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(NASA-Case-LAR-15041-1)
POLY(ARYLENE ETHER)S CONTAINING PENDENT ETHYNYL GROUPS Patent Application (NASA, Langley Research Center) 24 p

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Poly(arylene ether)s are condensation polymers that can be prepared by various routes. The most common route involves the reaction of an aromatic bisphenol with an activated aromatic dihalide to form the polymer. The synthesis and characterization of poly(arylene ether)s containing ethynyl groups has been known to those skilled in the art. Ethynyl and substituted ethynyl groups have been placed on the ends of oligomers and pendent along the backbone of polymers and thermally reacted to induce chain extension, rigidization, branching and/or crosslinking. In addition, a series of phenyl ethynyl terminated arylene ether oligomers having good melt stability were prepared and thermally reacted to yield polymers exhibiting excellent solvent resistance and high adhesive properties.

By the present invention a series of novel bisphenols containing pendent ethynyl groups were synthesized. These bisphenols contain an ethynyl or substituted ethynyl group which undergoes a thermal reaction with other ethynyl groups at temperatures ranging from approximately 150°C to approximately 400°C. The bisphenols can react with activated dihalides 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 compounds to form polymers.

The novelty of the invention resides in the bisphenol structure which contains pendent ethynyl groups. Poly(arylene ether)s are prepared from the reaction of the ethynyl containing bisphenols with activated difluoro monomers. When heated, these polymers form a crosslinked structure which yields the unexpected properties of improved solvent resistance, glass transition temperature, and modulus. In addition these polymers are high molecular weight and form tough films before the ethynyl crosslinking reaction takes place.

Inventors:  
Paul M. Hergenrother  
Brian J. Jensen  
Address:  
304 Old Dominion Road  
127 Branscome Blvd.  
Yorktown, VA 23692  
Williamsburg, VA 23185  
Employer:  
NASA LaRC  
NASA LaRC

Initial Evaluator: Terry L. St. Clair

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POLY(ARYLENE ETHER)S 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 pendent ethynyl groups and new poly(arylene ether)s containing pendent ethynyl groups. These bisphenols are reacted with activated dihalide monomers to form poly(arylene ether)s with pendent ethynyl groups. Upon heating, the pendent 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 dihalide to form the polymer which has a repeat unit of the general type
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

\[
\begin{align*}
\text{Ar} & \quad \text{X} \\
\end{align*}
\]

where \( X = \text{nil, O, S, SO}_2, \text{C}=\text{O}, \text{C(CH}_3)_2, \text{C(CF}_3)_2, \) etc. Ar may be any other
appropriate divalent radical. Ar' is a divalent aromatic which contains an electron
withdrawing activating group para to the halide to be displaced. Ar' has the
general structure

\[
\begin{align*}
\text{Ar'} & \quad \text{X} \\
\end{align*}
\]

where \( X = \text{SO}_2, \text{C}=\text{O}, \) 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.

Ethynyl and substituted ethynyl groups have been placed on the ends of oligomers and pendent along the backbone of polymers and thermally reacted to induce chain extension, rigidization, branching and/or crosslinking. More recently, a series of phenylethynyl 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, *Polym. Prepr.*, 33(1), 910 (1992)].

**Summary of Invention**

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

\[
\text{C-C-R}
\]

where \( R = H, n-C_4H_9^-, \text{and } C_6H_5^- \).

These bisphenols contain an ethynyl or substituted ethynyl group which undergoes a thermal reaction with other ethynyl groups at temperatures from \(-150^\circ C\) to \(-400^\circ C\), depending on the \( R \) group. In comparing the curing behavior of two different materials, when \( R = H \), differential scanning calorimetry at a heating rate of \( 20^\circ C/\text{minute} \) indicates the reaction is initiated at \(-225^\circ C\) and is complete after \( 0.5 \) h at \( 250^\circ C \); but if \( R = f \), the reaction initiates at slightly less than \( 350^\circ C \) and is complete after a short period (<1 h) at \( 350^\circ C \). Other \( R \) groups would be expected to have different reaction initiation temperatures. The bisphenols can
react with activated dihalides 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 compounds to form polymers.

