ABSTRACT
Crystalline imide/arylene ether block copolymers are prepared by reacting anhydride terminated poly(amic acids) with amine terminated poly(arylene ethers) in polar aprotic solvents and chemically or thermally cyclodehydrating the resulting intermediate poly(amic acids). The block copolymers of the invention have one glass transition temperature or two, depending on the particular structure and/or the compatibility of the block units. Most of these crystalline block copolymers form tough, solvent resistant films with high tensile properties. While all of the copolymers produced by the present invention are crystalline, testing reveals that copolymers with longer imide blocks or higher imide content have increased crystallinity.

6 Claims, 2 Drawing Sheets
CROSS-REFERENCE

This is a continuation of application Ser. No. 07/575,738, filed on Aug. 31, 1990, now abandoned, which is a continuation-in-part of our application Ser. No. 07/439,317, filed Nov. 21, 1989, now U.S. Pat. No. 5,112,923.

BACKGROUND OF THE INVENTION

1. Technical Field of the Invention

The present invention relates generally to high performance structural resins for advanced aerospace applications. It relates particularly to a tough, solvent resistant, crystalline imide/arylene block copolymer with a broad melting point, and especially to adhesives resistant, crystalline imide/arylene block copolymers. It relates particularly to a tough, solvent resistant, crystalline imide/arylene block copolymer with aromatic diamines. The intermediate poly(amic acid) is either thermally or chemically cyclodehydrated with aromatic diamines. The intermediate poly(amic acid) is either thermally or chemically cyclodehydrated to form the polyimide, which has a repeat unit of the general type

\[ \text{Ar} \text{ is a tetravalent aromatic radical which can be as simple as } 1,2,4,5 \text{-tetrasubstituted benzene, or may be as complex as a bis-4-(o-diphenylene) having the general structure} \]

where \( X = \text{nil, O, S, SO}_2, \text{C} = \text{O}, \text{etc} \). As well, \( \text{Ar} \) may be any other appropriate tetravalent radical. \( \text{Ar}^\prime \) is a divalent aromatic radical which may be 1,3-phenylene, 1,4-phenylene, 4,4'-biphenylene, 4,4'-oxydiphenylene, 4,4'-thiodiphenylene, 4,4'-carbonyldiphenylene, 4,4'-methanediphenylene or any other appropriate divalent radical.


Wholly aromatic polyimides are known for their exceptional thermal, thermooxidative, and chemical resistance but are generally difficult to process as structural adhesives or composite matrices. Several polyimides such as Kapton® [DuPont], PI-2080 [Upjohn], XU-218 [Ciba-Geigy], Ultem® [General Electric], and LARC-TPI [Mitsui Toatsu] are commonly available commercially and used as films, moldings, adhesives, and composite matrices.

Poly(arylene ethers) are condensation polymers commonly synthesized by nucleophilic displacement of activated aromatic halides in polar solvents by alkali metal phenates to form a repeat unit of the general type

\[ \text{Ar is arylene and } y = \text{C} = \text{O}, \text{SO}_2, \text{etc}. \]


Poly(arylene ethers) are known for their good mechanical properties, good thermooxidative stability, relative ease of processing, and solubility in common organic solvents. For certain applications, resistance to common organic solvents is a requirement. Several poly(arylene ethers) such as Udel® polysulfone [Amoco], Kadel® polyketone [Amoco], PEEK® polyetherketone [ICI] are commercially available and used as films, moldings, adhesives, and composite matrices.

Amine terminated arylene ethers have been prepared by several different methods. The preparation of amine terminated polysulfone oligomers using p-aminophenol as the end-capping compound was reported in 1974 [J.
SUMMARY OF THE INVENTION

Accordingly, it is a primary object of the present invention to provide a series of block copolymers that contain polyimide and poly(arylene ether) segments.

Another object of the present invention is to provide a block copolymer that contains polyimide and poly(arylene ether) segments, such that the copolymer has a high degree of crystallinity.

Another object of the present invention is to provide a block copolymer that contains polyimide and poly(arylene ether) segments, wherein the length of the polyimide and poly(arylene ether) segments are easily controlled, so that copolymers with various desired physical and mechanical properties can be produced.

