Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermal Crosslinking of Poly(2,6-Diphenylphenylene Ether) Containing Acetylene Moieties

Hu Yang[a]; Allan S. Hay[a]
[a] Department of Chemistry, McGill University, Montreal, Quebec, Canada

To cite this Article Yang, Hu and Hay, Allan S.(1994) 'Thermal Crosslinking of Poly(2,6-Diphenylphenylene Ether) Containing Acetylene Moieties', Journal of Macromolecular Science, Part A, 31: 2, 155 — 169

To link to this Article: DOI: 10.1080/10601329409349725

URL: http://dx.doi.org/10.1080/10601329409349725

J.M.S.—PURE APPL. CHEM., A31(2), pp. 155–169 (1994)

THERMAL CROSSLINKING OF POLY(2,6-DIPHENYLPHENYLENE ETHER) CONTAINING ACETYLENE MOIETIES

HU YANG and ALLAN S. HAY*

Department of Chemistry
McGill University
801 Sherbrooke St. W., Montreal, Quebec H3A 2K6, Canada

ABSTRACT

Thermally crosslinkable poly(2,6-diphenylphenylene ether) has been prepared by synthesizing copolymers containing ethynyl or phenylethynyl groups on the pendant phenyls of the comonomer units.

INTRODUCTION

Poly(2,6-diphenylphenylene ether) (P_3O) is a semicrystalline polymer with a high glass transition temperature (230°C) and high melting point (480°C) [1–4] characterized by having very high thermal stability and excellent electrical properties over a wide temperature range. P_3O cannot be molded because of its very high melting point which is close to the decomposition temperature [5]. In previous studies we demonstrated that substitution on the pendant phenyl rings can reduce the melting point of the polymer or convert it to an amorphous polymer so that melt processing is feasible.

We were interested in synthesizing an inherently amorphous P_3O-based polymer, or a polymer with significantly less crystallinity, which would be melt processible and in which there is incorporated thermally crosslinkable functionality which would allow the crosslinking of the polymer to take place well above the glass transition temperature. From previous results [6] on P_3O copolymers, it is indicated that approximately 10 mol% of comonomer units incorporated into the P_3O backbone would be sufficient to give a processible polymer with less crystallinity. By analogy to the physical crosslinking in the presence of crystalline domains in a polymer matrix, intermolecular chemical crosslinks have been recognized as having similar effects in terms of strengthening the polymer matrix at elevated temperature and improving solvent resistance [7–9].

The temperature range of the crosslinking reaction is a more critical parameter. Among the variety of cure functionalities used in thermosets, the acetylene group has been extensively employed to crosslink and/or extend polymer chains for many different polymer classes including polyimides [10, 11], poly(aryl ether sulfone)s [12], and poly(phenylquinoxaline)s [13]. One of the advantages of the acetylenic moieties as cure sites is that no volatile by-products are evolved during the cure cycle, resulting in void-free polymer structures. The thermally induced reaction of substituted acetylene groups is extremely complex; however, the resulting crosslinked polymers are thermoxidatively stable since the principal result of the crosslinking reaction appears to be the formation of aromatic moieties in the molecule [14]. The crosslinking reaction temperatures vary with the substituent on the acetylene group, as has been described in a review by Hergenrother [15].

Based on the above considerations, we proposed to design P_3O polymers incorporating small amounts of comonomer units bearing either an ethynyl or phenylethynyl group on the pendant phenyl groups and to study the thermal crosslinking of these polymers.

EXPERIMENTAL

Monomer Preparation

Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Flash chromatography was done on silica gel 60 from BDH. ^1H-NMR spectra were recorded in $CDCl_3$ solution at 200 MHz on a Varian XL-200 NMR spectrometer and reported in ppm from tetramethylsilane on the δ scale. Mass spectra were recorded at 70 eV with a direct insertion probe. Microanalyses were obtained from the Galbraith Laboratory Inc., Tennessee. All chemicals and solvents were reagent grade and used without further purification.

2,6-Bis(4-trimethylsilylethynylphenyl)phenol, 2

To a solution of 2,6-bis(4-iodophenyl)phenol (1) (6.25 g, 12.5 mmol) in diisopropylamine (100 mL) was added dichlorobis(benzonitrile)palladium (0.24 g, 0.625 mmol), triphenylphosphine (0.33 g, 1.25 mmol), and copper(II) acetate hydrate (0.125 g, 0.625 mmol). The solution was degassed by passing a rapid stream of argon through it. Trimethylsilylacetylene (TMSA) (2.95 g, 4.25 mL, 30 mmol) was added in 10 minutes at room temperature. The color changed rapidly to gray with the formation of a heavy precipitate. The mixture was heated to reflux for 2 hours. The dark brown mixture was cooled to room temperature, diluted with diisopropylamine (75 mL), and the precipitate was removed by filtration. The solvent was removed at reduced pressure, and the residue was taken up in methylene chloride (100 mL). The solution was washed with dilute HCl (5%, 150 mL) and water (2 × 100 mL). The solution was dried ($MgSO_4$), the solvent was evaporated, and the dark oil residue was purified by flash chromatography (hexane:ethyl acetate 10:1). The product was further purified by crystallization from ethanol to afford **2** as white crystals: yield, 3.4 g (62%); mp 120–122°C.

