Diamines containing pendent ethynyl and substituted ethynyl groups are synthesized. These diamines are reacted with dianhydrides to form polyamide acids, which are chemically or thermally cyclodehydrated to form polyimides and copolyimides with pendent ethynyl groups. Upon heating, the pendent ethynyl groups react to form crosslinked resins that are useful as adhesives, composite matrices, coatings, moldings and films.
CH₃CHO, C–CF₃

-78°C

(1)Br

nBuLi

-78°C

(1)Br

mp 194-196°C, 77% yield (Br)

mp 171-172°C, 59% yield (l)

mp 194-196°C, 77% yield (Br)

mp 171-172°C, 59% yield (l)

H₂N

reflux

NH₂ • HCl

NH₂

88% yield (Br)

81% yield (l)
C₆H₅-
\[ \text{NMP} \quad \text{El}_3\text{N} \]
\[ \text{Cu} \quad \text{I} \quad \text{Pd} \quad (\text{S}_3\text{P})_4 \quad 70-80^\circ \text{C} \]

\[ \text{C}_4\text{H}_9, \quad \text{C}_4\text{H}_9, \quad \text{mp} \quad 93^\circ \text{C} \quad 76\% \text{ yield} \]

\[ \text{R}' = (\text{CH}_3)_3\text{Si} \]
\[ \text{R} = \text{H} \quad \text{mp} \quad 161-163^\circ \text{C} \quad 78\% \text{ yield} \]
where R' = C

FIG. 3

where R = H, C₄H₉,
Copolymers where 10% of the repeat units contain pendant ethynyl groups.

where $R = H$, $C_4H_9$, 10%
DIAMINES AND POLYIMIDES CONTAINING PENDENT ETHYNYL GROUPS

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to condensation polymers. It relates in particular to polymides containing pendent ethynyl groups. It relates also in particular to diamines containing pendent ethynyl groups, which diamines are used in the preparation of the polyimides containing pendent ethynyl groups.

2. Description of Related Art

Polyimides are condensation polymers that can be prepared by various synthetic routes. The most popular route involves the reaction of an aromatic dianhydride with an aromatic diamine. The intermediate polyamide acid is either thermally or chemically cyclodehydrated to form the polyimide, which has an overall unit of the general type

![Polyimide Structure]

where Ar is a tetravalent aromatic radical, which can be as simple as a 1,2,4,5-tetrasubstituted benzene. Alternatively, Ar may be a bis-(1,2-methylene)phenylene having the general structure

![Bis(1,2-methylene)phenylene]

where X = nil, O, S, SO₂, C==O, etc. Moreover, Ar may be any other appropriate tetravalent radical. Ar' is a divalent aromatic radical which may be 1,3-phenylene, 1,4-phenylene, 4,4'-oxydiphenylene, 4,4'-biphenylene, 4,4'-thiodiphenylene, 4,4'-carbonyldiphenylene, diphenyliimethane, or any other appropriate divalent radical.


SUMMARY OF THE INVENTION

An object of this invention is to provide diamines containing a pendent ethynyl group.

Another object of this invention is to provide diamines containing a pendent phenylethynyl group.

Another object of this invention is to provide diamines containing a pendent substituted ethynyl group.

Another object is to provide polyimides which crosslink to form a network structure by heating at elevated temperatures.

Another object is to provide polyamides which crosslink to form a network structure by heating at elevated temperatures.

Another object is to provide polyamides and substituted ethynyl groups from the reaction of the above diamines with dianhydrides.

These objects and the attending benefits are achieved according to the present invention by providing a series of diamines having the general structural formula:
pendent ethynyl groups have a high molecular weight to form high molecular weight resins from polyimides containing pendent ethynyl imide oligomers (ATI) is that the polyimides containing ethynyl groups compared to acetylene-terminated glass transition temperature and modulus. These properties are important for electronic and aerospace applications. Furthermore, the crosslink density of the cured reaction products generally increase, accompanied by a corresponding decrease in tensile elongation and toughness. These cured polymers can be used as films, coatings, moldings, adhesives, and composite matrices.