Poly(arylene ether)s are prepared from the reaction of the ethynyl containing bisphenols with activated difluoro 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 pendent ethynyl groups compared to linear poly(arylene ether)s 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 pendent ethynyl groups compared to acetylene-terminated arylene ether oligomers (ATAE) is that the poly(arylene ether)s containing pendent ethynyl groups are high molecular weight and form tough films before the ethynyl crosslinking reaction takes place. The ATAEs typically form brittle films. Furthermore, the crosslink density of the cured resins from poly(arylene ether)s containing pendent ethynyl groups can be controlled by copolymerizing bisphenol without ethynyl groups and bisphenol containing the pendent ethynyl groups to form high molecular weight polymers.

With ATAEs 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 pendent ethynyl group.

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

Another object of this invention is to provide bisphenols containing pendent substituted ethynyl groups.

Another object is to provide bisphenols containing pendent ethynyl groups which undergo a crosslinking reaction at temperatures from ~150°C to ~400°C.

Another object is to provide poly(arylene ether)s with pendent ethynyl or
substituted ethynyl groups from the reaction of these bisphenols with activated
dihalide monomers.

Another object is to provide poly(arylene ether)s containing pendent ethynyl
groups which crosslink to form a network structure by heating at elevated

5
temperatures.

Another object is to provide copolymers containing pendent 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 ethynylphenyl)-2,2,2-trifluoroethane, 1,1-bis(4-hydroxyphenyl)-1-
(4 phenylethynylphenyl)-2,2,2-trifluoroethane and 1,1-bis(4-hydroxyphenyl)-1-(4-
hexynylphenyl)-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 pendent ethynyl or substituted ethynyl groups according to the present
invention.

Description of the Preferred Embodiments

A series of novel bisphenols containing pendent ethynyl or substituted ethynyl
groups were synthesized. These bisphenols have been reacted with various
activated dihalide monomers to provide poly(arylene ether)s containing pendent

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 pendent 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. Specific examples follow.

**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, 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. 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 min and the resulting white suspension was stirred at -78°C for 2h. After the 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 h.

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 to
room temperature. The reaction mixture was transferred to a separatory funnel and the aqueous layer was removed. The ether solution was washed carefully with saturated aqueous sodium bicarbonate (NaHCO₃), until all 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 lachrymatory 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. 'H NMR: an AB quartet centered at 7.66 ppm.

4-Iodotrifluoroacetophenone was prepared by a similar procedure in 81% yield from p-diiodobenzene. 'H NMR: an AB quartet centered at 7.65 ppm.

Example 2

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane (BBP) (FIG. 1)

4-Bromotrifluoroacetophenone (3.00 g, 12 mmol) and phenol (18.6 g, 20 mmol), trifluoromethanesulfonic acid (0.04 g, 2 mol %) 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 deep brown color. The reaction was steam distilled and the product formed a dark brown solid which was dissolved in warm methylene chloride. Addition of MgSO₄ and Norit-A with stirring and filtration provided a light orange solution. The solution was concentrated to about 65% of the original volume on a rotary evaporator and cooled in an ice bath. White crystals formed which were filtered and dried in a vacuum. A total of 4.0 g (80%) of product was collected: m.p. 187-189°C. 'H NMR (acetone-d₆): 6.6-7.0
(m, 8H); 7.3 (d, 4H); 8.3 (s, 2H); Mass Spectrum m/e (relative intensity) 422
(M+, 20), 424 (20), 353 (100), 355 (100); Calc'd for C_{n}H_{n}BrF_{3}O_{2}: 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 in 77% yield from 4-iodotrifluoroacetophenone: m.p.
210-212°C (after vacuum heat-drying). 'H NMR (acetone-d$_6$): 6.6 (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 C$_{20}$H$_{14}$IF$_{3}$O$_{2}$: C, 51.09%; H, 3.00%; I, 26.99%; Found: C
, 50.84%; H, 2.98%; I, 27.16%.