Analysis. Calculated for $C_{28}H_{30}OSi_2$ (438.7): C, 76.66; H, 6.89%. Found: C, 76.08; H, 6.31%. MS (70 eV) m/z = 438 (M+, 100), 423 (99.6), 204 (11.0). ^1H NMR ($CDCl_3$): δ = 0.26 (s, 18 H, $SiMe_3$), 5.29 (s, 1 H, OH), 7.05 (q, 1 H_{arom}), 7.25 (t, 2 H_{arom}), 7.48 (d, 4 H_{arom}, J = 8.5 Hz), 7.56 (d, 4 H_{arom}, J = 8.5 Hz).

2,6-Bis(4-ethynylphenyl)phenol, 3

To a solution of **2** (0.22g, 0.5 mmol) in THF (10 mL) was added tetrabutylammonium fluoride monohydrate (0.52 g, 2 mmol). The solution was allowed to stir at room temperature for 8 hours. The solution was poured into water (20 mL) and extracted with ether (2 × 30 mL). The ether solution was washed with water (2 × 50 mL) and dried ($MgSO_4$). Removal of solvent at reduced pressure gave a residue that was purified by crystallization from hexane–chloroform to afford **3** as white crystals: yield, 81 mg (55%); mp 154°C.

Analysis. Calculated for $C_{22}H_{14}O$ (294.4): C, 89.77; H, 4.79%. Found: C, 89.27; H, 4.43%. MS (70 eV) m/z = 294 (M+, 100), 263 (14.7), 147 (5.4). ^1H NMR ($CDCl_3$): δ = 3.12 (s, 2 H, $H_{acetylene}$), 5.29 (s, 1 H, OH), (t, 1 H_{arom}, J = 7.61 Hz), 7.27 (d, 2 H_{arom}, J = 6.88 Hz), 7.55 (q, 8 H_{arom}, J = 8.20 Hz).

2,6-Bis(4-phenylethynylphenyl)]phenol, 4

To a solution of **1** (3.11 g, 6.25 mmol) in diisopropylamine (50 mL) was added dichlorobis(benzonitrile)palladium (0.12 g, 0.31 mmol), triphenylphosphine (0.165 g, 0.625 mmol), and copper(II) acetate hydrate (62.5 mg, 0.31 mmol). The solution was degassed by passing a rapid stream of argon through it. Phenylacetylene (1.65 mL, 15 mmol) was added in 10 minutes at room temperature. The color changed rapidly to gray with the formation of a heavy precipitate. The mixture was heated to reflux for 1 hour. The dark brown mixture was diluted with diisopropylamine (50 mL) and filtered hot to remove solids. The solvent was removed under reduced pressure, and the residue was taken up in methylene chloride (100 mL). The solution was washed with dilute HCl (5%, 150 mL) and water (2 × 100 mL) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a residue that was purified by flash chromatography (hexane:ethyl acetate 10:1). The light colored product was further purified by crystallization from ethanol to afford **4** as white crystals: yield, 1.2 g (43%); mp 179°C.

Analysis. Calculated for $C_{34}H_{22}O$ (446.6): C, 91.45; H, 4.97%. Found: C, 91.20; H, 4.85%. MS (70 eV) m/z = 446 (M+, 100), 223 (13.9). ^1H NMR ($CDCl_3$): δ = 5.40 (s, 1 H, OH), 7.03–7.11 (m, 3 H_{arom}), 7.26–7.53 (m, 18 H_{arom}).

Polymer Preparation and Characterization

The inherent viscosities of the polymers were measured in chloroform (concentration 0.5%) at 25°C. Differential scanning calorimetry (DSC, Seiko 220 analyzer) was used to detect the thermal reactions and the variation in transition temperatures. Thermogravimetric analyses were conducted on a TG/DTA, Seiko 220 analyzer. The thermograms were recorded with a programmed heating accessory. Typically, 8–15 mg polymer samples were pressed into pellets and scanned at 20°C/min with dry nitrogen as the purging gas.