The advantage of polyimides containing pendent ethynyl groups compared to linear polyimide is their ability to react to form a crosslink structure which typically has an increased solvent resistance, and higher glass transition temperature and modulus. These properties are important for electronic and aerospace applications such as films, coatings, moldings, adhesives and composites.

The advantage of polyimides containing pendent ethynyl groups compared to acetylene-terminated imide oligomers (ATI) is that the polyimides containing pendent ethynyl groups have a high molecular weight and form tough films before the ethynyl crosslinking reaction takes place. The ATIs typically form brittle films. Furthermore, the crosslink density of the cured resins from polyimides containing pendent ethynyl groups can be controlled by copolymerizing a diamine without ethynyl groups and a diamine containing pendent ethynyl groups to form high molecular weight polymers. With ATIs, the crosslink density can be varied only by changing the molecular weight of the oligomer, which affects the ability to make films and moldings.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, including its objects and attending benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth below. This Description should be read together with the accompanying drawings wherein:

FIG. 1 is a representation of the reaction scheme for the preliminary stages of a process for preparing novel diamines containing pendent ethynyl groups or substituted ethynyl groups according to the present invention;

FIG. 2 is a representation of the reaction scheme for the final stage of a process for preparing novel diamines containing pendent ethynyl groups or substituted ethynyl groups according to the present invention;

FIG. 3 is a representation of the reaction scheme for preparing polyimides containing pendent ethynyl groups or substituted ethynyl groups according to the present invention; and

FIG. 4 is a representation of the reaction scheme for preparing imide copolymers containing pendent ethynyl groups or substituted ethynyl groups according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A series of novel diamines containing pendent ethynyl groups or substituted ethynyl groups were synthesized. See FIGS. 1 and 2 for the reaction schemes employed. The resulting diamines were then reacted with various dihydrides to form polyamic acids, which were cyclodehydrated to form polyimides containing pendent ethynyl groups or substituted ethynyl groups. See FIG. 3 for a schematic of the reaction employed. Finally, copolyimides from the diamines containing pendent ethynyl or substituted ethynyl groups and other diamines were also prepared. See FIG. 4 for the reaction scheme employed. The polyimides so produced were characterized (see Table 1 below), as were the copolyimides (see Table 2 below). Mechanical properties of films prepared from the polyimides and copolymers were determined, and the thermal stability and film properties of the copolymers were tabulated (see Table 3 below). Specific examples, which are for purposes of illustration only are presented as follows.

EXAMPLE 1

Synthesis of 4-bromotrifluoroacetophenone (see FIG. 1)

Into a flame-dried three-necked round bottomed flask, fitted with a pressure equalizing addition funnel and under nitrogen was added 1,4-dibromobenzene (20.04 g, 84.00 mmol). Using a syringe, 150 mL of anhydrous ether was added into the flask. Some of the 1,4-dibromobenzene dropped out of solution when the solution was cooled to -78 °C. in a dry-ice/acetone bath. An amount of n-butyl lithium (n-BuLi) (1.6M in hexane, 55 mL; 88 mmol) was introduced into the addition funnel with a syringe, and the funnel was adjusted for dropwise addition of the n-BuLi solution into the reaction flask. The addition was completed in 30 minutes,
and the resulting white suspension was stirred at -78°C for two hours. After two hours, the reaction vessel was removed from the bath and allowed to warm to 0°C to ensure complete metal-halogen exchange. The reaction mixture changed from a suspension to a solution on warming. On recoiling to -78°C, the suspension reappeared. To this white suspension was added dropwise, through the addition funnel, 13.47 g (95.00 mmol) of ethyl trifluoroacetate. The suspension became a solution before complete addition of the ester and the solution was left to warm to room temperature in about 12 hours.

To quench the reaction, the solution was cooled to between -30°C and -20°C, and then 40 mL of aqueous saturated ammonium chloride (NH₄Cl) was added dropwise through the addition funnel. To ensure complete hydrolysis, 40 mL of 1N hydrochloric acid (HCl) was added and the mixture was allowed to warm up to room temperature. The reaction mixture was transferred to a separatory funnel and the aqueous layer was removed. A yellow-colored, slightly lacrimatory liquid which was a colorless liquid. The liquid solidified on warming. On recooling to -78°C, the suspension reappeared. To this white suspension was added 1H NMR: an AB quartet centered at 7.66 ppm.

