0 mL) were used. ATR-IR (film, cm⁻¹): 3066, 2966, 2873, 1777, 1716, 1619, 1599, 1495, 1476, 1444, 1350, 1265, 1233, 1172, 1100, 1072, 1013, 920, 837, 776, 741, 682, 624, 543.

Example 21

Ultrem®-1000 Cast Films

Cast films of commercial Ultrem®-1000 were prepared from either chloroform or DMAc solution (10 w/w %), and similarly dried prior to characterization experiments. With reference to Fig. 8, IR spectra of PEI-ES, PEI-ES-A: A-4 hr, PEI-A and PEI-N (Ultrem) are provided. The ν_asymSO₂ (~1350 cm⁻¹) and ν_symSO₂ (~1310 cm⁻¹) stretches are present in PEI-ES, are obscured by nearby strong bands in PEI-ES-A: A-4 hr, and are absent in both PEI-A and PEI-N (Ultrem) samples.

With reference to Fig. 9, thermogravimetric analysis (TGA) thermograms of PI-ES, PI-A and PI-N samples (a) in air and (b) in N₂.

With reference to Fig. 10, TGA thermograms of PEI-ES and PEI-ES-A:xhr samples in air. The extent of retro-Michael reaction that varies with heating time at 250°C is determined by is determined by calculating the percentage of weight loss at 400°C., i.e., ES→A Conversion %=(Weight %PEI-A−Weight %PEI-ES)/Weight %PEI-ES. With reference to Fig. 11, TGA monitoring of retro-Michael reaction by following the ester-sulfonic acid conversion after the respective PEI-ES samples had been heated at 250°C for the predetermined durations.

Example 22

TABLE 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diamine</th>
<th>Dianhydride</th>
<th>T_a²</th>
<th>T_b²</th>
<th>T_a³</th>
<th>T_b³</th>
<th>in air</th>
<th>in N₂</th>
<th>E² (GPa)</th>
<th>Water Absorption</th>
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</thead>
<tbody>
<tr>
<td>PEI-ES (7a)</td>
<td>ES-Diamine</td>
<td>BPADA</td>
<td>193</td>
<td>221</td>
<td>282</td>
<td>300</td>
<td>1.38 ± 0.14</td>
<td>2.24 ± 0.05</td>
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<td></td>
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<tr>
<td>6F-PEI-ES (7b)</td>
<td>ES-Diamine</td>
<td>6F-BPADA</td>
<td>221</td>
<td>231</td>
<td>321</td>
<td>335</td>
<td>1.07 ± 0.10</td>
<td>2.39 ± 0.08</td>
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<tr>
<td>6FDI-ES (7c)</td>
<td>ES-Diamine</td>
<td>6FDA</td>
<td>254</td>
<td>313</td>
<td>322</td>
<td>1.27 ± 0.24</td>
<td>2.31 ± 0.11</td>
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<tr>
<td>DSF-DI-ES (7d)</td>
<td>ES-Diamine</td>
<td>DSFDA</td>
<td>UD²</td>
<td>UD²</td>
<td>302</td>
<td>1.75 ± 0.16</td>
<td>4.81 ± 0.07</td>
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<tr>
<td>BTDI-ES (7e)</td>
<td>ES-Diamine</td>
<td>BTDA</td>
<td>UD²</td>
<td>UD²</td>
<td>284</td>
<td>292</td>
<td>2.15 ± 0.25</td>
<td>4.86 ± 0.21</td>
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<td>PEI-N (14a)</td>
<td>m-PDA</td>
<td>BPADA</td>
<td>217</td>
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<td>513</td>
<td>2.68 ± 0.18</td>
<td>1.23 ± 0.06</td>
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<tr>
<td>Ultem (14a)</td>
<td>m-PDA</td>
<td>BPADA</td>
<td>217</td>
<td>248</td>
<td>504</td>
<td>509</td>
<td>2.74 ± 0.19</td>
<td>1.22 ± 0.04</td>
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<tr>
<td>6FDI-N (14c)</td>
<td>m-PDA</td>
<td>6FDA</td>
<td>280</td>
<td>492</td>
<td>497</td>
<td>1.67 ± 0.23</td>
<td>1.31 ± 0.03</td>
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<tr>
<td>PEI-A (15a)</td>
<td>m-DABA</td>
<td>BPADA</td>
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<td>273</td>
<td>441</td>
<td>443</td>
<td>3.08 ± 0.28</td>
<td>2.86 ± 0.12</td>
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TABLE 2-continued

Polymerization and Imidization conditions, polyimide molecular weights, polydispersity, and film quality.