General Procedure for the Polymerization

To a test tube was added 12.3 mg CuCl, 9.3 mg *N,N,N′,N′*-tetramethylethylene diamine (TMEDA), 0.6 g anhydrous magnesium sulfate, and 10 mL *o*-dichlorobenzene. The test tube was put in an oil bath at 65°C, and the mixture was agitated with a magnetic stirrer. Oxygen was bubbled into the mixture for 10 minutes. When the solution became green colored, a solution containing a combined total of 1.5 g 2,6-diphenylphenol (DPP) and functionalized monomer in a molar ratio of 20:1 or 10:1 in 12 mL *o*-dichlorobenzene was added slowly over 20 minutes. A dark red color developed instantly. The reaction was continued for 8 hours. When the reaction was finished, the mixture was diluted with 10 mL chlorobenzene, and several drops of anhydrous hydrazine were added to the reaction mixture to reduce the diphenoquinone by-product, whereupon the deep red-orange color of the diphenoquinone disappeared. The inorganic solids were removed by filtration through a layer of Celite (1 cm), and the solution was added dropwise to 200 mL methanol containing several drops of hydrazine. After stirring for several hours, the polymer was collected by filtration. The polymer was dissolved in about 20 mL chloroform and precipitated in 200 mL methanol. The polymer was collected again by filtration and dried in a vacuum oven at 80°C for 24 hours.

η_{inh}, dL/g: PESi5, 0.53; PESi10; 0.50; PEϕ5, 0.45; PEϕ10, 0.47.

Preparation of PE5 and PE10

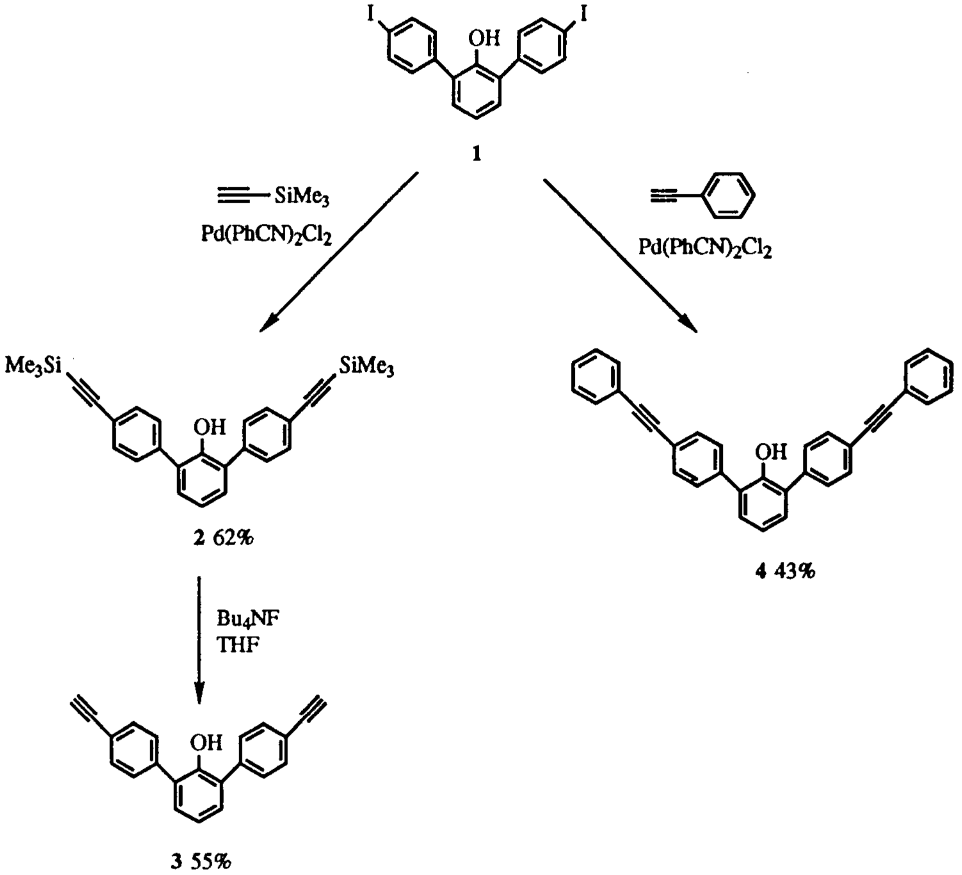
To a solution of polymer PESi5 or PESi10 (1.0 g) in tetrahydrofuran (30 mL), was added 3 equivalents (per ethynyl function) of tetrabutylammonium fluoride monohydrate, and the resultant solution was stirred at room temperature for 8 hours. The solution was concentrated under reduced pressure to 2/3 volume and added dropwise into methanol (150 mL). The fibrous polymer was dissolved in chloroform (100 mL), washed with water (2 × 100 mL), and dried ($MgSO_4$). The solution was concentrated to approximately 20 mL and precipitated into methanol (100 mL). The polymer was collected as a white fiber and dried in a vacuum oven at 80°C for 24 hours.