Example 3

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-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-bromophenyl)-2,2,2-trifluoroethane (3.00 g, 7.1 mmol),
triethylamine (40 mL), copper(I)iodide (CuI, 0.054 g, 0.28 mmol, 4 mol%),
tetrakis(triphenylphosphine)palladium(0) (0.33 g, 0.28 mmol, 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 methanol (80 mL) in the
presence of Na$_2$CO$_3$ (2.12 g, 20 mmol) overnight at room temperature (RT). The
reaction was filtered, the methanol removed on a rotary evaporator and 100 mL of
1N HCl was added to the flask. The acid solution was extracted with ether, dried
over MgSO$_4$, then ether was removed to provide a solid which was purified by
column chromatography using silica gel and a mixture of 80% benzene and 20%
diethyl ether. After drying under vacuum, 2.2 g (73%) of product was recovered:
m.p. 158-160°C. 'H NMR (acetone-d$_6$): 1.00 (br s, 3 H), 1.57 (br s, 4 H), 2.33
(br s, 2 H), 5.00 (br s, 2 H), 6.66 - 7.33 (m, 12 H), 8.33 (br s, 2 H); 'H NMR
(CDC$_3$): 1.00 (br s, 3 H), 1.57 (br s, 4 H), 2.33 (br s, 2 H), 5.00 (br s, 2 H),
6.57 - 7.3 (m, 12 H); Mass Spectrum, m/e (relative intensity): 368 (M$^+$, 23), 299
(100); Calc'd for C$_{22}$H$_{15}$F$_3$O$_2$: C, 71.73%; H, 4.10%; Found: C, 71.43%; H,
4.09%.

Example 4

Synthesis of 1,1-bis(4-hydroxyphenyl)-1-(4-phenylethynylphenyl)-2,2,2-
trifluoroethane (PEBP)(FIG. 2)

Into a 50 mL single-neck round bottom flask were added 1,1-bis(4-
hydroxyphenyl)-1-(4-iodophenyl)-2,2,2-trifluoroethane (3.50 g, 7.40 mmol),
phenylacetylene (1.51 g, 14.80 mmol, 100% excess), bis(triphenylphosphine)-
palladium(II) chloride (0.208 g, 0.300 mmol, 4 mol%), CuI (0.056 g, 0.300
mmol; 4 mol%) and triethylamine (30 mL). The solution was sealed in the flask
with a rubber septum and the magnetically stirred mixture was heated at 80°C. A
precipitate formed (the amine hydroiodide 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 dissolved in diethyl ether and washed with 1N HCl
followed by extraction with aqueous NaOH. The product was regenerated by the
dropwise addition of HCl to the neutralization point, filtered, then redissolved in
diethyl ether. After drying over MgSO$_4$, the ether was removed and the product
was purified by column chromatography using silica gel and a mixture of 80%
benzene and 20% diethyl ether. After drying under vacuum at 80°C for 1h, 2.7 g
(82%) of product was recovered: m.p. 205-207°C. 'H NMR acetone-d$_6$: 6.3 -
7.6 (m, 17 H), 8.3 (br s 2H); Mass Spectrum, m/e (relative intensity): 444 (M$^+$,
Example 5

**Synthesis of 1,1-Bis(4-hydroxyphenyl)-1-(4-hexynylphenyl)-2,2,2-trifluoroethane (HBP)** (FIG. 2)

This compound was prepared from 1,1-(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane and 1-hexyne by the same procedure as for the phenylethynylphenyl analog. After drying under vacuum at 80°C for 1 h, 2.2 g (73%) of product was recovered: m.p. 142-144°C. \(^1^H\) NMR (acetone-\(d_6\)): 3.6 (s, 1 H), 6.6-7.39 (m, 12 H), 8.3 (br s, 2 H); \(^1^H\) NMR (CDCl\(_3\)): 3.15 (s, 1 H), 5.0 (br s, 2 H); 6.6-7.6 (m, 12 H); Mass Spectrum, m/e (relative intensity) 424 (M+, 20), 355 (100); Calc’d for C\(_{36}\)H\(_{21}\)F\(_3\)O\(_2\): C, 73.57%; H, 5.46%. Found: C, 73.88%; H, 5.38%.

