Poly(arylene ether)s containing pendent ethynyl and substituted ethynyl groups and poly(arylene ether) copolymers containing pendent ethynyl and substituted ethynyl groups are readily prepared from bisphenols containing ethynyl and substituted ethynyl groups. The resulting polymers are cured up to 350°C to provide crosslinked poly(arylene ether)s with good solvent resistance, high strength and modulus.

88% yield (Br) [81% yield (I)]
m.p. 187-189°C, 80% yield (Br)
[210-212°C, 77% yield (I)]

Fig. 1
Fig. 3

where R = H, C₄H₉,

DMAC
Toluene
K₂CO₃
155°C
Copolymers Containing 10 to 30 Mole % Ethynyl Containing Monomer

where R = H, CH₃.
POLYARYLENE ETHERS CONTAINING PENDENT ETHynyL GROUPS

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and 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 to a series of new bisphenols containing pendant ethynyl groups and new poly(arylene ether)s containing pendant ethynyl groups. These bisphenols are reacted with activated difluoride monomers to form poly(arylene ether)s with pendant ethynyl groups. Upon heating, the pendant ethynyl groups react to form crosslinked resins that are useful as adhesives, composite matrices, moldings and films.

2. Description of Related Art

Poly(arylene ether)s are condensation polymers that can be prepared by various routes. The most popular route involves the reaction of an aromatic bisphenol with an activated aromatic difluoride to form the polymer which has a repeat unit of the general type

\[(O-Ar-O-Ar')\]

where Ar is a divalent aromatic radical, which can be as simple as 1,3- or 1,4-disubstituted benzene, or it may be a bis-3 or 4-(diphenylene) having the general structure

![Structure](image)

where X=nil, O, S, SO₂, C=O, C(CH₃)₂, C(CF₃)₂, etc. Ar' may be any other appropriate divalent radical. Ar' has the general structure

![Structure](image)

where X=SO₂, C=O, etc.

Synthesis and characterization of poly(arylene ether)s containing ethynyl groups have been reported in the literature and summarized in two reviews [P. M. Hergenrother, **J. Macromol. Sci. Rev. Macromol. Chem.**, C19, 1 (1980) and P. M. Hergenrother, in H. Mark, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 1, John Wiley & Sons, Inc., New York, 61 (1985)]. Ethynyl and substituted ethynyl groups have been placed on the ends of oligomers and pendant along the backbone of polymers and thermally reacted to induce chain extension, rigidization, branching and/or crosslinking. More recently, a series of phenylethynylnyl terminated arylene ether oligomers having good melt stability were prepared and thermally reacted to yield polymers exhibiting excellent solvent resistance and high adhesive properties [R. G. Bryant, B. J. Jensen and P. M. Hergenrother, *Polymer Prepr.*, 33(1), 910 (1992)].

SUMMARY OF INVENTION

According to the present invention, a series of novel bisphenols containing pendant ethynyl groups were synthesized having the following general structure:

![Structure](image)

where R=H, n-C₆H₄—, and C₆H₄—. These bisphenols contain an ethynyl or substituted ethynyl group which a thermal reaction with other ethynyl groups at temperatures from about -150°C to about 400°C, depending on the R group. In the temperature range, the reaction initiates at slightly less than 350°C and is complete after a short period (<1 h) at 350°C. Other R groups would be expected to have different reaction initiation temperatures. The bisphenols can react with activated difluorides or activated dinitro compounds to form arylene ethers, or react with acid chlorides to form esters. Since these bisphenols are difunctional, they can react with other difunctional groups to form polymers.

Poly(arylene ether)s are prepared from the reaction of the ethynyl containing bisphenols with activated difluoride monomers. Upon heating these polymers at elevated temperatures, the ethynyl groups react with one another to form a crosslinked structure. The advantage of poly(arylene ether)s containing pendant ethynyl groups compared to linear poly(arylene ether) is the ability to react forming a crosslinked structure which typically increases the solvent resistance, glass transition temperature, and modulus. These properties are important for various applications as films, moldings, adhesives and composites.

