NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is, therefore, available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.2).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant licenses to commercial concerns. Although NASA encourages nonexclusive licensing to promote competition and achieve the widest possible utilization, NASA will consider the granting of a limited exclusive license, pursuant to the NASA Patent Licensing Regulations, when such a license will provide the necessary incentive to the licensee to achieve early practical application of the invention.

Address inquiries and all applications for license for this invention to NASA Patent Counsel, Langley Research Center, Mail Code 279, Langley Station, Hampton, VA 23665. Approved NASA forms for application for nonexclusive or exclusive license are available from the above address.
This invention relates to novel polyarylene ethers which possess the combination of high strength, toughness, and high use temperature with ease of extrusion and formation into complex objects. These polyarylene ethers are suitable for use in adhesives, coatings, films, membranes, and composite matrices.

The polyarylene ethers of this invention are the polycondensation products from the reaction of either 1,3-bis (4-chloro or fluoro-benzoyl) benzene or 1,4-bis (4-chloro or fluorobenzoyl) benzene with any one of the following bisphenolic compounds:

- bis (3-hydroxyphenyl) methane,
- bis (4-hydroxyphenyl) methane,
- 1,1-dimethyl-bis (4-hydroxyphenyl)methane,
- or 9,9-bis (4-hydroxyphenyl) fluorene.

Random and block copolymers are also comprehended. These are prepared by (a) reacting varying molar quantities of 1,3-bis (4-chloro or fluoro-benzoyl) benzene and 1,4-bis (4-chloro or fluorobenzoyl) benzene with substantially stoichiometric amounts of any one of the bisphenolic compounds; or (b) reacting a substantially stoichiometric amount of either 1,3-bis (4-chloro or fluorobenzoyl) benzene or 1,4-bis (4-chloro or fluorobenzoyl) benzene with varying molar quantities of any two of the bisphenolic compounds.

The novelty of this invention appears to reside in the composition of the polymers and copolymers, which possess a highly desirable combination of properties not available in the prior art.
Origin of the Invention

The invention described herein was made in the performance of work under a NASA Contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958 (72 Stat. 435; 42 USC 2457).

Field of the Invention

The present invention relates generally to aromatic polymers. It relates particularly to polyarylene ethers, which are condensation polymers having a repeating unit represented by $\overline{(-O-Ar-O-Ar')_n}$, wherein Ar is an aromatic divalent radical, and Ar' is an aromatic divalent radical which contains an electron withdrawing group such as carbonyl or sulfonyl.

Background of the Invention

A variety of polyarylene ethers are known and several are commercially available for use in different applications such as adhesives, composite matrices, moldings, films and membranes. Specific commercial examples include UDEL® P-1700 polysulfone and RADEL® from Union Carbide Corporation; VICTREX® PES200 and 300P polyethersulfones, and PEEK® polyetheretherketone from Imperial Chemical Industries; and Stylan® polyetherketone from Raychem Corporation.

The synthesis and properties of polyarylene ethers have been studied and are reported. Representative publications are: H. Lee et al, Chapter 5, entitled "Aromatic Polysulfones" in New Linear Polymers, McGraw-Hill Book Company, New York 1967; R. N. Johnson et al, Journal of Polymer Science, Part A-1, 5, 2375 (1967); T. E. Attwood et al, Polymer 22, 1096 (1981) and R. N. Johnson in Encyclopedia of Polymer Science and Technology (H. F. Mark,
Amorphous polyarylene ethers, as exemplified by the polysulfones and polyethersulfones, are relatively tough materials with moderate tensile strengths and moduli, moderate processability, and poor solvent resistance.

Polyetheretherketone and polyetherketone are semi-crystalline polyarylene ethers with a high degree of toughness, difficult processability, excellent solvent resistance and excellent tensile properties. There is a need for a polyarylene ether which is relatively inexpensive, easily extruded and formed into various complex objects, and which exhibits higher strength properties than the amorphous polyarylene ethers while having the toughness offered by the semi-crystalline polyarylene ethers. In addition, there is also a need for a polyarylene ether which offers a higher use temperature and at least comparable mechanical properties with respect to either the amorphous or semi-crystalline polyarylene ethers, and which can be extruded and shaped into complex objects.

It is accordingly an object of the present invention to provide a new, relatively inexpensive polyarylene ether which affords what has not been available in the prior art, viz., the combination of high strength, toughness, and high use temperature with ease of extrusion and formation into complex objects.