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<thead>
<tr>
<th>Sample</th>
<th>Step 1 Solvent</th>
<th>Step 2 Solvent</th>
<th>$M_n$ a</th>
<th>$M_w$ a</th>
<th>$M_w/M_n$ a</th>
<th>PDI b</th>
<th>Film Quality</th>
</tr>
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<tbody>
<tr>
<td>6F-PEI-ES (7b)</td>
<td>NMP SC c</td>
<td>SC c</td>
<td>15,450</td>
<td>41,500</td>
<td>2.67</td>
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<td>Tough, creasable</td>
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<tr>
<td>6F-PEI-ES (7b)</td>
<td>NMP T1 c</td>
<td>SC c</td>
<td>7,070</td>
<td>29,100</td>
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<td>Brittle</td>
</tr>
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<td>6F-PEI-ES (7c)</td>
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<td>SC c</td>
<td>14,300</td>
<td>58,500</td>
<td>4.09</td>
<td></td>
<td>Tough, creasable</td>
</tr>
<tr>
<td>6F-PEI-ES (7c)</td>
<td>DMAc T1 c</td>
<td>DMAc SC c</td>
<td>5,410</td>
<td>17,800</td>
<td>3.30</td>
<td></td>
<td>Brittle</td>
</tr>
<tr>
<td>6F-PEI-ES (7c)</td>
<td>DMAc SC c</td>
<td>DMAc SC c</td>
<td>19,900</td>
<td>59,400</td>
<td>2.98</td>
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<td>Tough, creasable</td>
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<td>DMAc T1 c</td>
<td>DMAc SC c</td>
<td>6,240</td>
<td>18,900</td>
<td>3.03</td>
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<td>Brittle</td>
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TABLE 3

Thermal and mechanical properties of thermally derived copolyamide films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Convert. (%)</th>
<th>$T_g$ c</th>
<th>$T_{gmp}$ c</th>
<th>$T_{gmp}$ c</th>
<th>$E'$ (GPa)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-ES (7a)</td>
<td>0</td>
<td>221</td>
<td>282</td>
<td>300</td>
<td>1.38 ± 0.14</td>
<td>1.332 ± 0.003</td>
</tr>
<tr>
<td>PEI-ES-A-1 hr d</td>
<td>13.0</td>
<td>247</td>
<td>334</td>
<td>342</td>
<td>1.86 ± 0.24</td>
<td>1.326 ± 0.004</td>
</tr>
<tr>
<td>PEI-ES-A-2 hr d</td>
<td>32.1</td>
<td>267</td>
<td>337</td>
<td>343</td>
<td>1.30 ± 0.12</td>
<td>ND c</td>
</tr>
<tr>
<td>PEI-ES-A-4 hr d</td>
<td>64.1</td>
<td>279</td>
<td>345</td>
<td>361</td>
<td>1.28 ± 0.17</td>
<td>ND c</td>
</tr>
<tr>
<td>PEI-ES-A-8 hr d</td>
<td>83.5</td>
<td>286</td>
<td>417</td>
<td>429</td>
<td>1.27 ± 0.15</td>
<td>ND c</td>
</tr>
<tr>
<td>PEI-ES-A-16 hr d</td>
<td>100</td>
<td>287</td>
<td>463</td>
<td>472</td>
<td>1.31 ± 0.22</td>
<td>1.323 ± 0.005</td>
</tr>
<tr>
<td>PEI-A (12a)</td>
<td>100</td>
<td>273</td>
<td>441</td>
<td>443</td>
<td>3.08 ± 0.28</td>
<td>1.320 ± 0.003</td>
</tr>
<tr>
<td>PEI-N (15a)</td>
<td>—</td>
<td>247</td>
<td>502</td>
<td>513</td>
<td>2.68 ± 0.19</td>
<td>1.271 ± 0.007</td>
</tr>
</tbody>
</table>