The advantage of poly(arylene ether)s containing pendant ethynyl groups compared to acetylene-terminated arylene ether oligomers (ATAEs) is that the poly(arylene ether)s containing pendant ethynyl groups are high molecular weight and form tough films before the ethynyl crosslinking reaction takes place. The ATAAs typically form brittle films. Furthermore, the crosslink density of the cured resins from poly(arylene ether)s containing pendant ethynyl groups can be controlled by copolymerizing bisphenol without ethynyl groups and bisphenol containing the pendant ethynyl groups to form high molecular weight polymers. With ATAAs the crosslink density can be varied only by changing the molecular weight of the oligomer, which affects the ability to make films and moldings.

An object of this invention is to provide a bisphenol containing a pendant ethynyl group.

Another object of this invention is to provide a bisphenol containing a pendant phenylethynylnyl group.
Another object of this invention is to provide bisphenols containing pendant substituted ethynyl groups. Another object is to provide bisphenols containing pendant ethynyl groups which undergo a crosslinking reaction at temperatures from −150°C to −400°C.

Another object is to provide polyarylene ether copolymers containing pendant ethynyl or substituted ethynyl groups which crosslink to form a network structure by heating at elevated temperatures.

Another object is to provide polyarylene ether copolymers containing pendant ethynyl groups which undergo a crosslinking reaction at temperatures above −20°C to form insoluble films when heated above −20°C. These crosslinked films also have high modulus and high temperature use properties due to the reaction of the ethynyl groups. The polymers containing pendant ethynyl groups react with anhydrous magnesium sulfate (MgSO₄) and the liquid solidified on storing in the refrigerator. The liquid solidified on storing in the refrigerator.

The invention is to provide bisphenols containing pendant ethynyl or substituted ethynyl groups which crosslink to form a network structure by heating at elevated temperatures.

The invention is to provide polyarylene ether copolymers containing pendant ethynyl or substituted ethynyl groups which crosslink to form a network structure by heating at elevated temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an equation showing the synthesis of 4-bromotrifluoroacetophenone and 1,1-bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane according to the present invention.

FIG. 2 is an equation showing the synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-ethylphenyl)-2,2,2-trifluoroethane, 1,1-bis(4-hydroxyphenyl)-1-(4-phenylethynylphenyl)-2,2,2-trifluoroethane and 1,1-bis(4-hydroxyphenyl)-1-(4-ethylphenyl)-2,2,2-trifluoroethane according to the present invention.

FIG. 3 is an equation showing the synthesis of polyarylene ethers according to the present invention; and

FIG. 4 is an equation showing the synthesis of arylene ether copolymers containing pendant ethynyl or substituted ethynyl groups according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A series of novel bisphenols containing pendant ethynyl or substituted ethynyl groups were synthesized. These bisphenols have been reacted with various activated dihalide monomers to provide poly(arylene ether) containing pendant ethynyl groups. Copoly(arylene ether)s of these bisphenols and other bisphenols have also been prepared. The poly(arylene ether)s and copoly(arylene ether)s have been characterized and mechanical properties determined on films. The polymers containing pendant ethynyl groups react to form insoluble films when heated above −200°C. These crosslinked films also have high modulus and high temperature use properties due to the reaction of the ethynyl groups.

EXAMPLE 1

Synthesis of 4-bromotrifluoroacetophenone (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, ethyl trifluoroacetate (3.00 g, 7.1 mmol), triethylamine (40 mL) and a magnetic stirrer were placed in a 250 mL single-neck round bottom flask equipped with a condensing column. The reaction mixture was heated to 100°C and maintained at reflux for 48 h becoming a dark brown solid which was dissolved in warm diiodobenzene (13.47 g, 95.00 mmol) of diiodobenzene. The ether solution was transferred to a flask and dried. A total of 4.0 g (80%) of product was collected: m.p. 187°C–189°C. 1H NMR: (acetone-d₆): 6.6–7.0 (m, 8H); 7.3 (d, 4H); 8.3 (s, 2H); Mass Spectrum m/e (relative intensity) 424 (M⁺, 20), 424 (20), 353 (100), 355 (100); Calc'd for C₂₇H₂₆Br₂F₂O₂: C, 56.76%; H, 3.33%; Found: C, 57.12%; H, 3.24%. 1,1-Bis(4-hydroxyphenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane (IBP) was prepared in a similar manner to yield 4-iodotrifluoroacetophenone: m.p. 210°C–212°C. (after vacuum heat-drying); 1H NMR (acetone-d₆): (s, 10H), 7.3–7.6 (d, 2H), 8.0 (br s, 2H); Mass Spectrum m/e (relative intensity) 470 (M⁺, 11), 401 (100); Calc'd for C₂₉H₂₆Br₂F₂O₂: C, 51.00%; H, 3.00%; Found: 37.10%; I, 29.00%. 5,498,803