4-iodotrifluoroacetophenone was prepared by a similar procedure in 81% yield from p-diiodobenzene. 1H NMR: an AB quartet centered at 7.66 ppm.

EXAMPLE 2

Synthesis of 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluorothane (See FIG. 1)

4-Bromotrifluoroacetophenone (33.53 g, 132 mmol) was placed in a 500 mL single-necked round bottomed flask followed by 23 g (178 mmol) of purified aniline hydrochloride. After freshly distilled aniline (93 mL) was added, the flask was fitted with a reflux condenser and the suspension was stirred at -78°C for about 30 minutes. On cooling to room temperature, a brittle orange glass was left which was ground, giving the monomer as a yellow colorless, slightly lacrimatory liquid which was a colorless liquid. The liquid solidified on warming. On recooling to -78°C, the suspension reappeared. To this white suspension was added dropwise, through the addition funnel, 13.47 g (95.00 mmol) of ethyl trifluoroacetate. The suspension became a solution before complete addition of the ester and the solution was left to warm to room temperature in about 12 hours.

To quench the reaction, the solution was cooled to between -30°C and -20°C, and then 40 mL of aqueous saturated ammonium chloride (NH₄Cl) was added dropwise through the addition funnel. To ensure complete hydrolysis, 40 mL of 1N hydrochloric acid (HCl) was added and the mixture was allowed to warm up to room temperature. The reaction mixture was transferred to a separatory funnel and the aqueous layer was run off. The ether solution was washed carefully with saturated aqueous sodium bicarbonate (NaHCO₃), until the acid was neutralized (no effervescence on adding fresh amounts of the aqueous bicarbonate). The ether solution was transferred to a flask and dried over anhydrous magnesium sulfate (MgSO₄). Suction filtration, followed by rotary evaporation of the solvent, left a yellow-colored, slightly lacrimatory liquid which was vacuum distilled (0.2 Torr, 80°C) to obtain 19.75 g (88%) of 4-bromotrifluoroacetophenone as a dense, colorless liquid. The liquid solidified on storing in the refrigerator. 1H NMR: an AB quartet centered at 7.66 ppm.

4-Iodotrifluoroacetophenone was prepared by a similar procedure in 81% yield from p-diiodobenzene. 1H NMR: an AB quartet centered at 7.66 ppm.

EXAMPLE 3

Synthesis of 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluorothane (See FIG. 2)

1,1-Bis(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluorothane was prepared in a similar manner in 59% yield from 4-iodotrifluoroacetophenone: mp 171°-172°C (after vacuum heat-drying). 1H NMR: 83.50 (br s, 4H), 6.44 (d, 4H), 6.80 (d, 6H), 7.46 (d, 2H); Mass Spectrum, m/e (relative intensity) 468 (M+,40), 399 (100), 272 (20); Calc'd for C₂₀H₁₆BrF₃N₂: C, 51.30; H, 3.44; N, 5.98. Found: C=51.40; H=3.36; N=5.97.

EXAMPLE 4

Synthesis of 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluorothane (See FIG. 1)

4-Bromotrifluoroacetophenone (33.53 g, 132 mmol) was placed in a 500 mL single-necked round bottomed flask followed by 23 g (178 mmol) of purified aniline hydrochloride. After freshly distilled aniline (93 mL) was added, the flask was fitted with a reflux condenser and the suspension was stirred at -78°C for about 30 minutes. On cooling to room temperature, a brittle orange glass was left which was ground, giving the monomer as a yellow colorless, slightly lacrimatory liquid which was vacuum distilled (0.2 Torr, 80°C) to obtain 19.75 g (88%) of 4-bromotrifluoroacetophenone as a dense, colorless liquid. The liquid solidified on storing in the refrigerator. 1H NMR: an AB quartet centered at 7.66 ppm.