η_{inh}, dL/g: PE5, 0.54; PE10, 0.52.

RESULTS AND DISCUSSION

Monomer Synthesis

The introduction of ethynyl and phenylethynyl groups onto DPP was carried out by reacting 2,6-bis(4-iodophenyl)phenol, which had been prepared previously [16], with trimethylsilylacetylene or phenylacetylene by the palladium-catalyzed coupling reaction outlined in Scheme 1. The trimethylsilyl functionalized monomer **2** and the phenylethynyl-substituted monomer **4** were readily obtained from the coupling reactions. The deprotection of monomer **2** with fluoride anion afforded **3**, which was used in a model study of the crosslinking reaction.



SCHEME 1.

Monomer **3**, when heated in the DSC (Fig. 1, Curve a), displays a sharp melting endotherm at 179°C and a broad exotherm due to reaction of the ethynyl group. The exotherm commences in the melt region and peaks at 227°C. A DSC trace of **4** (Fig. 1, Curve b) shows a melting endotherm at 154°C and a reaction exotherm onset near 345°C, peaking at 392°C. These data indicate that the ethynyl-substituted analog decomposes near the glass transition of the polymer, which would make it very difficult to process. Therefore, the polymers bearing phenylethynyl groups, which cure at much higher temperatures, are the most attractive to pursue. The actual onset temperature of the crosslinking reaction for the corresponding polymers would be expected to be further increased due to the restricted mobility and much lowered density of cure sites in the polymer systems.

Polymer Preparation

The acetylene-functionalized monomers were incorporated into P_3O by copolymerization with 2,6-diphenylphenol, DPP, as shown in Scheme. 2. Either 5 or 10 mol% of the functional monomers was used in the copolymers.

