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POLY(ARYLENE ETHER)S WITH PENDANT ETHYNYL GROUPS

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ABSTRACT

Three novel bisphenols containing pendant ethynyl, hexynyl, and phenylethynyl groups were synthesized and used to prepare arylene ether polymers and copolymers. When heated to 250–350°C, the ethynyl groups react. After curing, the homopolymers were brittle due to the high crosslink density. Copolymers prepared using either 10 or 30 mol% of the ethynyl-containing bisphenol and either 90 or 70 mol% of the bisphenol with no ethynyl groups were relatively tough and formed creasible films. After a thermal cure, the copolymers became insoluble and exhibited high T_gs and good thin film tensile properties.

INTRODUCTION

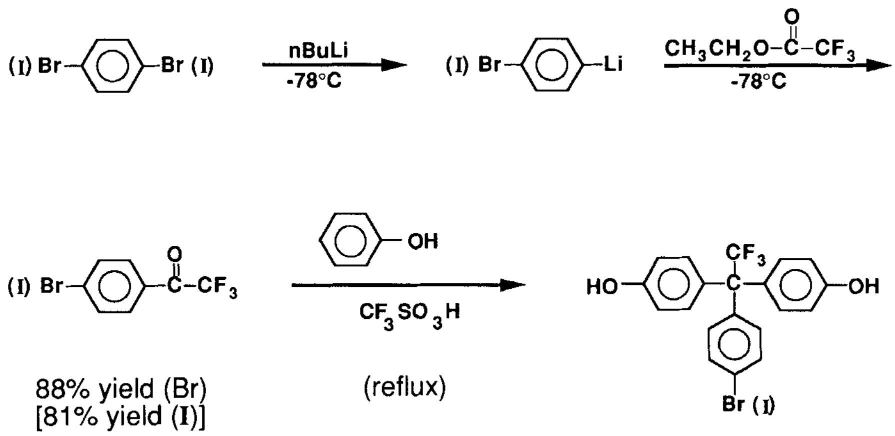
The work reported herein concerns the use of novel ethynyl-containing bisphenols to prepare a series of poly(arylene ether)s containing pendant ethynyl groups. This work was done as part of a study on chemical structure/property relationships to provide information to help design better materials for a variety of aerospace applications.

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. This work has been summarized in two reviews [1, 2]. 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 [3]. As an extension of this work, several poly(arylene ether)s containing pendant ethynyl, hexynyl, and phenylethynyl groups were prepared and characterized. Their chemical, physical, and mechanical properties are discussed herein.

EXPERIMENTAL

Monomer Synthesis

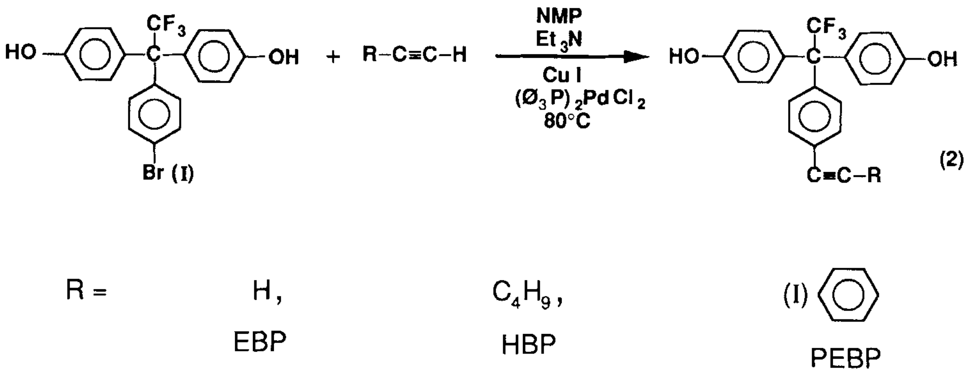
The monomers containing pendant bromo, ethynyl, hexynyl, and phenylethynyl groups were synthesized as shown in Eqs. (1) and (2). The synthetic procedure for each reactant and monomer is described.



(1)

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

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



(2)

4-Bromotrifluoroacetophenone

Into a flame-dried, three-neck round-bottom flask, fitted with a pressure equalizing addition funnel and under nitrogen, was added 1,4-dibromobenzene (20.04 g, 85.00 mmol). Using a syringe, 150 mL anhydrous ether was added into the flask. Some of the 1,4-dibromobenzene precipitated when the solution was cooled to −78°C in a dry-ice/acetone bath. *n*-Butyllithium (*n*-BuLi) (1.6 M 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. The addition was completed in 30 minutes and the resulting white suspension was stirred at −78°C for 2 hours. The reaction vessel was removed from the bath and allowed to warm to 0°C to ensure complete metal–halogen exchange, changing from a suspension to a solution on warming. On recooling to −78°C, the suspension reappeared. Ethyl trifluoroacetate (13.47 g, 95.00 mmol) was added dropwise to this white suspension. The suspension became a solution before complete addition of the ester, and the solution was left to warm to room temperature.