It is another object of the present invention to provide a new polyarylene ether which is useful in adhesives, coatings, films, membranes, and composite matrices.

Summary of the Invention

According to the present invention, the foregoing and additional objects are attained by providing a polyarylene ether which is formed as the polycondensation product from the reaction of either 1,3-bis(4-chloro or fluorobenzoyl)benzene or 1,4-bis(4-chloro or fluorobenzoyl)benzene with any one of the following
bisphenolic compounds: bis(3-hydroxyphenyl)methane, bis(4-hydroxyphenyl)methane, 1,1-dimethyl-bis(4-hydroxyphenyl)methane, or 9,9-bis(4-hydroxyphenyl)fluorene. The use of other activated dihalo monomers and bisphenolic compounds resulted in polyarylene ethers which did not possess the desired combination of properties.

Random and block copolymers were also prepared by reacting varying molar quantities of 1,3-bis(4-chlorobenzoyl)benzene and 1,4-bis(4-chlorobenzoyl)benzene with substantially stoichiometric amounts of any one of bis(3-hydroxyphenyl)methane, bis(4-hydroxyphenyl)methane, 1,1-dimethyl-bis(4-hydroxyphenyl)methane, or 9,9-bis(4-hydroxyphenyl)fluorene. These copolymers also possessed the desired combination of high strength, toughness, solvent resistance, and high use temperature with ease of extrusion and formation into complex objects. Moreover, random and block copolymers were also prepared by reacting a stoichiometric amount of either 1,3-bis(4-chlorobenzoyl)benzene or 1,4-bis(4-chlorobenzoyl)benzene with varying molar quantities of any two of the following bisphenolic compounds: bis(3-hydroxyphenyl)methane, bis(4-hydroxyphenyl)methane, 1,1-dimethyl-bis(4-hydroxyphenyl)methane, or 9,9-bis(4-hydroxyphenyl)fluorene. These copolymers also possessed the desired combination of properties set forth above. All of the polyarylene ethers of the present invention, including the random and block copolymers, are eminently suitable for use in adhesives, coatings, films, membranes, and composite matrices.

**Detailed Description of the Invention**

For a more complete understanding of the present invention, including its objects and benefits, the following detailed description is set forth. In the Examples, which are presented for illustrative purposes only, all parts and percentages are by weight.
Example I

Provision of Monomers

A. 1,3-bis(4-chlorobenzoyl)benzene (referred to hereinafter as "1,3-CBB")

Powdered anhydrous aluminum chloride (160 g, 1.2 moles) was added to a cold (10 to 15°C) stirred solution of isophthaloyl chloride (101.5 g, 0.5 mole) in chlorobenzene (904 g, 8.0 moles), during ten minutes, and the reaction was stirred at this temperature for one hour. The reaction was then stirred for 16 hours at room temperature, followed by heating to 70 to 80°C and stirring for an additional three hours. The reaction product was precipitated in cold, aqueous hydrochloric acid, washed with water twice and methanol once. Filtration separated a white solid which was dried at 100°C to yield 162 g of crude product (91 percent yield). The crude product was recrystallized twice from toluene to afford 1,3-bis(4-chlorobenzoyl)benzene as white crystals (m.p. 210.5 - 211.5°C, 85 percent yield).

Elemental analyses - calculated for C\textsubscript{20}H\textsubscript{12}C\textsubscript{12}O\textsubscript{2}: C, 67.63 percent; H, 3.40 percent; Cl, 19.96 percent. Found: C, 67.62 percent; H, 3.36 percent; Cl, 20.04 percent.

B. 1,3-Bis(4-fluorobenzoyl)benzene (referred to hereinafter as "1,3-FBB")

Anhydrous powdered aluminum chloride (164.7 g, 1.24 moles) was added during 5 minutes to a stirred solution of isophthaloyl chloride (101.5 g, 0.5 mole) in fluorobenzene (480.5 g, 5.0 moles). The reaction became exothermic with the temperature increasing to about 60°C. After the exotherm subsided, the reaction was maintained at about 75°C for 4 hours, and then precipitated in cold, aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene, and the residual solid was collected by filtration. The crude product was recrystallized from toluene to afford 1,3-bis(4-fluorobenzoyl)benzene as white crystals (m.p. 178-179°C, 81% yield). Elemental analysis calculated for C\textsubscript{20}H\textsubscript{12}F\textsubscript{2}O\textsubscript{2}: C, 74.53%; H, 3.75%; F, 11.79%. Found: C, 74.33%; H, 3.59%; F, 11.42%.
C. 1,4-bis(4-chlorobenzoyl)benzene (referred to hereinafter as "1,4-CBB")