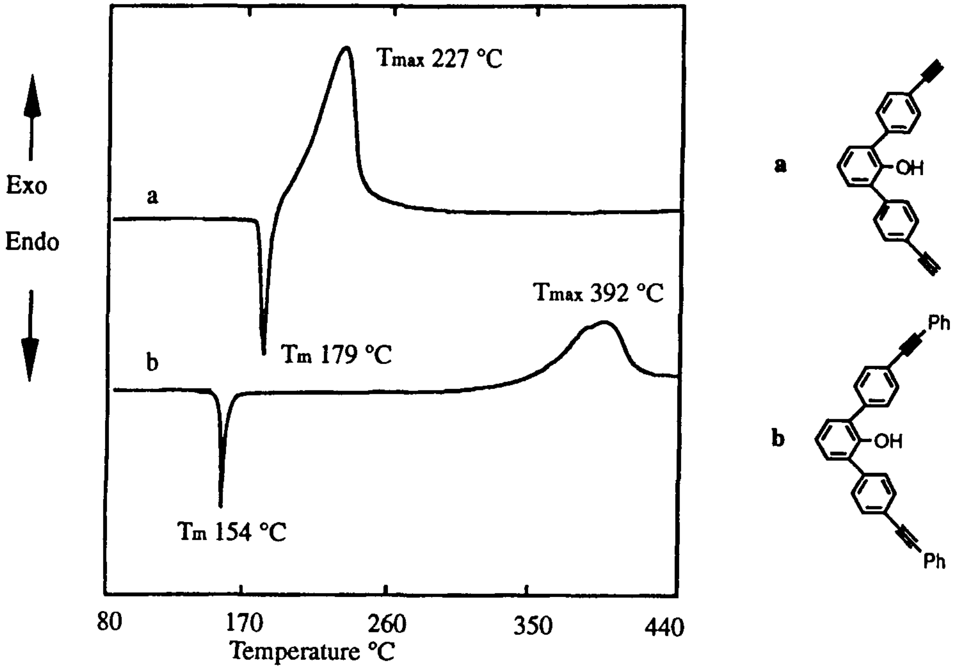
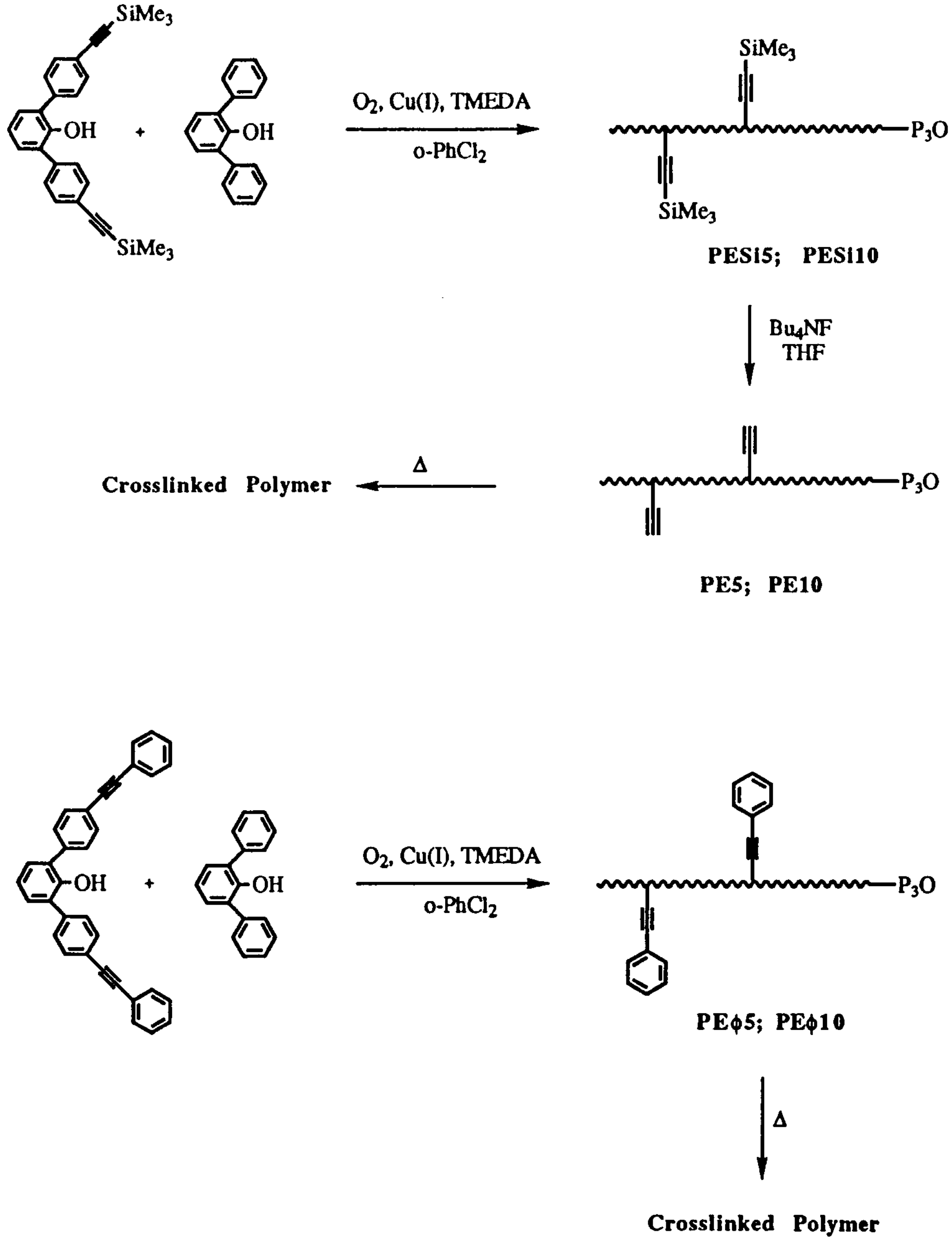


FIG. 1. DSC traces of monomer containing acetylene groups. Heating rate: 20°C/min.

Since the ethynyl group will undergo an oxidative coupling reaction under these conditions, and therefore will interfere with the polymerization, TMS-protected monomer **2** was subjected to copolymerization with DPP. The protecting group was subsequently removed by treating the resultant copolymers with tetrabutylammonium fluoride in THF yielding cure precursors PE5 (5% mole of ethynyl-substituted monomer) and PE10 (10% mole of ethynyl-substituted monomer). The proton NMR (Fig. 2) shows the incorporation of trimethylsilylacetylene-substituted monomer in P_3O as indicated by the extra peaks near 6.3 ppm from the identical hydrogens of the central phenylene ring (Curve b) whereas P_3O homopolymer only shows a single peak at 6.3 ppm (Curve a). The complete removal of the protecting group is also indicated by the disappearance of absorption at 0.12 ppm from the TMS group (Curve b) and the new peak at 3.0 ppm (Curve c) after treatment with fluoride in THF.