Notes:
- Percentage of carboxylic acid converted from ester-sulfuryl groups or present in polymer.
- $T_g$ measured from the peak of tan delta (DMA) as an average value taken from 3 measurements, reported in °C.
- Temperature at which 5% weight loss recorded on TGA thermogram obtained with a heating rate of 10°C/min in air, reported in °C.
- Temperature at which 5% weight loss recorded on TGA thermogram obtained with a heating rate of 10°C/min in air, reported in °C.
- Modulus determined at stress mode at 25°C as an average value taken from 3 specimens per sample.
- Density was measured by floating the samples in CCl₄/Methanol mixture. A 5.00 ml of the mixture was divided by a pipette and weighed. An average value was taken from 3 measurements.
- PEI-ES-A films were heated at 250°C for 1-1.5 hr under N₂ to yield PEI-ES-A copolymers via retro-Michael reaction.
- Not determined (ND).
### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>EtOH</th>
<th>ACE</th>
<th>DCM</th>
<th>CHCl₃</th>
<th>THF</th>
<th>DMSO</th>
<th>DMAc</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEl-ES (7a)</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>6F-PEI-ES (7b)</td>
<td>-</td>
<td>+/−</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>0FDI-ES (7c)</td>
<td>-</td>
<td>+/−</td>
<td>+</td>
<td>-</td>
<td>-</td>
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<td>+</td>
</tr>
<tr>
<td>DSDD-ES (7d)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BTDD-ES (7e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEl-A (14a)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ultem (14a)</td>
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<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
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<tr>
<td>6FDI-N (14c)</td>
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<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>PEl-A (15a)</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>0FDI-A (15c)</td>
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<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

EtOH is ethanol; ACE is acetonitrile; DCM is dichloromethane; THF is tetrahydrofuran; DMSO is dimethylsulfoxide; DMAc is dimethylacetamide; NMP is N-methylpyrrolidone; solubility designations are: Soluble; − Insoluble; +/− Partially soluble.

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### Thermal and Mechanical Properties:

The glass transition temperatures (Tₐ's) were determined by both DSC and DMA techniques. Tₐ's were measured from inflection in baseline on DSC thermograms and from the peak of tan δ (DMA), respectively. Generally, the Tₐ's values from DMA are higher than the DSC values (see Table 1 as Example 22). Of the three types of polyimides and given the same dianhydride, the “ES” series exhibit the lowest Tₐ's, most probably due to the plasticizing effect of ES groups, and PI-A’s show the highest Tₐ's because of the inter-chain hydrogen bonding of carboxylic acids. Derived from the most rigid dianhydride, the glass transition of BTDD-ES was undetected below 300°C, and the degradation of the polymer started just slightly above 300°C. The Tₐ’s of the other members of “ES” are 193-279°C, according to the DSC results, and 221-291°C by DMA experiments. On the whole, the Tₐ’s of the “ES” series increased with increasing rigidity of dianhydride monomers, BTDD-DSDD-6FDI-6F-PEI-PEI, in agreement with the trend observed for other structurally similar polyimides.

The thermal stability was evaluated by TGA. As expected, the PI-ES samples showed the lowest thermal stability due to the aliphatic ES side chains. They all exhibited a two-stage degradation process (see Figs. 9A-9B). Their 5 wt % degradation temperatures are in the range of 282-321°C in air (Fig. 9A) and 292-335°C in N₂ (Fig. 9B). The non-functional PEI-N (Ultem®) and 6FDI-N exhibited the best thermal and thermos-oxidative stabilities. Their 5 wt % degradation temperatures are in the range of 492-504°C in air and 497-509°C in N₂ (see Fig. 10). The PI-A samples showed lower thermal stability than PI-N’s since the carboxylic groups underwent decarboxylation above 300°C.

The thermomechanical properties of the polyimide films were characterized by DMA to confirm the expected trends (Table 1 as Example 22). For “ES” series, all the films of the most rigid BTDD-ES have the largest Young’s modulus (2.15 GPa) and the lowest modulus belongs to the most flexible member, 6F-PEI-ES (1.07 GPa), in agreement with the observed Tₐ trend. However, 0FDI-A and PEl-A have even higher moduli, 2.13 and 3.08 GPa, respectively, apparently stemming from effective crosslinking and close packing driven by the inter-chain hydrogen bonding of the COOH pendant.

The morphology of the materials was characterized with wide-angle X-ray diffraction (WAXD). The results indicated that all the polyimides were completely amorphous as evidenced by the featureless diffraction patterns of these materials. Thus, the influence of any crystallinity on the humidity-driven response of these materials is deemed to be negligible.