To a solution of terephthaloyl chloride (101.5g, 0.5 mole) and chlorobenzene (738g, 6.5 moles), anhydrous powdered aluminum chloride (160g, 1.2 moles) was added with stirring. After an exothermic reaction raising the temperature to 30°C, the solution was heated to 95°C and held for three hours. Upon cooling, the solution was poured into cold, aqueous hydrochloric acid to precipitate a cream colored solid, which was isolated by filtration. The cream colored solid was thoroughly washed with methanol and dried at 100°C in air (90 percent crude yield). Recrystallization from N,N'-dimethylacetamide afforded a yellow crystalline solid (m.p. 257 - 258°C) [lit. m.p. 256°C, C.D. Marrable, British Patent 1,139,296].

D. 1,4-Bis(4-fluorobenzoyl)benzene (referred to hereinafter as "1,4-FBB")

Anhydrous powdered aluminum chloride (80.0 g, 0.60 moles) was added during 10-15 minutes to a stirred solution of terephthaloyl chloride (50.8 g, 0.25 mole) in fluorobenzene (241 g, 2.5 moles). The reaction became exothermic with the temperature increasing to about 60°C. After the exotherm subsided, the reaction was maintained at about 75°C for 4 hours, and then precipitated in cold, aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene, and the residual solid was collected by filtration. The crude product was recrystallized from toluene to afford 1,4-bis(4-fluorobenzoyl)benzene as white plates (m.p. 218.5-219.5°C, 88% yield). Elemental analysis calculated for C_{20}H_{12}F_{2}O_{2}: C, 74.53%; H, 3.75%, F, 11.79%. Found: C, 74.60%; H, 3.80%, F, 11.83%.

E. Bis(3-hydroxyphenyl)methane (referred to hereinafter as "3-HPM")

A cold solution of concentrated sulfuric acid (88ml,
1.58 moles) in ice water (900ml) was added to bis(3-aminophenyl)methane (39.65g, 0.20 mole). While the suspension was maintained at 0°C, a solution of sodium nitrite (27.95g, 0.405 mole) in water (68ml) was slowly added with stirring and the reaction vessel was maintained in an ice bath for an additional 30 minutes. Afterward, the entire reaction mixture was slowly added to a boiling mixture of sulfuric acid (270ml) and water (200ml). A black oil, which separated from the hot mixture, was dissolved in a small amount of methylene chloride and dried over magnesium sulfate. The dark oil was vacuum distilled and a yellow solid was recovered. Recrystallizing from toluene afforded bis(3-hydroxyphenyl)methane as light yellow needles (m.p. 101-103°C, 30 percent yield) [lit. m.p. 102-103°C, H. L. Bender, A. G. Farnham, J. W. Guyer, U. S. 2,464,207].

F. Bis(4-hydroxyphenyl)methane (referred to hereinafter as "4-HPM")

This monomer was obtained commercially (Aldrich Chemical Company, Milwaukee, Wisconsin), and was recrystallized from water to yield a white crystalline solid (m.p. 158 - 159°C).

G. 1,1-dimethyl-bis(4-hydroxyphenyl)methane (referred to hereinafter as "BPA")

This monomer was obtained commercially (Aldrich Chemical Company, Milwaukee, Wisconsin), and recrystallized from toluene to yield a white crystalline solid (m.p. 156 - 157°C).

H. 9,9-bis(4-hydroxyphenyl)fluorene (referred to hereinafter as "9,9-HPF")

9-Fluorenone (135.15g, 0.75 mole) was reacted with phenol (282.34g, 3.0 moles) in the presence of a small amount of 3-mercaptopropionic acid. The mixture was heated to approximately 50°C with stirring, at which time hydrogen chloride gas was bubbled into the mixture. The bubbling was continued for four hours at a temperature of about 50°C,
after which the reaction mixture became light amber and viscous. The reaction was terminated when a light green solid precipitated, and the mixture became too viscous to stir. The solid was steam distilled and subsequently air dried at about 100°C. A strong phenol smell was observed. This crude product was recrystallized twice from toluene to yield an off-white solid (m.p. 222-223.5°C, approximately 40 percent yield) [lit, m.p. 223-224°C, I. Smedley, J. Chem. Soc., 87, 1249 (1905)].