Another object of the present invention is to provide a block copolymer that contains polyimide and poly(arylene ether) segments, wherein the copolymer forms a tough, solvent resistant film and coating material.

Another object of the present invention is to provide a block copolymer that contains polyimide and poly(arylene ether) segments, wherein the copolymer forms a film and coating material with high tensile properties.

Another object of the present invention is to provide a film and coating material useful for both industrial and aerospace applications requiring adhesives and composites, with good solvent resistance and high tensile properties, such as strength, modulus and elongation.

By the present invention, the foregoing and additional objects were obtained by synthesizing imide/arylene copolymers from the reaction of anhydride terminated poly(amic acids) and amine terminated poly(arylene ethers). After curing, the resulting block copolymers had glass transition temperatures ranging from 165 °C to 220 °C. Some had two glass transitions, corresponding to the arylene/ether segment and the imide segment, indicating a phase separation in the films due to polymer-to-polymer incompatibility. The block copolymers also had broad crystalline melting points (Tm) from 335 °C to 355 °C. Some had two Tm's and, therefore, possibly two crystalline forms. Solution cast films of the block copolymers were tough and flexible with tensile strength, tensile moduli, and elongation at break up to 16,200 psi, 535,000 psi, and 8% respectively at 25 °C. And, depending on the glass transition temperatures of the arylene/ether segment, some block copolymers maintained good mechanical properties at 93 °C and 177 °C.

Moldings were prepared from polymers which were solution imidized, by distilling a toluene/water azotropic mixture from the reaction at 155 °C for 16 hours, to form powders. The powders were compression molded in stainless steel molds in hydraulic presses with electrically heated platens. The moldings were machine into compact tension specimens and tested for toughness. The values of fracture toughness, KIC, and fracture energy, GIC, for the homopolymers are extremely high and values for the copolymers are excellent and increase with increasing block length.

Wide-angle x-ray scattering data indicated that block and segmented copolymer films cured up to 300 °C for 1 hour and solution imidized powders were crystalline. Furthermore, copolymers with longer imide blocks or higher imide content had more intense and sharper x-ray peaks, indicating more crystallinity than the others.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 demonstrates wide-angle x-ray scattering data for a copolymer film of the present invention; and FIG. 2 demonstrates wide-angle x-ray scattering data for a copolymer powder of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The general reaction sequence for the block copolymers of the present invention is represented by the following equation:

\[
\text{RT, SOLVENT}
\]

\[
\text{FIG.}
\]

\[
\text{1}
\]

\[
\text{2}
\]
wherein n is an integer from 4 to 100. The solvent is preferably N,N-dimethylacetamide, but it may be N-methylpyrrolidinone, m-cresol, N,N-dimethylformamide, dimethyl sulfoxide, or ether solvents such as diglyme.

Cyclodehydration is accomplished chemically or by heating the intermediate poly(amic acid) at temperatures exceeding 150°C.

PAA is representative of a poly(amic acid) synthesized by reacting excess dianhydride with a diamine as generically shown below:

\[
\text{(n+1)}O \quad \text{Ar} \quad O + \quad (c)H_2N-Ar'-NH_2
\]

\[
\text{cylodehydration}
\]

\[
\text{Ar is selected from a group of radicals consisting of:}
\]

wherein n is an integer from 4 to 100. The solvent is preferably N,N-dimethylacetamide, but it may be N-methylpyrrolidinone, m-cresol, N,N-dimethylformamide, dimethyl sulfoxide or ether solvents such as diglyme.

PI is representative of a polyimide synthesized by the cyclodehydration of the PAA component as generically shown below:
wherein \( Y \) is not a substituent or is a substituent selected from the group consisting of \( \text{O, C}=\text{O, and C(CF}_3\text{)}_2 \).

\( \text{Ar}' \) is selected from a group of radicals consisting of:

\[ PAE \text{ is representative of a poly(arylene ether) synthesized by reacting an activated aromatic dihalide with a bisphenol as generically shown below:} \]

\[ (n + \frac{m}{2})X\text{Ar}Y \text{Ar}Y + (m)\text{HOAr} - \text{OH} + (m)\text{NH}_2\text{Ar} - \text{OH} \]

\[ \text{H}_2\text{N}-\text{O}[\text{Ar}R\text{YAr}]\text{O}[\text{Ar}R\text{YAr}]\text{O}[\text{Ar}R\text{YAr}]\text{O}[\text{Ar}R\text{YAr}]\text{O}\text{NH}_2 \]

wherein \( n \) is an integer from 4 to 100. The solvent is preferably \( \text{N, N-dimethylacetamide} \), but may be other solvents such as \( \text{N-methylpyrrolidinone, N,N-dimethylformamide, or dimethyl sulfoxide} \).