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### Solubility:

Eight organic solvents, i.e., ethanol, acetone, CH₂Cl₂, CHCl₃, THF, DMSO, DMAc and NMP, were used to evaluate the solubilities of polyimides and the results are summarized in Table 4 as Example 25. All the polymers are insoluble in ethanol, which was used as a precipitating solvent after chemicalimidization. With the exception of BTDD-ES, they are all soluble in polar aprotic solvents such as DMSO, DMAc and NMP. PEl-ES, 6F-PEI-ES, 6FDI-ES and PEI-N (Ultem®) are soluble in chlorinated solvents (CH₂Cl₂, CHCl₃). It is noteworthy that the CO₂H-containing PI-A’s, with higher polarity and hydrogen-bonding capability than other polyimides in this work shows excellent solubility in both THF and acetone, especially the latter which is an uncommon solvent for polyimides.

### Film Fabrication:

For ES-containing polyimides, we found that the choice of imidization methods, i.e., chemical and thermal imidization, and conditions had direct impact on the film quality, likely because of the equilibrium nature of poly(amic acid) solution that is sensitive to the imidization conditions and pathways and influences the outcome of polyimide molecular weight. For example, the cast films of PI-ES obtained from chemical imidization in solution at room temperature are creasable while those obtained from thermal imidization at 175°C are brittle (see Table 2 as Example 23).

### Thermally-Derived PI-Es:

Copolyimides by Retro-Michael Reaction: The thermal, solid-state, retro-Michael reaction of ES-PI’s with an excellent combination of temperature- and time-dependence (i.e. allowing control of the initiation and extent of reaction), and stereospecificity (i.e. no side reactions) was found to be a simple method to generate a series of copolyimides having the same polymer backbone and containing variable ratio of ES and COOH (A) pendants. Thus, PEI-ES (7a) was selected and its film samples were heated in an oven under N₂ at 250°C at a set of durations (0-16 hr). The resulting copolyimides are designated as PEI-ES-A-xhr, where xhr corresponds to number of heat-treatment hours at 250°C. In TGA (air) experiments, the samples first started to degrade at 270°C due to the side-chain cleavage and reached a plateau at 350-440°C (Fig. 10). Aromatic components degraded above 440°C. The percentage of ester-sulfone to carboxylic acid conversion was calculated based on the weight loss at 400°C, and the results are plotted in Fig. 11. There are two linear degradation processes (0-4 and 4-16 hr). The conversion rate is much faster between 0 and 4 hr than 4-16 hr. About 64% of ester sulfonate was converted into carboxylic acid in the first 4-hr heating at 250°C (Fig. 11). Possibly, the rate is lower because of higher concentration of
COOH formed to slow down the escape of methylvinylsulfone molecule via the transition state of Michael adduct.

Humidity-Driven Actuation

Water uptake testing was conducted on all the polymers in an attempt to find the correlation between the water sorption and hygromorphic properties of the films (Table 1 as Example 22). Generally speaking, polar groups such as sulfonyl (—SO$_3$—) and carboxylic acid (—CO$_2$H) groups, increase the polymer's ability to absorb the moisture. BTDI-ES, DSDDI-ES, and 6FDI-A show the highest water uptake (~4.8%). Non-functional polymers (PEI-N and 6FDI-N) absorb the least amount of water in the range of 1.22 and 1.31 while the more polar counterparts in Table 1 have uptake values between 2.39 and 2.86%. Overall, these polyimides have much lower water affinity than perchlorate-doped, electrochemically polymerized polyphosphazene (Ppy.C1O$_2$N$_4$ 9.9% uptake at 94% RHi) and Nafion (15-25% uptake).

Previous comparisons by others of the mechanochemical behavior of Ppy.C1O$_2$N$_4$ films made of non-ionic polymers such as polyolefin, polyurethane, and polyethylene and reported that no humidity induced deformation. However, it has been observed that a thin polymer film (~3 cm x 3 cm and 30 um thick) of PEI-ES (also non-ionic) has the ability to self-actuating and locomotive on a wet surface (see Fig. 12, where arrows designate sequential photographs). Briefly, upon being laid flat on a piece of water-wet paper towel, two opposite parts of the film were able to curl up like a pair of wings while standing still, and then moved to another spot by flipping over when the “wings” are in close contact, following by a quick roll-over and flattening action. The apparently self-propelling movement continued across the wet surface until when the film reached the edge of the humidity field. In addition, we found that similarly fabricated film from an unmodified polyetherimide (Ultem®) or a highly hydroscopic polymer, namely Nafion, were practically unresponsive under the same testing conditions. Apparently, the former lacks suitable functional group with high affinity for polar molecules (e.g. H$_2$O and MeOH), and the water molecules are known to tenaciously bind to the sulfonic acid groups in the latter at room temperature.