EXAMPLE 3

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-ethylphenyl)-2,2,2-trifluoroethane (EBP) (FIG. 2)

Into a 50 mL single-neck round bottom flask were added 1,1-bis(4-hydroxyphenyl)-1-(4-ethylphenyl)-2,2,2-trifluoroethane (3.00 g, 7.1 mmol), triethylamine (40 mL), cop.
per(1)iodide (CUI, 0.054 g, 0.28 retool, 4 mol %) and trimethylsilylacetylene (1.39 g, 14.2 mmol). The solution was sealed in the flask with a rubber septum and the magnetically stirred mixture was heated at 80°C. A dark precipitate formed (the amine hydrobromide salt), which increased in quantity with time. After 48 h, the solvent mixture was filtered to remove the salt and transferred to a 250 mL flask whereby the triethylamine was removed on a rotary evaporator. The product was desilylated by stirring in a magnetically stirred mixture was heated at 80°C. A dark precipitate formed (the amine hydroiodide salt), which increased in quantity with time. After 48 h, the solvent DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (20 g), and DMAc (22 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction appeared to gel. After diluting with DMAc (20 g), the reaction was heated to ~150°C. During 4 h, held for 1 h when the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form within ~2 h. If the reaction temperature was reduced in an effort to prepare high molecular weight, soluble polymers containing pendant ethynyl groups during synthesis. Therefore, both reaction time and temperature were reduced in an effort to form an azeotropic mixture with any water present in the reaction and maintain an anhydrous environment by collection in a Dean-Stark trap. Table 1 shows inherent viscosities (ηinh) of the PAE homopolymers. Specific examples of these polymers follow.

**EXAMPLE 6**

The following example illustrates the synthesis of PAE with pendant bromo groups. BBP (0.8465 g, 2.00 mmol), DFB (0.4364 g, 2.00 mmol), potassium carbonate (0.61 g, 4.40 mmol), toluene (12 mL) and DMAc (12 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to ~155°C. During 5 h and maintained at this temperature for 16 h. The reaction was filtered, neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was washed in water and boiling methanol and dried at 100°C overnight to provide a near-quantitative yield of polymer with inherent viscosity (ηinh) of 1.15 dL/g. The polymer was dissolved in chloroform (15% solids) and this solution was cast onto plate glass and cured in air for 1 h each at 100, 200 and 350°C to form a film with a Tg of 162°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely soluble in DMAc or chloroform.

**EXAMPLE 7**

The following example illustrates the synthesis of PAE with pendant ethynyl groups. EBP (1.8418 g, 5.00 mmol), DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (20 mL) and DMAc (22 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to ~150°C. During 4 h, held for 1 h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at ~150°C for 1 h. After the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form when ~2 h. Several other attempts using different conditions were also unsuccessful in producing high molecular weight polymer.

**EXAMPLE 8**

The following example illustrates the synthesis of PAE with pendant hexynyl groups. HBP (2.1224 g, 5.00 mmol), DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (20 mL) and DMAc (18 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to ~150°C. During 4 h, held for 1 h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at ~150°C for 1 h. After the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form when ~2 h. Several other attempts using different conditions were also unsuccessful in producing high molecular weight polymer.