Example II
Preparation of Polyarylene Ethers According to the Present Invention

A. A polyarylene ether having the following structural representation was prepared:

\[
\begin{align*}
\text{This polymer, which is referred to hereinafter as "1,3-CBB/3-HPM", was produced according to the following procedure:} \\
1,3\text{-Bis(4-chlorobenzoyl)benzene (3.5522g, 0.01 mole),} \\
\text{bis(3-hydroxyphenyl)methane (2.0024g, 0.01 mole), and} \\
\text{potassium carbonate (3.45g, 0.025 mole) were stirred in a mixture of N,N-dimethylaceta} \\
\text{mide (30ml) and toluene (30ml) to azeotrope the water formed, and the reaction was heated} \\
\text{to approximately 155°C during three hours, and held at 155°C for about 16 hours. The reaction was cooled to 80°C, and} \\
\text{the product was filtered through a sintered glass funnel. After being neutralized with a 50/50 mixture of acetic} \\
\text{acid/N,N-dimethylacetamide, the product was precipitated in water in a blender, washed successively with water and} \\
\text{methanol, and boiled in methanol. Drying in air about 100°C for four hours afforded an off-white polymer (n}_{inh} = 0.39} 
\end{align*}
\]
dL/g, 0.5 percent solution in chloroform at 25°C; Tg = 114°C, DSC at 20°C/minute) in greater than 95 percent yield.

B. A polyarylene ether having the following structural representation was prepared:

\[
\begin{array}{c}
\text{O} \\
\text{C} \quad \text{O} \\
\text{O} \quad \text{C} \\
\text{CH}_2 \\
\text{O} \\
\end{array}
\]

This polymer, which is referred to hereinafter as "1,3-CBB/4-HPM", was produced according to the following procedure:

1,3-Bis(4-chlorobenzoyl)benzene (5.3284 g, 0.015 mole), bis(4-hydroxyphenyl)methane (3.0036 g, 0.015 mole), and potassium carbonate (4.57 g, 0.033 mole) were stirred in a mixture of N,N-dimethylacetamide (30 ml) and toluene (35 ml) under a Dean-Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed and the reaction was heated to approximately 155°C during about three hours, and held at 155°C for about 16 hours. The reaction was cooled to 80°C, diluted with 25 ml of N,N-dimethylacetamide and filtered through a sintered glass funnel. After the reaction was neutralized with 50/50 mixture of acetic acid/N,N'-dimethylacetamide, the polymer was precipitated in water in a blender, washed successively with water and methanol, and boiled in methanol. Drying in air at about 100°C for 4 hours afforded an off-white polymer (n\text{inh} = 0.71 dL/g, 0.5% solution in chloroform at 25°C; Tg = 145°C, DSC at 20°C/minute) in greater than 95% yield.

C. A polyarylene ether having the following structural representation was prepared:
This polymer which is referred to hereinafter as "1,3-CBB/BPA", was produced according to the following procedure:

1,3-Bis(4-chlorobenzoyl)benzene (26.642g, 0.075 mole), 1,1-dimethyl-bis(4-hydroxyphenyl)methane (17.122g, 0.075 mole), and potassium carbonate (25g, 0.18 mole) in N,N-dimethylacetamide (175ml) and toluene (75ml) were stirred under a Dean-Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed, and the reaction was heated to approximately 155°C during about three hours, where it was held for about 16 hours. The reaction was allowed to cool to 80°C, filtered through a sintered glass funnel, and neutralized with a 50/50 mixture of acetic acid/N,N'-dimethylacetamide. The polymer was precipitated in water in a blender, washed successively with water and methanol, and boiled in methanol. Drying in air at 100°C for 4 hours afforded an off-white polymer (η\text{inh} = 0.57 dL/g, 0.5% solution in chloroform at 25°C; Tg = 152°C, DSC at 20°C/minute) in greater than 95% yield.