\( X \) is either a fluorine or chlorine atom. The \( \text{Base} \) is an alkali metal hydroxide or carbonate selected from the group consisting of \( \text{NaOH, KOH, Na}_2\text{CO}_3 \) and \( \text{K}_2\text{CO}_3 \).

\( R \) and \( R' \) are selected from a group of aromatic radicals consisting of:
wherein $Y$ is not a substituent or is a substituent selected from the group consisting of $O$, $S$, $C=O$, $SO_2$, $CH_2$, $C(CH_3)_2$, and $C(CF_3)_2$.

$X$ is $F$, and

$R^1$ is

represents either 3-aminophenol or 4-aminophenol.

The following examples illustrate the reaction sequence for the synthesis of several polyimides according to the present invention. However, the invention is not limited to these examples.

**EXAMPLE 1**

The following example illustrates the reaction sequence for the synthesis of imide/arylene ether block copolymer

The theoretical number average molecular weight ($M_n$) of both the poly(amic acid) block and the poly(arylene ether) block is 6545 g/mole. This copolymer is designated ATPAE 6545//1,3-BABB/BTDA 6545.

Amine Terminated Poly(Arylene Ether)

1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB) (0.1 m, 32.231 g), 2,2-bis(4-hydroxyphenyl)propane (BPA) (0.0925 m, 21.1172 g), 4-aminophenol (0.015 m, 1.637 g), powdered potassium carbonate (0.22 m, 30.4 g), N,N-
5,418,300

Amine Terminated Poly(Arylene Ether)

1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB) (0.07 m, 22.562 g), 2,2-bis(4-hydroxyphenyl)propane (BPA) (0.0595 m, 13.583 g), 4-aminophenol (0.021 m, 2.292 g), powdered potassium carbonate (0.154 m, 21.3 g), N,N-dimethylacetamide (DMAc) (15 ml) and toluene (40 ml) were added to a three-neck flask equipped with a Dean-Stark trap and nitrogen purge. The reaction was heated to 155°C during approximately 4 hours while collecting a toluene/water azeotropic mixture and held at 155°C overnight. The reaction was filtered, neutralized with a small amount of acetic acid and precipitated in water. After washing and boiling in water, drying at 80°C in vacuum provided a light tan solid in greater than 95% yield. The resulting amine-terminated arylene ether oligomer had $\eta_{inw} = 0.16$ dL/g in DMAc at 25°C.

Anhydride Terminated Poly(amic acid)

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA) (0.0035 m, 1.1276 g) was added to a solution of 1,3-bis(4-fluorobenzoyl)benzene (1,3-BABB) (0.003087 m, 1.5452 g) and DMAc (15.2 g) and stirred for 3 hours to provide a clear yellow solution.

Imide/Arylene Ether Block Copolymer

The amine-terminated arylene ether (2.6730 g) was dissolved in DMAc (15.2 g) to provide a clear brown solution which was added to the anhydride-terminated poly(amic acid) solution. The combined solution became viscous immediately and gelled within approximately 10 minutes. Stirring overnight provided a viscous orange solution ($\eta_{inw} = 0.89$ dL/g, DMAc at 25°C). Casting onto plate glass and curing 1 hour each at 100°C, 200°C, and 300°C provided a tough, flexible, clear yellow film (Tg=165°C, Tm=335°C and 350°C, DSC at 20°C/min).

EXAMPLE II

The following example illustrates the reaction sequence for the synthesis of imide/arylene ether block copolymer where

\[
\text{Ar} \quad \text{X is F, and} \\
\text{Ar'} \quad \text{R' is} \\
\text{R} \\
\]

X is F, and

R' is

The theoretical number average molecular weight ($M_n$) of both the poly(amic acid) block and the poly(arylene ether) block is 3110 g/mole. This copolymer is designated ATPE 3110/1,3-BABB/BTDA 3110.