4-Iodotrifluoroacetophenone was prepared by a similar procedure in 81% yield from p-diiodobenzene. 1H NMR: an AB quartet centered at 7.66 ppm.
Synthesis of Polymides. FIG. 3 shows the synthesis of polyimides containing pendent ethynyl or substituted ethynyl groups. Table 1 shows the inherent viscosities ($\eta_{inh}$) of six polyamide acids prepared using diamines containing pendent ethynyl groups. Specific examples of these polymers follow.

EXAMPLE 4

Synthesis of 1,1-bis(4-aminophenyl)-1-(4-phenylethynylphenyl)-2,2,2-trifluoroethane (see FIG. 2).

Into a single-necked round bottom flask were added 6.27 g (13.39 mmol) of 1,1-bis(4-aminophenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane, 0.52 g (0.45 mmol); 3.36 mol % of tetrakis(triphenylphosphine)palladium (O), and 0.11 g (0.58 mmol; 4.3 mol %) of Cul. After the addition of 24 mL of triethylamine and 8 mL of N,N-dimethylpyrrolidinone, 2.80 g (27.45 mmol) of phenylacetylene was introduced into the flask. A reflux condenser, connected to a nitrogen line, was attached to the flask and the stirred mixture was maintained at 70° C. with an oil bath for three days. The solvent mixture was removed on a rotary evaporator and the dark red oily residue was extracted with ether continuously until further extraction with fresh ether gave a colorless organic layer. All the ether extracts were collected, washed with water and dried over anhydrous MgSO4. Suction filtration and solution concentration on the rotary evaporator gave a dark-red oil which foamed up to give a fluffy yellow solid on leaving on the evaporator for two-three hours.

The crude product was applied onto a column of silica gel and eluted initially with benzene. After the faster moving components of the crude mixture had eluted (this fraction was a dark red oil), elution was continued with a 9:1 (v/v) mixture of benzene and ether respectively. The product was obtained from this fraction, on rotary evaporation of the solvent and leaving the residue for three hours at 53° C., as a bright yellow foamy solid weighing 3.45 g (58%). 1H NMR spectrum of this product indicated that some occluded benzene was still left in the solid. The product was therefore subjected to vacuum heat-drying at 80° C. for 30 minutes. An orange glass was left on cooling to room temperature, which was ground into a yellow powder; top: the compound started to shrink at 85° C., became a glassy ball at 90°-92° C. and melted into an orange liquid at 100°-2° C. 1H NMR: 83.66 (br s, 4H), 6.36-7.36 (m, 17H); Mass Spectrum, M+ (relative intensity); 442 (M+, 20), 373 (100); Calc’d for C28H21F3N2: C, 73.93; H, 5.96; N, 6.33. Found: C, 75.63; H, 4.95; N, 6.15.

EXAMPLE 5

Synthesis of 1,1-Bis(4-aminophenyl)-1-(4-hexynylphenyl)-2,2,2-trifluoroethane (See FIG. 2).

This compound was prepared in 76% yield from 1,1-(4-aminophenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane and 1-hexyne by the same procedure as for the phenylethynylvphenyl analog. Mp: the compound started to soften and shrink at 53° C., becomes a transparent mass at 62° C. and melted at 93° C. 1H NMR: 80.90 (unresolved, 3H); 1.50 (unresolved, 4H); 2.32 (unresolved, 2H); 3.42 (br s, 4H); 6.55 (AB q, 4H); 7.02 (AB q, 4H); Mass Spectrum, m/e (relative intensity); 424 (M+, 20), 353 (100); Calc’d for C36H23F3N3: C, 73.93; H, 5.96; N, 6.63. Found: C, 74.29; H, 6.13; N, 6.63.

The corresponding 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl, phenylethynylphenyl and 4-hexynylphenyl) can be prepared through the same procedure by starting with acetophenone in place of trifluorocacetophenone.
EXAMPLE 9

The following example illustrates the synthesis of an imide copolymer where 10 mole percent of the diamine used contains pendent ethynyl groups. 1,1-Bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (0.001 m, 0.366 g), BDAF (0.009 m, 4.6625 g), 6FDA (0.01 m, 4.4425 g) and DMAc (54.1 g) were added to a three neck flask equipped with a stirring motor and nitrogen purge. The reaction was stirred for eight hours at RT to form a polyamide acid with η_{inh}=1.54 dL/g. This solution was cast onto plate glass and cured in air for one hour each at 100°, 200° and 300° C. to form a creasible, lightly crosslinked yellow imide copolymer film with T_g=273° C. by DSC. This film was completely insoluble in DMAc or chloroform but did swell.