To quench the reaction, the solution was cooled between −30 and −20°C and 40 mL of aqueous saturated ammonium chloride (NH_4Cl) was added dropwise. To ensure complete hydrolysis, 40 mL of 1 N 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 with saturated aqueous sodium bicarbonate ($NaHCO_3$) until all the acid was neutralized. The ether solution was transferred to a flask and dried over anhydrous magnesium sulfate ($MgSO_4$). Suction filtration, followed by rotary evaporation of the solvent, left a yellow-colored, slightly lachrimatory liquid which was vacuum distilled (0.2 torr, 80°C) to obtain 19.75 g (88%) of 4-bromotrifluoroacetophenone as a dense, colorless liquid. The liquid solidified on storing in the refrigerator. ^1H NMR: An AB quartet centered at 7.66 ppm.

4-Iodotrifluoroacetophenone was prepared by a similar procedure in 81% yield from *p*-diiodobenzene. ^1H NMR: An AB quartet centered at 7.65 ppm.

1,1-Bis(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane (BBP)

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 hours 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 $MgSO_4$ 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: mp 187–189°C. ^1H NMR (acetone-d_6): 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).

Calculated for $C_{20}H_{14}BrF_3O_2$: 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 was prepared in a similar manner in 77% yield from 4-iodotrifluoroacetophenone: mp 210–212°C (after vacuum heat-drying). ^{1}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).

Calculated for $C_{20}H_{14}IF_3O_2$: C, 51.09%; H, 3.00%; I, 26.99%. Found: C, 50.84%; H, 2.98%; I, 27.16%.

1,1-Bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (EBP)

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 hours, 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_2CO_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 1 N 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: mp 158–160°C. ^{1}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, 2H); ^{1}H NMR ($CDCl_3$): 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).

Calculated for $C_{22}H_{15}F_3O_2$: C, 71.73%; H, 4.10%. Found: C, 71.43%; H, 4.09%.

1,1-Bis(4-hydroxyphenyl)-1-(4-phenylethynylphenyl)-2,2,2-trifluoroethane (PEBP)

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 hours, 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 1 N 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 1 hour, 2.7 g (82%) of product was recovered: mp 205-207°C. ^{1}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^+, 30), 375 (100).

Calculated for $C_{28}H_{19}F_3O_2$: C, 75.67%; H, 4.31%. Found: C, 75.56%; H, 4.42%.

1,1-Bis(4-hydroxyphenyl)-1-(4-hexynylphenyl)-2,2,2-trifluoroethane (HBP)

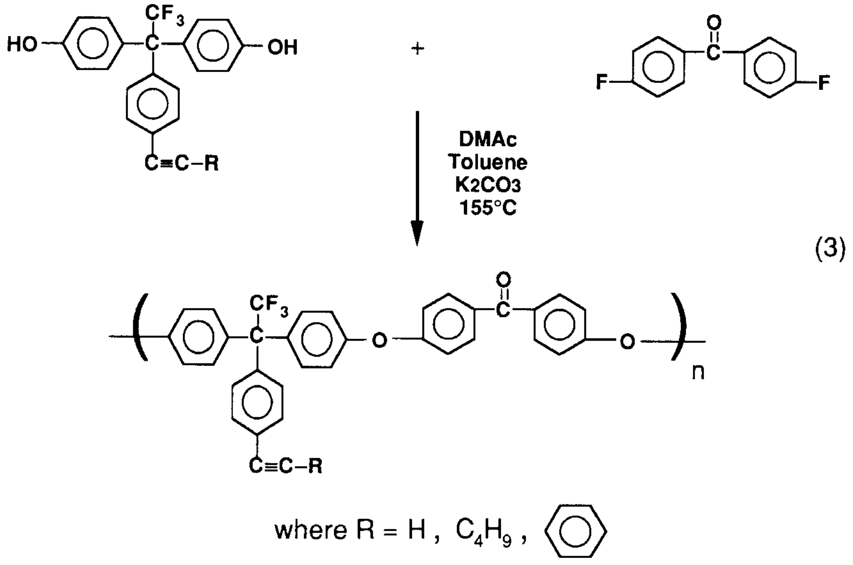
This compound was prepared from 1,1-(4-hydroxyphenyl)-1-(4-bromophenyl)-2,2,2-trifluoroethane and 1-hexyne by the same procedure as for the phenylethynylphenyl analog. After drying under vacuum at 80°C for 1 hour, 2.2 g (73%) of product was recovered: mp 142-144°C. ^{1}H NMR (acetone-d_6): 3.6 (s, 1 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).