<table>
<thead>
<tr>
<th>Example</th>
<th>Final Product</th>
<th>M.p. or Tg (°C)</th>
<th>Viscosity (dL/g)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td>Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-phenylethynylphenyl)-2,2,2-trifluoroethane (PEBP) (FIG. 2)</td>
<td>155</td>
<td>1.15</td>
<td>Completely soluble in DMAc or chloroform.</td>
</tr>
<tr>
<td>Example 6</td>
<td>The poly(arylene ether) (PAE) were synthesized as shown in FIG. 3 by the nucleophilic substitution of DFB with a bisphenol using potassium carbonate in DMAc at 155°C. Toluene was added at the beginning of the reaction to form an azeotropic mixture with any water present in the reaction and maintain an anhydrous environment by collection in a Dean-Stark trap. Table 1 shows inherent viscosities (ηinh) of the PAE homopolymers. Specific examples of these polymers follow.</td>
<td>155</td>
<td>1.15</td>
<td>Completely soluble in DMAc or chloroform.</td>
</tr>
<tr>
<td>Example 7</td>
<td>The following example illustrates the synthesis of PAE with pendant ethynyl groups. EBP (1.8418 g, 5.00 mmol), DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (20 mL) and DMAc (22 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to ~150°C. During 4 h, held for 1 h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at ~150°C for 1 h. After the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form when ~2 h. Several other attempts using different conditions were also unsuccessful in producing high molecular weight polymer.</td>
<td>155</td>
<td>1.15</td>
<td>Completely soluble in DMAc or chloroform.</td>
</tr>
<tr>
<td>Example 8</td>
<td>The following example illustrates the synthesis of PAE with pendant hexynyl groups. HBP (2.1224 g, 5.00 mmol), DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (20 mL) and DMAc (18 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to ~150°C. During 4 h, held for 1 h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at ~150°C for 1 h. After the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form when ~2 h. Several other attempts using different conditions were also unsuccessful in producing high molecular weight polymer.</td>
<td>155</td>
<td>1.15</td>
<td>Completely soluble in DMAc or chloroform.</td>
</tr>
</tbody>
</table>
The reaction was heated to -155°C during 5 h and not obtained.

-145°C for up to 4 h, high molecular weight polymer was hexynyl groups. When the reaction was held at or below -2°C within 2 h. Several other attempts using different conditions were also unsuccessful in producing high molecular weight polymer.

EXAMPLE 9

The following example illustrates the synthesis of PAE with pendant phenylethynyl groups. PEBF (2.2223 g, 5.00 mmol), DFB (1.0910 g, 5.00 mmol), potassium carbonate (1.52 g, 11.0 mmol), toluene (30 mL) and DMAc (21.7 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to -150°C for 5 h and maintained at this temperature for 16 h. The reaction was filtered, neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was washed in water and boiling methanol and dried at 100°C overnight to provide a polymer with Tg of 0.38°C/g. The polymer was completely insoluble in DMAc or chloroform. A composite of the bisphenol containing a pendent phenylethynyl group. PEBP (1.0910 g, 5.00 mmol), BPAF (3.5305 g, 10.5 mmol), DFB (3.2731 g, 15.00 mmol), potassium carbonate (3.04 g, 22 mmol), toluene (20 mL) and DMAc (22 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to -150°C for 5 h and maintained at this temperature for 2.5 h. The reaction was filtered, neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was washed in water and boiling methanol and dried at 100°C overnight to provide a polymer with Tg of 0.89°C/g. The polymer was dissolved in chloroform (15% solids) and this solution was cast onto plate glass and cured in air for 1 h each at 100°C, 200°C and 350°C to form a yellow film with a Tg of 185°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely insoluble in DMAc or chloroform.

EXAMPLE 10

The following example illustrates the synthesis of an PAE copolymer where one out of ten repeat units contains a pendant phenylethynyl group. PEBP (2.0001 g, 4.5000 mmol), BPAF (1.5131 g, 4.5000 mmol), DFB (1.0910 g, 5.0000 mmol), potassium carbonate (1.52 g, 11 mmol), toluene (20 mL) and DMAc (22 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to -150°C for 5 h and maintained at this temperature for 5 h. The reaction was filtered, neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was washed in water and boiling methanol and dried at 100°C overnight to provide a polymer with Tg of 0.89°C/g. The polymer was dissolved in chloroform (15% solids) and this solution was cast onto plate glass and cured in air for 1 h each at 100°C, 200°C and 350°C to form a yellow film with a Tg of 185°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely insoluble in DMAc or chloroform but did swell.