D. A polyarylene ether having the following structural representation was prepared:
This polymer, which is referred to as "1,3-FBB/BPA", was produced according to the following procedure:

1,3-Bis(4-fluorobenzoyl)benzene (3.2232 g, 0.010 mole), 1,1-dimethyl-bis(4-hydroxyphenyl)methane (2.2829 g, 0.010 mole), and potassium carbonate (3.45 g, 0.025 mole) in N,N-dimethylacetamide (30 ml) and toluene (30 ml), were stirred under a Dean-Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed, and the reaction was heated to about 155°C during about 3 hours, where it was held for about 16 hours. The reaction was allowed to cool to approximately 80°C, filtered through a sintered glass funnel, and neutralized with a 50/50 mixture of acetic acid/N,N'-dimethylacetamide. The polymer was precipitated in water in a blender, washed successively with water and methanol, and boiled in methanol. Drying in air at 100°C for 4 hours afforded an off-white polymer (inh=1.23 dL/g, 0.5% solution in chloroform at 25°C; Tg = 155°C, DSC at 20°C/minute) in greater than 95% yield.

E: A polyarylene ether having the following structural representation was prepared.

This polymer which is referred to hereinafter as "1,3-CBB/9,9-HPF", was produced according to the following procedure.
1,3-Bis(4-chlorobenzoyl)benzene (7.104g, 0.02 mole), 9,9-bis(4-hydroxyphenyl)fluorene (7.008g, 0.02 mole) and potassium carbonate (5.94g, 0.043 mole) were stirred in a mixture of N,N-dimethylacetamide (56ml) and toluene (35ml) under a Dean-Stark trap in a nitrogen atmosphere. Toluene was used to azeotrope the water formed and the reaction was heated to approximately 155°C during five hours, and held at 155°C for about 16 hours. The reddish brown viscous solution was diluted with N,N-dimethylacetamide (50ml), allowed to cool to about 80°C, and filtered through a sintered glass funnel. The solution was poured into dilute aqueous acetic acid in a blender, successively washed with water and methanol and boiled in methanol. Drying in air at 100°C afforded an off-white polymer ($\eta_{inh} = 0.95$ dL/g, 0.5% solution in chloroform at 25°C; $T_g = 223^\circ$C, DSC at 20°C/minute) in greater than 95% yield.

F. A random polyarylene ether copolymer having the following structural representation was prepared.

This random copolymer, which is referred to hereinafter as "1,3-CBB/BPA/9,9-HPF (random)" was produced according to the following procedure:
1,3-Bis(4-chlorobenzoyl)benzene (7.102g, 0.02 mole),
1,1-dimethyl-bis(4-hydroxyphenyl)methane (2.283g, 0.01 mole),
9,9-bis (hydroxyphenyl)fluorene (3.504g, 0.01 mole), and
potassium carbonate (5.94g, 0.043 mole) were stirred in a
mixture of N,N-dimethylacetamide (42ml) and toluene (20ml)
under a Dean-Stark trap in a nitrogen atmosphere. Toluene
was used to azeotrope the water formed and the reaction was
heated to 155°C during about three hours, and held at 155°C
for about 16 hours. The reaction was allowed to cool to
about 80°C, filtered through a sintered glass funnel, and
poured into dilute aqueous hydrochloric acid in a blender.
The precipitated polymer was successively washed with water
and methanol, and finally boiled in methanol. Drying in air
at 100°C for 4 hours afforded a light beige polymer ($\eta_{inh} =
0.75$ dL/g, 0.5% solution in chloroform at 25°C; $T_g = 187°C$,
DSC at 20°C/minute) in greater than 95% yield.

G. Additional polymers and copolymers were prepared
according to procedures similar to those employed in
Examples II A through II E above. These polymers and
copolymers are listed below in Table I.

Example III
Determination of Properties of Polyarylene
Ethers According the Present Invention

A. Fundamental physical properties of all of the
polymers and copolymers of Example II were determined.
These properties are set forth below in Table I.