Calculated for $C_{26}H_{23}F_3O_2$: C, 73.57%; H, 5.46%. Found: C, 73.88%; H, 5.38%

Other monomers used in this study, 4,4′-difluorobenzophenone (DFB) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (BPAF), were obtained from commercial sources and were recrystallized prior to use. *N,N*-Dimethylacetamide (DMAc), toluene, and potassium carbonate were obtained from commercial sources and were used as received.

Polymer Synthesis

The poly(arylene ether)s (PAE) were synthesized as shown in Eq. (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 to maintain an anhydrous environment by collection in a Dean-Stark trap.



(3)

The following example illustrates the synthesis of PAE with pendant 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 5 hours and maintained at this temperature for 16 hours. 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 (η_{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 hour 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 either DMAc or chloroform.

The same procedure was used with BBP, EBP, and HBP in place of PEBP. The reaction using BBP provided a PAE with η_{inh} of 1.15 dL/g while the other reactions formed gels, indicating reaction of the ethynyl and hexynyl groups during synthesis.

Copolymer Synthesis

Arylene ether copolymers containing pendant ethynyl or substituted ethynyl groups were prepared using either 10 or 30 mol% of the bisphenol containing a pendant ethynyl group and either 90 or 70 mol%, respectively, of BPAF (a bisphenol without a pendant ethynyl group), although any ratio of these bisphenols could be used. Table 1 gives the η_{inh}s and the original and final T_gs of these PAE copolymers.

The following example illustrates the synthesis of a 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 condensor. The reaction was heated to ~155°C during 5 hours and maintained at this temperature for 16 hours. 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 η_{inh} 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 hour 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 insoluble in either DMAc or chloroform but did swell.

The same procedure was used with EBP in place of PEBP to provide a PAE, with η_{inh} 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 hour 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 either DMAc or chloroform but did swell.

Characterization

Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in chloroform at 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent T_g taken at the inflection point of the ΔT versus temperature curve. Thermogravimetric analysis (TGA) was conducted on film specimens at a heating rate of 2.5°C/min in flowing air or nitrogen. ^{1}H-NMR spectra were measured on a Varian EM 360 A spectrometer with chemical shifts reported in ∂ units from tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained in the electron impact mode at 70 eV on a VG 7070 E-HF mass spectrometer. Elemental analyses were performed by Galbraith Microanalytical Laboratory, Nashville, Tennessee.

Films

Chloroform solutions (15% solids) of the polymers and copolymers were centrifuged, the decantate doctored onto plate glass and dried at RT to a tack-free form in a low humidity chamber. The films on glass were dried 1 hour each at 100, 200, and 350°C in air. Mechanical tests were preformed according to ASTM D882 on four or more specimens per test condition.

RESULTS AND DISCUSSION

The ethynyl and substituted ethynyl bisphenols were prepared in relatively high crude yields, but purification by simple recrystallization was difficult. Column chromatography proved more successful and afforded bisphenols whose elemental analyses agreed well with the theoretical values. The DSC melting points of these bisphenols were sharp, and visual melting occurred over a 2°C range. The exothermic peaks in the DSC curves due to reaction of the ethynyl groups occurred at 265°C for EBP, 300°C for HBP, and 370°C for PEBP, showing that the substituent on the ethynyl group influenced the curing reaction. The chemical structure and purity of all of the ethynyl-containing bisphenols were further verified by mass spectroscopy and ^{1}H NMR.

The PAEs were prepared by aromatic nucleophilic substitution using exact monomer stoichiometry in DMAc at 20-25% solids content (weight to weight) with potassium carbonate as base and toluene to remove any water present or formed by azeotropic distillation. Initially, the reactions were heated to ~155°C during 5 hours and held at 155°C for 16 hours under an N_2 atmosphere. As shown in Table 1, these conditions provided a high molecular weight PAE from BBP and a moderate

TABLE 1. Inherent Viscosity of Poly(Arylene Ether)s

Bisphenol	Bisfluoro monomer	η_{inh}, dL/g
BBP	DFB	1.15
EBP	DFB	Insoluble
HBP	DFB	Insoluble
PEBP	DFB	0.38

TABLE 2. Characterization of DFB/BPAF-Based Copolymers

Bisphenol with BPAF	η_{inh}, dL/g	DSC T_g, °C Initial	DSC T_g, °C Final[a]
10% BBP	1.4	170	170
10% EBP	0.89	172	185
10% PEBP	0.92	165	179
30% PEBP	0.52	162	184
100% BPAF	0.35	168	168

[a] After heating to 350°C for 1 hour.

molecular weight PAE from PEBP. However, polymers prepared in this manner using EBP or HBP and DFB formed insoluble materials, indicating reaction of the ethynyl and hexynyl groups during synthesis. Therefore, both reaction time and temperature were reduced in an effort to prepare high molecular weight, soluble polymers containing these pendant groups. When the reaction was held at or below ~145°C for up to 4 hours, 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 ~2 hours. Several other attempts using different conditions were also unsuccessful in producing high molecular weight. Furthermore, the PEBP polymer produced a very brittle film after curing for 1 hour at 350°C as expected because of the high crosslink density. This film was completely insoluble in chloroform and did not swell. Therefore, no further work was done with these polymers because of their limited utility.