TABLE 1
CHARACTERIZATION OF POLYMERS

<table>
<thead>
<tr>
<th>R =</th>
<th>R' =</th>
<th>Polyamide Acid η_{inh}, dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CO</td>
<td>0.94</td>
</tr>
<tr>
<td>H</td>
<td>C(CF_3) =</td>
<td>0.80</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>CO</td>
<td>0.77</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>C(CF_3) =</td>
<td>0.68</td>
</tr>
<tr>
<td>C_7H_8</td>
<td>CO</td>
<td>0.40</td>
</tr>
<tr>
<td>C_7H_8</td>
<td>C(CF_3) =</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Note: No T_g's were detected by DSC for the polyimides.

EXAMPLE 10

The following example illustrates the synthesis of an imide copolymer where 10 mole percent of the diamine used contains pendent phenylethynyl groups. 1,1-Bis(4-aminophenyl)-1-(4-phenylethynyl)-2,2,2-trifluoroethane (0.001 m, 0.4425 g), BDAF (0.009 m, 4.6625 g), 6FDA (0.01 m, 4.4425 g) and DMAc (54.1 g) were added to a three neck flask equipped with a stirring motor and nitrogen purge. The reaction was stirred for eight hours at RT to form a polyamide acid with η_{inh}=1.47 dL/g. This solution was cast onto plate glass and curved in air for one hour each at 100°, 200° and 350° C. to form a creasible, lightly crosslinked yellow 65 imide copolymer film with T_g=273° C. by DSC. This film was completely insoluble in DMAc or chloroform but did swell.

TABLE 2
CHARACTERIZATION OF COPOLYMERS

where 90 mole % of Ar = BDAF and 10 mole % of Ar =

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Polyamide Acid η_{inh}, dL/g</th>
<th>DSC T_g, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R =</td>
<td></td>
<td>Original</td>
</tr>
<tr>
<td>H</td>
<td>1.54</td>
<td>265</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>1.47</td>
<td>265</td>
</tr>
</tbody>
</table>
### TABLE 2-continued

<table>
<thead>
<tr>
<th>Characterization of Copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer</td>
</tr>
<tr>
<td>CaH5</td>
</tr>
</tbody>
</table>

*DMAC at 25°C and 0.5% concentration.
*DSC at a heating rate of 20°C./min.
*Chemically imidized, acetic anhydride and triethylamine.
*After heating to 400°C.

### TABLE 3

**THERMAL STABILITY AND FILM PROPERTIES OF COPOLYMERS**

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Loss, °C.</th>
<th>Strength, Ksi</th>
<th>Modulus, Ksi</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>468</td>
<td>493</td>
<td>14.8b</td>
<td>416b</td>
</tr>
<tr>
<td>CaH5</td>
<td>450</td>
<td>493</td>
<td>17.7c</td>
<td>518c</td>
</tr>
<tr>
<td>CaH4</td>
<td>401</td>
<td>493</td>
<td>17.8b</td>
<td>534b</td>
</tr>
</tbody>
</table>

*TGA at a heating rate of 2.5°C./min in flowing atmosphere, 15 ml/min.
*Cured at 350°C. in air for 1 hr.
*Cured at 300°C in air for 1 hr.

We claim:

1. A diamine having a pendant ethynyl or substituted ethynyl group and having the following structural formula:

   ![Structural formula](image)

   where 90 mole % of Ar = BDAF and 10 mole % of Ar =

   ![Structural formula](image)

   wherein R is a member selected from the group consisting of hydrogen, alkyl, and phenyl, and R' is a member selected from the group consisting of CH3 and CF3.

2. A diamine according to claim 1, wherein R is hydrogen.

3. A diamine according to claim 1, wherein R is a butyl group.

4. A diamine according to claim 1, wherein R is a phenyl group.

*****

TGA* 5% Weight Tensile Tensile