Amine Terminated Poly(Arylene Ether)

1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB) (0.07 m, 22.562 g), 2,2-bis(4-hydroxyphenyl)propane (BPA) (0.0595 m, 13.583 g), 4-aminophenol (0.021 m, 2.292 g), powdered potassium carbonate (0.154 m, 21.3 g), N,N-dimethylacetamide (DMAc) (115 ml) and toluene (40 ml) were added to a three-neck flask equipped with a Dean-Stark trap and nitrogen purge. The reaction was heated to 155°C during approximately 4 hours while collecting a toluene/water azeotropic mixture and held at 155°C overnight. The reaction was filtered, neutralized with a small amount of acetic acid and precipitated in water. After washing and boiling in water, drying at 80°C in vacuum provided a light tan solid in greater than 95% yield. The resulting amine-terminated arylene ether oligomer had $\eta_{inw} = 0.16$ dL/g in DMAc at 25°C.

Anhydride Terminated Poly(amic acid)

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA) (0.0035 m, 1.1276 g) was added to a solution of 1,3-bis(4-fluorobenzoyl)benzene (1,3-BABB) (0.00266 m, 1.13315 g) and DMAc (13.9 g) and stirred for 3 hours to provide a clear yellow solution.

Imide/Arylene Ether Block Copolymer

The anhydride-terminated arylene ether (2.4593 g) was dissolved in DMAc (13.9 g) to provide a clear brown solution which was added to the anhydride-terminated poly(amic acid) solution. The combined solution became viscous within 1 hour ($\eta_{inw} = 0.63$ dL/g, DMAc at 25°C). Casting onto plate glass and curing 1 hour each at 100°C, 200°C, and 300°C provided a tough, flexible, clear yellow film (Tg=175°C, Tm=354°C, DSC at 20°C/min).

EXAMPLE III

The following example illustrates the reaction sequence for the synthesis of the imide/arylene ether segmented copolymer when
The theoretical $M_r$ of the poly(arylene ether) block is 6545 g/mole while the poly(amic acid) segment is of random length but has an average $M_r$ of 6545 g/mole. The method of addition of starting materials leads to a final structure for this copolymer of a type which is different from the copolymer described in Example I. This copolymer is designated ATPAE 6545+1,3-BABB+BTDA (6545).

**Amine Terminated Poly(Arylene Ether)**

This material is the same as the material prepared in Example I.

**Imide/Arylene Ether Semi-Block Copolymer**

This copolymer was prepared with the poly(amic acid) segment synthesized in the presence of the AT-PAE, not separately as in Example I.

1,3-BABB (0.002205 m, 1.1037 g) and ATPAE (0.0025 m, 1.9093 g) were dissolved in DMAC (21.6 g). Addition of BTDA (0.0025 m, 0.8056 g) produced a viscous solution immediately that gelled within approximately 15 minutes. Stirring 24 hours at 45°C produced a clear viscous solution ($\eta_{inh} = 1.15$ dL/g, DMAC at 25°C). Casting onto plate glass and curing 1 hour each at 100°C, 200°C, and 300°C provided a tough, flexible, clear yellow film ($T_g = 165°C$ and $220°C$, $T_m = 338°C$ and $353°C$, DSC at 20°C/min).

Data for polymer and copolymer inherent viscosities and glass transition temperatures are presented in Tables I and II.

### TABLE I

<table>
<thead>
<tr>
<th>Oligomer or Polymer</th>
<th>$\eta_{inh}$, dL/g</th>
<th>$T_g$, °C. by DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATPAE 3110</td>
<td>0.16 (CHCl₃)</td>
<td>133</td>
</tr>
<tr>
<td>ATPAE 6545</td>
<td>0.29 (CHCl₃)</td>
<td>146</td>
</tr>
<tr>
<td>ATPAE 3110 + BTDA</td>
<td>0.79 (DMAC)</td>
<td>165</td>
</tr>
<tr>
<td>ATPAE 6545 + BTDA</td>
<td>1.10 (DMAC)</td>
<td>222 (350)</td>
</tr>
<tr>
<td>1,3-BABB + BTDA</td>
<td>0.80 (DMAC)</td>
<td>155</td>
</tr>
<tr>
<td>FBB + BPA</td>
<td>0.70 (CHCl₃)</td>
<td>155</td>
</tr>
<tr>
<td>PI + PAE (1:1 blend)</td>
<td>1.15 (DMAC)</td>
<td>165, 220 (338, 353)</td>
</tr>
<tr>
<td>ATPAE 6545 + 1,3-BABB + BTDA (6545)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE II