**Synthesis of Polymers**

The poly(arylene ether)s (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 (\(\eta\)) of the PAE homopolymers. Specific examples of these polymers follow.

Example 6

The following example illustrates the synthesis of PAE with pendent 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 \( \sim 155^\circ C \) during 5h and maintained at this temperature for 16h. 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 (\( \eta_{inh} \)) 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 \( T_g \) 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 pendent 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 \( \sim 150^\circ C \) during 4h, held for 1h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at \( \sim 150^\circ C \) for 16h in an unsuccessful effort to dissipate the gel, indicating a reaction of the ethynyl groups during synthesis. Therefore, both reaction time and temperature were reduced in an effort to prepare high molecular weight, soluble polymers containing pendent ethynyl groups. When the reaction was held at or below \( \sim 145^\circ C \) for up to 4h, high molecular weight polymer was not obtained. If the reaction temperature was allowed to increase even a few degrees (to \( \sim 148^\circ C \)), a gel would form within \( \sim 2h \). 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 pendent 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 4h, held for 1h when the reaction appeared to gel. After diluting with DMAc (20 g), the reaction was held at ~150 for 16h in an unsuccessful effort to dissipate the gel, indicating a reaction of the hexynyl groups during synthesis. Therefore, both reaction time and temperature were reduced in an effort to prepare high molecular weight, soluble polymers containing pendent hexynyl groups. When the reaction was held at or below ~145°C for up to 4h, high molecular weight polymer was not obtained. If the reaction temperature was allowed to increase even a few degrees (to ~148°C), a gel would form within ~2h. 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 pendent phenylethynyl groups. PEBP (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 ~155°C during 5h and maintained at this temperature for 16h. 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 inherent viscosity (\(\eta_{inh}\)) of 0.38 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 yellow film with no \( T_g \) detected by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely insoluble in DMAc or chloroform.

### Synthesis of Copolymers

Arylene ether copolymers containing pendant ethynyl or substituted ethynyl groups were prepared as shown in FIG. 4 using 10 or 30 mole % of the bisphenol containing a pendant ethynyl group and 90 or 70 mole %, respectively, of BPAF (a bisphenol without a pendant ethynyl group), although any ratio of these bisphenols could be used. Table 2 gives the \( \eta_{inh} \) and the original and final \( T_g \)'s of these PAE copolymers. Table 3 gives data on the thermal stability and film properties (tensile strength, modulus and elongation) of the same copolymers. For reference, the homopolymer of BPAF and DFB is included and is soluble in DMAc and CHCl₃. When cured at 250-350°C, the ethynyl groups react and the copolymers become insoluble in DMAc and CHCl₃. Specific examples of these copolymers follow.

#### Example 10

The following example illustrates the synthesis of an PAE copolymer where one out of ten repeat units contains a pendant bromo group. BBP (0.4232 g, 1.00 mmol), BPAF (3.0262 g, 9.00 mmol), DFB (2.1821 g, 10.00 mmol), potassium carbonate (3.04 g, 22 mmol), toluene (30 mL) and DMAc (30 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 \( \sim 155°C \) during 5h and maintained at this temperature for 16h. 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 \( \eta_{inh} \) of 1.4 dL/g. The polymer was dissolved in chloroform (15%
Example 11

The following example illustrates the synthesis of an PAE copolymer where one out of ten repeat units contains a pendent 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 5h and maintained at this temperature for 16h. 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 $\eta_{in}$ of 0.92 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 light yellow film with a T$_g$ of 179°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely soluble in DMAc or chloroform.