The phenylethynyl-substituted monomer can be directly incorporated into P_3O by simultaneous oxidation of a mixture of 2,6-diphenylphenol (DPP) and phenylethynyl-substituted monomer **4**. The incorporation of substituted monomer units in P_3O is also confirmed from NMR (Fig. 3) as indicated by the extra peaks near 6.3 ppm which correspond to the absorption of hydrogen on the central phenylene rings along the copolymer chain. The resulting copolymers PEϕ5 (5% mol of **4**) and PEϕ10 (10% mol of **4**) were then subjected to thermal curing.


SiMe3
OH
+
OH
SiMe3
O2, Cu(I), TMEDA
o-PhCl2
SiMe3
P3O
SiMe3
PESi5; PESi10
Bu4NF
THF
P3O
PE5; PE10
Δ
Crosslinked Polymer
OH
+
OH
O2, Cu(I), TMEDA
o-PhCl2
P3O
PEϕ5; PEϕ10
Δ
Crosslinked Polymer

SCHEME 2.

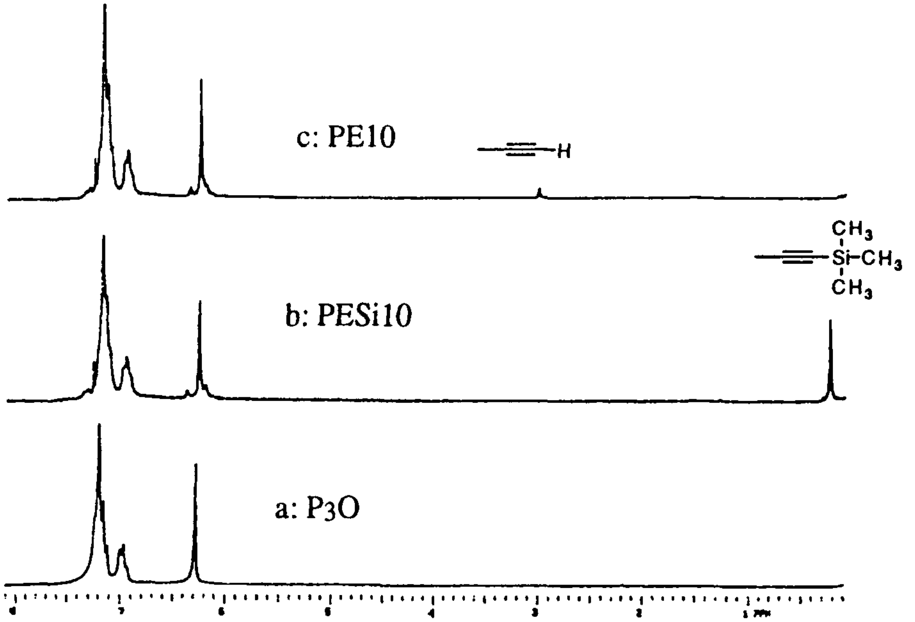


FIG. 2. ^{1}H-NMR spectra: (a) P_3O homopolymer (single peak at 6.3 ppm, hydrogens on central phenylene rings; (b) PESi10 (single peak at 0.2 ppm, $Ar-C{\equiv}C-Si(CH_3)_3$; multiple peaks around 6.3 ppm correspond to substituted and unsubstituted monomer units along the copolymer chains; (c) PE10 (single peak at 3.0 ppm, $Ar-C{\equiv}C-H$).

Copolymers Bearing Ethynyl Groups

Table 1 lists the transition temperatures and reaction exotherms from DSC scans of as-made samples PE5 and PE10. The onset temperature (T_{onset}) of the crosslinking reaction was found to be in the same region as T_g and reached a maximum near 280°C (T_{max}). The exotherm maxima (T_{max}) for both PE5 and PE10 are about 50°C higher than observed for the corresponding monomers. The much broader thermal reaction temperature ranges of PE5 (Fig. 4, Curve a) and PE10 (Fig. 5, Curve a) presumably arise from the much more restricted mobility in the polymer system than in the small molecules. We found that 5% of comonomer **3** in the P_3O backbone (PE5, Fig. 4, Curve a) does not suppress crystallinity completely since a melting endotherm was detected at 401°C.

The cure experiments for sample PE5 are shown in Fig. 4. Curing at 290°C for 2 hours (Curve b) and 350°C for 1 hour (Curve c) causes the glass transition temperatures to shift up to 255 and 266°C, respectively, and the intensity of the transition is significantly decreased. In addition, the increases in intensity of the melting endotherms indicate that crystallization also occurs upon thermal treatment. This suggests a competitive process between crosslinking and crystallization upon thermal treatment. Therefore the increase in T_g might be attributed to increased crystallinity as well as crosslinking in the system.