**CHARACTERIZATION OF BLOCK COPOLYMERS**

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Polyamic Acid, $\eta_{inh}$ (dL/g)</th>
<th>DSC $T_g$, °C.</th>
<th>$T_b$ Transition, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA</td>
<td>0.63, 0.90</td>
<td>175, 175</td>
<td>193</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA 6545</td>
<td>0.87, 1.73</td>
<td>170 (354)</td>
<td>249</td>
</tr>
<tr>
<td>ATPAE 6545/1,3-BABB/BTDA 6545</td>
<td>0.81, 1.00</td>
<td>168 (354)</td>
<td>185</td>
</tr>
<tr>
<td>ATPAE 6545/1,3-BABB/BTDA 4565</td>
<td>0.89, 1.03</td>
<td>165 (335)</td>
<td>168, 205 (343, 355)</td>
</tr>
</tbody>
</table>

This copolymer was prepared with the poly(amic acid) segment synthesized in the presence of the AT-PAE, not separately as in Example I.

Data for polymer and copolymer properties, including tensile strength, tensile modulus, elongation, fracture toughness, and fracture energy, are presented in Table III.

### TABLE III

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength, Ksi</th>
<th>Tensile Modulus, Ksi</th>
<th>Elongation, %</th>
<th>$K_{ic}$ psi V/in</th>
<th>$G_{ic}$ in-lb/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATPAE 3110/BTDA</td>
<td>10.9, 9.1</td>
<td>1.2, 367</td>
<td>333</td>
<td>4.0, 3.3</td>
<td>80, 5.2</td>
</tr>
<tr>
<td>ATPAE 6545/BTDA</td>
<td>11.1, 8.5</td>
<td>367, 329</td>
<td>—</td>
<td>5.7, 5.2</td>
<td>&gt;100, 5.2</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA</td>
<td>15.0, 12.7</td>
<td>3.4, 514</td>
<td>449</td>
<td>3.5, 3.2</td>
<td>38, 3370</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA 6545</td>
<td>16.2, 14.5</td>
<td>5.9, 535</td>
<td>516</td>
<td>3.8, 3.7</td>
<td>30, 3900</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA 4565</td>
<td>16.2, 14.5</td>
<td>5.9, 535</td>
<td>516</td>
<td>3.8, 3.7</td>
<td>30, 3900</td>
</tr>
</tbody>
</table>

**FILM PROPERTIES**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength, Ksi</th>
<th>Tensile Modulus, Ksi</th>
<th>Elongation, %</th>
<th>$K_{ic}$ psi V/in</th>
<th>$G_{ic}$ in-lb/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATPAE 3110/BTDA</td>
<td>10.9, 9.1</td>
<td>1.2, 367</td>
<td>333</td>
<td>4.0, 3.3</td>
<td>80, 5.2</td>
</tr>
<tr>
<td>ATPAE 6545/BTDA</td>
<td>11.1, 8.5</td>
<td>367, 329</td>
<td>—</td>
<td>5.7, 5.2</td>
<td>&gt;100, 5.2</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA</td>
<td>15.0, 12.7</td>
<td>3.4, 514</td>
<td>449</td>
<td>3.5, 3.2</td>
<td>38, 3370</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA 6545</td>
<td>16.2, 14.5</td>
<td>5.9, 535</td>
<td>516</td>
<td>3.8, 3.7</td>
<td>30, 3900</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTDA 4565</td>
<td>16.2, 14.5</td>
<td>5.9, 535</td>
<td>516</td>
<td>3.8, 3.7</td>
<td>30, 3900</td>
</tr>
</tbody>
</table>
### TABLE III-continued