During the course of this work, it became apparent that amorphous polymers containing other simple and highly polar moieties such as COOH pendants can be hygromorphic and motile as well under non-equilibrating humidity conditions. A series of representative snapshots of the actuation and locomotion sequence of the 6FDI-A film is depicted in Fig. 13.

Humidity Gradient Actuation Assessment

A steady state humidity response of circular films with diameter of 2.7 cm was quantified using a custom built humidity gradient chamber. The humidity gradient was generated by using deionized water as the source and a saturated aqueous solution of lithium chloride (LiCl$_{aq}$) as the sink. The separation between the source and the sink was maintained at 4 cm. Deionized water generates an equilibrium relative humidity of 100% while LiCl$_{aq}$ generates an equilibrium relative humidity of 11% (see Fig. 14A). Therefore, a linear estimate of the steady state humidity gradient is ~22%cm. The films were placed in the chamber and the equilibrium curvature of the films was imaged.

No actuation was observed in the absence of a humidity gradient, as tested by using deionized water as the source and sink. However, under a constant flux of water vapor from the source, the films actuated and maintained a constant conformation. The relative actuation was observed to be dependent on the molecular configuration. Overall, the presence of hydrophilic groups in the polymer structure had a positive effect on actuation when compared to films containing no hydrophilic polymer backbone or side chain, e.g. PEI-ES vs PEI-N (see Fig. 14B). While both PEI-N and 6FDI-N contain no hydrophilic pendants, the 6FDI-N backbone has been reported to be rather hydrophilic, and would account for the observed curvature angle (vs. zero curvature for PEI-N), which is still smaller than those polyimides containing hydrophilic pendants and being hygromorphic/ motile. When the rigidity of the backbone increased, with the pendant groups remaining unchanged, a general increase in the actuation was observed (Fig. 14B). 6FDI-ES somewhat falls out of line likely because of the added effect of its relatively more hydrophilic backbone as noted for 6FDI-N. There were slight changes in the film curvature when the film group was changed from ester-sulfone to carboxylic acid. The effect of pendant groups and backbone architecture on film curvature was highlighted in Fig. 14B. Together, these results highlight that humidity-driven actuation can be generated from a non-ionic polymer by simply grafting a sufficient amount of highly polar methylsulfonylethyl ester groups to the PEI backbone. Advantages of our approach include the convenient solubility of PEI polymer and the monolithic nature of the product, which eliminates phase separation or other interfacial issues of a multi-component system.

While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, they are not intended to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modification will be readily apparent to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative apparatus and methods and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the scope or the spirit of the general inventive concept exemplified herein.

What is claimed is:

1. An aryl diamine monomer comprising a sulfone moiety and having a general chemical formula:

```
H2N
\[\text{N}\]
\[\text{O}\]
\[\text{W}\]
\[\text{SO}_3R_2\]
```

wherein W is selected from the group consisting of NH and NR, wherein R and R are independently selected from the group consisting of substituted or unsubsti
tuted C1-C7 alkyl groups and substituted or unsubstituted phenyl groups.

2. The aryl diamine monomer of claim 1, wherein R is a methyl group or an unsubstituted phenyl group.

3. The aryl diamine monomer of claim 2, wherein R is a methyl group, and wherein R is a methyl group or an unsubstituted phenyl group.

4. The aryl diamine monomer of claim 1, wherein R is an unsubstituted C2-C7 alkyl groups methyl group or an unsubstituted phenyl group.

5. A method of synthesizing the aryl diamine monomer of claim 1, comprising:

reducing a 3,5-dinitrobenzoic acid derivative comprising a sulfone moiety and having a general chemical formula:
6. The method of claim 5, further comprising: reacting 3,5-dinitrobenzoic acid or 3,5-dinitrobenzoic acid halide with a sulfonyl ethyl moiety having a general chemical formula:

7. The method of claim 6, wherein the sulfonyl ethyl moiety is selected from the group consisting of 2-(methylsulfonyl)ethanol, 2-(methylsulfonyl)ethylamine, 2-(methylsulfonyl)-N-methyl-ethylamine, 2-(methylsulfonyl)-N-phenyl-ethylamine, and salts thereof.