The cure experiments on PE10 studied by DSC are shown in Fig. 5. The amorphous nature of as-made sample PE10 was confirmed by the absence of a

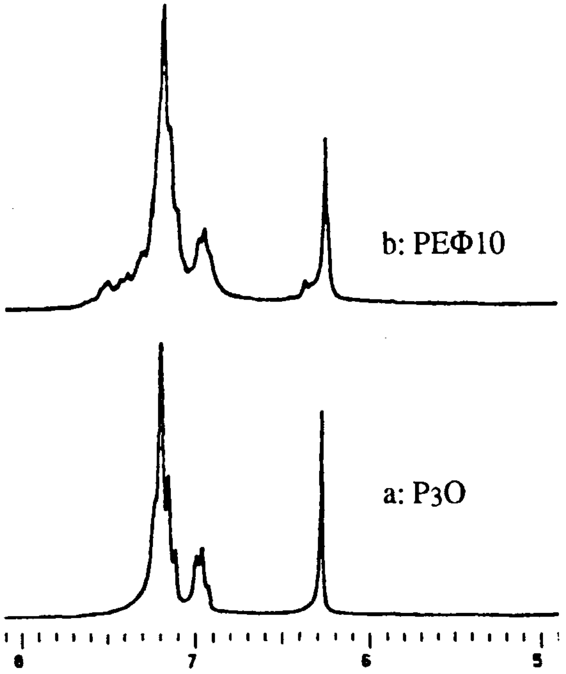


FIG. 3. ^{1}H-NMR spectra: (a) P_3O homopolymer; (b) PEϕ10, extra peaks near 6.3 ppm indicate random incorporation of substituted monomer unit into P_3O.

melting endotherm (Curve a). Curing at 260°C resulted in a glass transition temperature shift from 229 to 274°C (Curve b). Curing at 350°C gave no evident glass transition (Curve c), which indicates intensive crosslinking in the sample.

Copolymer Bearing Phenylethnyl Groups

Table 2 lists the transition temperatures and reaction exotherms from DSC scans for as-made samples PEϕ5 and PEϕ10. In these systems there was an approximately 30°C up-shift of T_{max} compared to the corresponding phenylethynyl-substituted monomers.

TABLE 1. Thermal Behavior of P_3O-Bearing Ethynyl Group[a]

Copolymer	T_g, °C	T_c, °C	T_{onset}, °C[b]	T_{max}, °C[c]	T_m, °C
PE5	230	–	230	287 (227[d])	401
PE10	229	–	230	276 (227[d])	–

[a] Heating rate: 20°C/min.

[b] Onset of crosslinking exotherm.

[c] Maxima of crosslinking exotherm.

[d] T_{max} of ethynyl-substituted monomer 3.

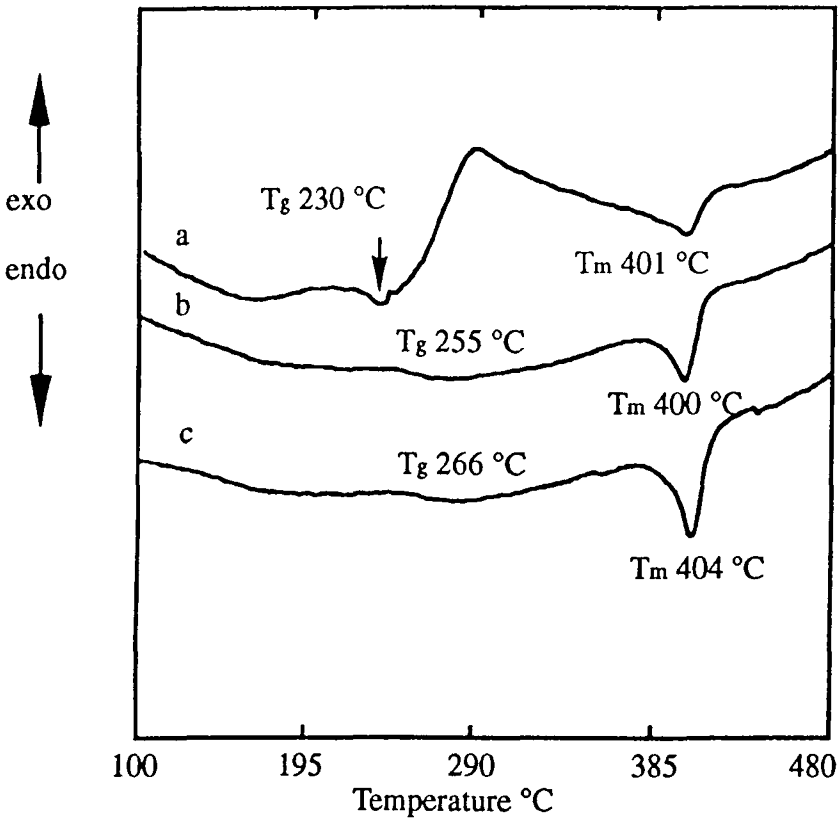


FIG. 4. DSC traces of cured PE5 samples (heating rate: 20°C/min), 5 mol% of functional comonomer: (a) sample as made; (b) cured at 290°C for 2 hours; (c) cured at 350°C for 1 hour.