The focus shifted to the preparation of copolymers that would yield more usable materials with a lower crosslink density. Copolymers were prepared from the reaction of 90 mol% of BPAF and 10 mol% of either BBP, EBP, or PEBP with DFB. Characterization of the copolymers is presented in Table 2. The BBP copolymer gave the highest η_{inh} (1.4 dL/g) and produced a tough film. Since no ethynyl groups were present, this material had the same T_g before and after heating to 400°C. The copolymers containing 10% pendant ethynyl groups also produced high η_{inh}s and tough films after curing. The materials, however, show an increase of 13-14°C in T_g due to crosslinking after heating to 400°C in the DSC or curing in an oven for 1 hour at 350°C. The films also become totally insoluble in chloroform or DMAc but did swell in these solvents.

In an effort to increase crosslink density and thereby reduce swelling, copolymers containing 30 mol% of EBP and PEBP were synthesized. However, the same problems occurred for the copolymer containing 30 mol% EBP as the EBP homopolymer. Again, attempts to synthesize high molecular weight copolymer without gel formation were unsuccessful, so the focus shifted to the 30 mol% PEBP copolymer. This copolymer was readily synthesized and produced a tough film although the η_{inh} was lower than the previous copolymers. As expected, the T_g of this copolymer increased after curing from 162 to 184°C, the largest increase recorded for the copolymers due to a higher concentration of ethynyl groups and, accordingly, higher crosslink density. A film from this copolymer cured 1 hour at 350°C showed only slight swelling in chloroform.

TABLE 3. Thermal Stability and Thin Film Properties of Polymers and Copolymers

	Temperature of 5% weight loss by TGA, °C		23 °C tensile properties (150 °C)		
Bisphenol components	Air	N_2	Strength, MPa	Modulus, GPa	Elongation, %
10% BBP, 90% BPAF	484	490	54.5 (28.9)	1.80 (1.58)	60 (76)
10% EBP, 90% BPAF	461	484	71.0 (33.8)	2.36 (1.79)	6.1 (9.1)
10% PEBP, 90% BPAF	455	487	68.9 (33.8)	1.96 (1.48)	96 (180)
30% PEBP, 70% BPAF	452	484	65.5 (31.0)	2.35 (1.60)	4.8 (76)
100% BPAF	476	493	65.5 (27.6)	2.24 (1.37)	9.9 (1.3)

Thin films were cast from the chloroform solutions and subsequently cured 1 hour each at 100, 200, and 350°C. Previous work on phenylethynyl-containing arylene ethers indicated that the reaction was complete after this cure schedule [3]. The thin film tensile properties of the PAEs containing pendant bromo or ethynyl groups and a homopolymer containing no ethynyl groups are reported in Table 3. Room temperature tensile strengths, moduli, and elongations of the lightly crosslinked PAE films ranged from 54.5 to 71.0 MPa, 1.80 to 2.36 GPa, and 4.8 to 96% at RT, and 28.9 to 33.8 MPa, 1.48 to 1.79 GPa, and 9.1 to 180% at 150°C, respectively. These values, especially strength and modulus, were slightly higher than those of the polymers containing no ethynyl groups.

Also presented in Table 3 is the temperature of 5% weight loss by TGA for the polymers and copolymers. The copolymers containing either pendant bromo or ethynyl groups had thermal stabilities only slightly lower than the homopolymer when tested in either air or nitrogen.

CONCLUSIONS

Polymers and copolymers prepared from bisphenols containing pendant ethynyl and substituted ethynyl groups and a commercially available monomer, 4,4′-difluorobenzophenone, formed films which could be thermally crosslinked to improve solvent resistance. The toughness and solubility of the copolymers could be systematically controlled by varying the amount of ethynyl-containing bisphenol used in the synthesis, which controls the final crosslink density. Thermal stabilities for the ethynyl- and phenylethynyl-containing copolymers were equivalent to the homopolymers.

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REFERENCES

[1] P. M. Hergenrother, *J. Macromol. Sci.—Rev. Macromol. Chem., C19*, 1 (1980).

[2] P. M. Hergenrother, in *Encyclopedia of Polymer Science and Engineering*, Vol. 1, 2nd ed. (H. Mark, ed.), Wiley, New York, 1985, p. 61.

[3] R. G. Bryant, B. J. Jensen, and P. M. Hergenrother, *Polym. Prepr., 33*(1), 910 (1992).

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