Example 12

The following example illustrates the synthesis of an PAE copolymer where one out of ten repeat units contains a pendent ethynyl group. EBP (0.1842 g, 0.500 mmol), BPAF (1.5131 g, 4.500 mmol), DFB (1.0910 g, 5.000 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 during 5h
and maintained at this temperature for 2.5h. 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 $\eta_{in}$ of 0.89 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 light yellow film with a $T_g$ 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 13**

The following example illustrates the synthesis of an PAE copolymer where three out of ten repeat units contains a pendent phenylethynyl group. PEBP (2.0001 g, 4.500 mmol), BPAF (3.5305 g, 10.5 mmol), DFB (3.2731 g, 15.00 mmol), potassium carbonate (4.56 g, 33 mmol), toluene (40 mL) and DMAc (35 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 5h and maintained at this temperature for 16h. 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 $\eta_{in}$ of 0.52 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 light yellow film with a $T_g$ of 184°C by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. This film was completely insoluble in DMAc or chloroform and showed only slight swelling.
TABLE 1. INHERENT VISCOSITY OF POLY(ARYLENE ETHERS)

<table>
<thead>
<tr>
<th>Bisphenol</th>
<th>Bisfluoro monomer</th>
<th>$\eta_{\text{inh}}$, 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 with BPAF</th>
<th>$\eta_{\text{inh}}$, dL/g</th>
<th>DSC Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>10% BBP</td>
<td>1.4</td>
<td>170</td>
</tr>
<tr>
<td>10% EBP</td>
<td>0.89</td>
<td>172</td>
</tr>
<tr>
<td>10% PEBP</td>
<td>0.92</td>
<td>165</td>
</tr>
<tr>
<td>30% PEBP</td>
<td>0.52</td>
<td>162</td>
</tr>
<tr>
<td>100% BPAF</td>
<td>0.35</td>
<td>168</td>
</tr>
</tbody>
</table>

*After heating to 350 °C for 1h.
TABLE 3. THERMAL STABILITY AND THIN FILM PROPERTIES OF POLYMERS AND COPOLYMERS

<table>
<thead>
<tr>
<th>5</th>
<th>Bisphenol Components</th>
<th>Temperature of 5% Wt. Loss by TGA, °C</th>
<th>23°C Tensile Properties (150°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Air</td>
<td>N₂</td>
</tr>
<tr>
<td>10</td>
<td>10%BBP, 90% BPAF</td>
<td>484</td>
<td>490</td>
</tr>
<tr>
<td></td>
<td>10% EBP, 90% BPAF</td>
<td>461</td>
<td>484</td>
</tr>
<tr>
<td></td>
<td>10% PEBP, 90% BPAF</td>
<td>455</td>
<td>487</td>
</tr>
<tr>
<td>15</td>
<td>30% PEBP, 70% BPAF</td>
<td>452</td>
<td>484</td>
</tr>
<tr>
<td></td>
<td>100% BPAF</td>
<td>476</td>
<td>493</td>
</tr>
</tbody>
</table>
POLY(ARYLENE ETHER)S CONTAINING PENDENT ETHYNYL GROUPS

Abstract of the Disclosure

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.
(I) \[ \text{Br} \xrightarrow{\text{nBuLi, -78°C}} \text{Li} \] 

(II) \[ \text{Br} \xrightarrow{\text{CH}_3\text{CH}_2\text{O-C=CF}_3, -78°C} \] 

88% yield (Br)  
[81% yield (I)]

(III) \[ \text{Br} \xrightarrow{\text{CF}_3\text{SO}_3\text{H, reflux}} \] 

m.p. 187-189°C, 80% yield (Br)  
[m.p. 210-212°C, 77% yield (I)]
\[ \text{Br (I)} + \text{R-C}=\text{C-H} \xrightarrow{\text{NMP, Et}_3\text{N, CuI, (O}_3\text{P)}_2\text{Pd Cl}_2, 80^\circ\text{C}} \text{HO-C}=\text{C-R} \]

\[ \begin{align*}
R &= \text{H, EBP} \\
   &= \text{C}_4\text{H}_9, \text{HBP} \\
   &= \text{(I) } \text{PEBP}
\end{align*} \]
where $R = H, C_4H_9, \bigcirc$
Copolymers Containing 10 to 30 Mole % Ethynyl Containing Monomer

where R = H, C₄H₉, O