EXAMPLE 11

The following example illustrates the synthesis of an PAE copolymer where one out of ten repeat units contains a pendant phenylethynyl group. PEBP (0.8889 g, 2.00 mmol), BPAF (6.0523 g, 18.00 mmol), DFB (4.3641 g, 20.00 mmol), potassium carbonate (6.08 g, 44 mmol), toluene (40 mL) and DMAc (40 g) were added to a three-neck flask equipped with a stirring motor, nitrogen purge and Dean-Stark trap with a condenser. The reaction was heated to -155°C during 5 h and maintained at this temperature for 16 h. The reaction was filtered, neutralized with acetic acid and poured into water to form a white precipitate. The precipitate was washed in water and boiling methanol and dried at 100°C overnight to provide a polymer with Tg of 0.92°C/g. The polymer was dissolved in chloroform (15% solids) and this solution was cast onto plate glass and cured in air for 1 h each at 100°C, 200°C and 350°C to form a yellow film with a Tg of 170°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely insoluble in DMAc or chloroform.
TABLE 1

INHERENT VISCOSITY OF POLY(ARYLENE ETHERS)

<table>
<thead>
<tr>
<th>Bisphenol</th>
<th>Bis/fluoro monomer</th>
<th>( \eta_{ns} ) ( \text{dL/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBP</td>
<td>DFB</td>
<td>1.15</td>
</tr>
<tr>
<td>EBP</td>
<td>DFB</td>
<td>insoluble</td>
</tr>
<tr>
<td>HBP</td>
<td>DFB</td>
<td>insoluble</td>
</tr>
<tr>
<td>PEBP</td>
<td>DFB</td>
<td>0.38</td>
</tr>
</tbody>
</table>

TABLE 2

CHARACTERIZATION OF DFB/BPAF BASED COPOLYMERS

<table>
<thead>
<tr>
<th>Bisphenol</th>
<th>DSC ( T_g ), °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>with BPAF</td>
<td>( \eta_{ns} ), dL/g</td>
</tr>
<tr>
<td>10% BBP</td>
<td>1.4</td>
</tr>
<tr>
<td>10% EBP</td>
<td>0.89</td>
</tr>
<tr>
<td>10% PEBP</td>
<td>0.92</td>
</tr>
<tr>
<td>30% PEBP</td>
<td>0.52</td>
</tr>
<tr>
<td>100% BPAF</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*After heating to 350° C. for 1 h.

TABLE 3

THERMAL STABILITY AND THIN FILM PROPERTIES OF POLYMERS AND COPOLYMERS

<table>
<thead>
<tr>
<th>Components</th>
<th>Air</th>
<th>( T_{5%} ), °C.</th>
<th>Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% BBP, 90% BPAF</td>
<td>484</td>
<td>490</td>
<td>7.9 (4.2)</td>
<td>261 (229)</td>
<td>60 (76)</td>
</tr>
<tr>
<td>10% EBP, 90% BPAF</td>
<td>461</td>
<td>484</td>
<td>10.3 (4.9)*</td>
<td>342 (260)</td>
<td>6.1 (9.1)</td>
</tr>
<tr>
<td>100% BBP, 90% BPAF</td>
<td>455</td>
<td>487</td>
<td>10.0 (4.9)</td>
<td>284 (214)</td>
<td>96 (180)</td>
</tr>
<tr>
<td>30% PEBP, 90% BPAF</td>
<td>452</td>
<td>484</td>
<td>9.5 (4.5)</td>
<td>341 (232)</td>
<td>4.8 (76)</td>
</tr>
<tr>
<td>70% BPAF, 100% BPAF</td>
<td>476</td>
<td>493</td>
<td>9.5 (4.0)</td>
<td>325 (198)</td>
<td>9.9 (1.3)</td>
</tr>
</tbody>
</table>

We claim:

1. A poly(arylene ether) containing pendent ethynyl or substituted ethynyl groups prepared by reacting a bisphenol containing an ethynyl or substituted ethynyl group and having the structure

\[
\text{HO-C-} \overset{\overset{\text{C-C-R}}{\text{X}}}{{\text{O}}}
\]

wherein \( X \) is a halogen.

2. A copoly(arylene ether) containing pendent ethynyl or substituted ethynyl groups prepared by reacting a mixture of a bisphenol containing an ethynyl or substituted ethynyl group and having the structure

\[
\text{HO-C-} \overset{\overset{\text{C-C-R}}{\text{X}}}{{\text{O}}}
\]

wherein \( R \) is selected from the group consisting of hydrogen, \( n_\text{C}_4\text{H}_9 \) and \( n_\text{C}_9\text{H}_{13} \), and a bisphenol having no ethynyl or substituted ethynyl groups having the structure

\[
\text{HO-C-} \overset{\overset{\text{C-C-R}}{\text{X}}}{{\text{O}}}
\]

with

wherein \( X \) is a halogen.

* * * *