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength, Ksi</th>
<th>Tensile Modulus, Ksi</th>
<th>Elongation, %</th>
<th>$K_{in}$ psi $V/\text{in}$</th>
<th>$G_{in}$ in-lb/in²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTDA 6545</td>
<td>RT 93°C 177°C</td>
<td>RT 93°C 177°C</td>
<td>RT 93°C 177°C</td>
<td>RT 93°C 177°C</td>
<td>RT 93°C 177°C</td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTD</td>
<td>13.2 10.5 1.4</td>
<td>435 433</td>
<td>35 3.1</td>
<td>15.1 74</td>
<td>3930 35</td>
</tr>
<tr>
<td>BTDA 3110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATPAE 3110/1,3-BABB/BTD</td>
<td>14.2 10.9 2.7</td>
<td>519 437</td>
<td>114 4.3</td>
<td>3.3 49</td>
<td>4750 44</td>
</tr>
<tr>
<td>ATPAE 6545 + 1,3-BABB +</td>
<td>16.0 12.7 2.2</td>
<td>457 443</td>
<td>85 6.1</td>
<td>3.8 53</td>
<td>3350 25</td>
</tr>
<tr>
<td>BTDA (6545)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-BABB + BTDA</td>
<td>22.0 15.2 630</td>
<td>540 8.3</td>
<td>21 4890</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>FBB + BPA</td>
<td>12.7 7.5 —</td>
<td>381 340</td>
<td>136 124</td>
<td>—</td>
<td>5570 62</td>
</tr>
</tbody>
</table>

*continued*

**FIGS. 1 and 2 show wide-angle x-ray scattering data for the ATPAE 6454//1,3-BABB/BTDA 6545 copolymer film and powder, respectively.**

What is new and desired to be secured by Letters Patent of the United States is:

1. A crystalline imide/arylene ether block copolymer prepared by reacting an anhydride terminated polyamic acid and an amine terminated poly(arylene ether) in a polar aprotic solvent and cyclodehydrating the intermediate poly(amic acid), the anhydride terminated poly(amic acid) having the formula:

   \[
   \text{R} = \left(\begin{array}{c}
   \text{O} \\
   \text{O} \\
   \text{Ar} \\
   \text{C} \quad \text{OH} \\
   \text{H} \quad \text{C} \\
   \text{NH} \quad \text{Ar'} \quad \text{NH} \\
   \text{O} \quad \text{O} \\
   \text{n}
   \end{array}\right)
   \]

   \(n\) is an integer from 4 to 100; wherein

   \(\text{Ar}\) is

   \(=\left(\begin{array}{c}
   \text{O} \\
   \text{O} \\
   \text{C} \quad \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H}
   \end{array}\right)
   \)

   and

   \(\text{Ar'}\) is

   \(=\left(\begin{array}{c}
   \text{O} \\
   \text{O} \\
   \text{C} \quad \text{H} \\
   \text{H} \\
   \text{H}
   \end{array}\right)
   \)

and the amine terminated poly(arylene ether) having the formula

\[
\text{H}_2\text{N} \left(\begin{array}{c}
\text{O} \\
\text{O} \\
\text{R} \quad \text{O} \\
\text{O} \\
\text{R'}
\end{array}\right)
\]

2. The crystalline imide/arylene ether block copolymer of claim 1, wherein the theoretical number average molecular weight of both the poly(amic acid) block and the poly(arylene ether) block is between about 1000 g/mole and 10,000 g/mole.

3. The crystalline imide/arylene ether block copolymer of claim 1, wherein the theoretical number average molecular weight of both the poly(amic acid) block and the poly(arylene ether) block is about 3000 g/mole.

4. The crystalline imide/arylene ether block copolymer of claim 1, wherein the theoretical number average molecular weight of both the poly(amic acid) block and the poly(arylene ether) block is about 6500 g/mole.

5. The crystalline imide/arylene ether block copolymer of claim 1, wherein the theoretical number average molecular weight of both the poly(amic acid) block and the poly(arylene ether) block is about 6545 g/mole.

6. The crystalline imide/arylene ether block copolymer of claim 1, wherein the theoretical number average molecular weight of the poly(arylene ether) block is between about 1000-10,000 g/mole, and the poly(amic acid) block is of random length, but whose number average molecular weight is about 1000-10,000 g/mole.

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