B. Thin film properties, fracture toughness, and
adhesive properties of representative polymers of Example II
were determined. These properties are set forth below in
Table II.
<table>
<thead>
<tr>
<th>Polymer or Copolymer</th>
<th>n_{inh}^1</th>
<th>T_{g}^3, °C (T_{m}, °C)</th>
<th>M_{n}, g/mole</th>
<th>Film^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>dihalo cpd.</td>
<td>dL/g</td>
<td>(T_m, °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>0.39</td>
<td>114</td>
<td>23,150</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,4-CBB</td>
<td>0.79</td>
<td>122</td>
<td>27,850</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>0.71</td>
<td>145</td>
<td>--</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,4-CBB</td>
<td>4-HPM</td>
<td>120 (275)</td>
<td>--</td>
<td>opaque, brittle</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>4-HPM</td>
<td>insoluble</td>
<td>28,500</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>9,9-HPF</td>
<td>152</td>
<td>28,300</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>9,9-HPF</td>
<td>166</td>
<td>26,950</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>9,9-HPF</td>
<td>223</td>
<td>39,850</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>1:1 BPA/9,9-HPF (Random)</td>
<td>187</td>
<td>--</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1:1 1,3-CBB/1,4-CBB</td>
<td>4-HPM (Random)</td>
<td>insoluble</td>
<td>152</td>
<td>--</td>
</tr>
<tr>
<td>1:1 1,3-CBB/4-CBB</td>
<td>4-HPM (Block DP about 4)</td>
<td>insoluble</td>
<td>150</td>
<td>--</td>
</tr>
<tr>
<td>1:3 1,3-CBB/1,4-CBB</td>
<td>4-HPM (Random)</td>
<td>insoluble</td>
<td>150 (280)</td>
<td>--</td>
</tr>
<tr>
<td>3:1 1,3-CBB/1,4-CBB</td>
<td>4-HPM (Random)</td>
<td>145</td>
<td>--</td>
<td>clear, tough, flexible</td>
</tr>
<tr>
<td>1:1 1,3-CBB/4-CBB</td>
<td>4-HPM (Random)</td>
<td>162</td>
<td>--</td>
<td>clear, tough, flexible</td>
</tr>
</tbody>
</table>

1. Inherent viscosity, 0.5% solution in chloroform at 25°C.
2. Inherent viscosity, 0.5% solution in m-cresol at 30°C.
3. Differential scanning calorimetry at a heating rate of 20°C/min.
4. Number average molecular weight by membrane osmometry using chloroform.
5. Solvent cast or melt pressed.
6. Crystalline melt.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>BPA</th>
<th>93</th>
<th>1,3-CBB</th>
<th>93</th>
<th>1,4-CBB</th>
<th>93</th>
<th>1,3-CBB</th>
<th>9,9-HPF</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin Film Properties</td>
<td>Test</td>
<td>Tensile Modulus psi</td>
<td>Fracture Toughness psi-in</td>
<td>Fracture Strength psi-in/in-0.001&quot;</td>
<td>Tensile Shear Modulus psi</td>
<td>Tensile Shear Strength psi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>25</td>
<td>12,600</td>
<td>380,000</td>
<td>12.7</td>
<td>7.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-CBB</td>
<td>25</td>
<td>9,350</td>
<td>310,000</td>
<td>145.0</td>
<td>128.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>25</td>
<td>13,450</td>
<td>380,000</td>
<td>4.6</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-CBB</td>
<td>25</td>
<td>9,990</td>
<td>350,000</td>
<td>2.6</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example IV
Comparison of Polymers According to the Present Invention With Those of the Prior Art

A. The polyarylene ether of Example II-D, viz., 1,3-CBB/9,9-HPF, was readily compression molded at 300°C under 100psi to form tough transparent orange plaques. Isothermal aging of this material was found to be significantly better than that of UDEL® P1700, a commercially available polysulfone. The 1,3-CBB/9,9-HPF exhibited a weight loss of only one percent after 1000 hours in air at 250°C, whereas UDEL® P1700 exhibited a weight loss of 3.5 percent under the same conditions.

B. Other properties of UDEL® P1700 polysulfone were compared with those of polyarylene ethers according to the present invention as set forth in Example II above. Polyarylene ethers according to the present invention had fracture toughness, tensile strength, modulus, elongation, and tensile shear strength higher than UDEL® P1700, and a melt viscosity slightly lower. That is to say, as compared with UDEL®, the polyarylene ethers of the present invention are stronger, tougher, and process more easily.

Because of the unique combination of properties which they possess, the polyarylene ethers of the present invention are eminently suitable for use in adhesives—for example, aerospace adhesives, in coatings, films, membranes, and composite matrices—for example, for structural use on aircraft.

Although the present invention has been described in detail with respect to certain preferred embodiments thereof, it is to be understood that variations and modifications in detail may be effected without departing from the spirit and scope of the present invention, as defined in the following claims.

What is new and desired to be secured by Letters Patent is:
Polyarylene ethers prepared by the polycondensation of particular dihalo compounds with specific bisphenols possess the combination of high strength, toughness, and high use temperature with ease of extrusion and formation into complex objects.