The DSC scan of as-made sample PEϕ5 shows that this sample has a crystallization exotherm at 284°C and a melting endotherm at 420°C (Fig. 6, Curve a). In this case the crystallization in PEϕ5 proceeded without competition from crosslinking due to the much higher onset temperature of crosslinking (400°C), and the crosslinking reaction commences in the melting region where the mobility restriction is removed.

The scan for PEϕ5, cured at 380°C for 2 hours (20°C below the onset of T_m), showed a melting endotherm peaking at 435°C. The crosslinking reaction commences in the melting region (Curve b). The relatively small amount of crosslinking during this curing treatment is believed to result from the restricted mobility due to crystallization in the system which is indicated by the absence of a crystallization exotherm and the increased content of melting endotherm (Curves a and b). By raising the curing temperature to the onset of melting (400°C, 2 hours) with the expected removal of the mobility restriction, the resulting sample gave a melting endotherm at 420°C without any further crosslinking reaction, which was indicated by the symmetrical melting peak (Curve c). Again, the disappearance of the glass

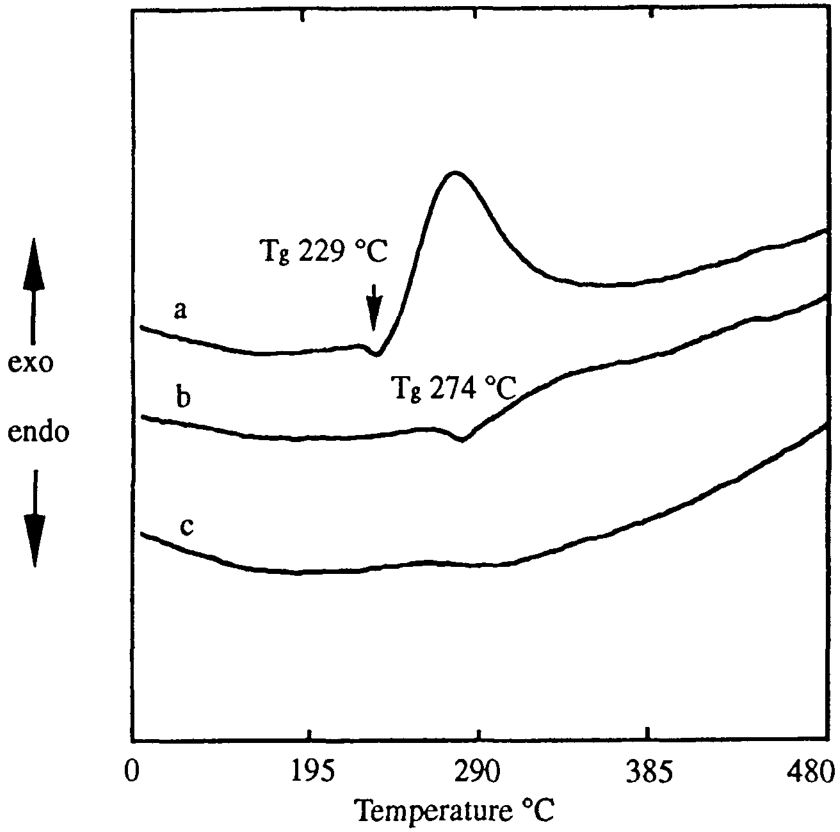


FIG. 5. DSC traces of cured PE10 samples (heating rate: 20°C/min), 10 mol% of functional comonomer: (a) sample as made; (b) cured at 290°C for 2 hours; (c) cured at 350°C for 1 hour.

TABLE 2. Thermal Behavior of Copolymer-Bearing Phenylethynyl Group[a]

Copolymer	T_g, °C	T_c, °C	T_{onset}, °C[b]	T_{max}, °C[c]	T_m, °C
PEϕ5	203	284	—[d]	—[d] (392[e])	420
PEϕ10	215	—	379	420 (392[e])	—

[a] Heating rate: 20°C/min.

[b] Onset of crosslinking exotherm.

[c] Maxima of crosslinking exotherm.

[d] Crosslinking exotherm falls in the melting temperature range.

[e] T_{max} of phenylethynyl-substituted monomer **4**.

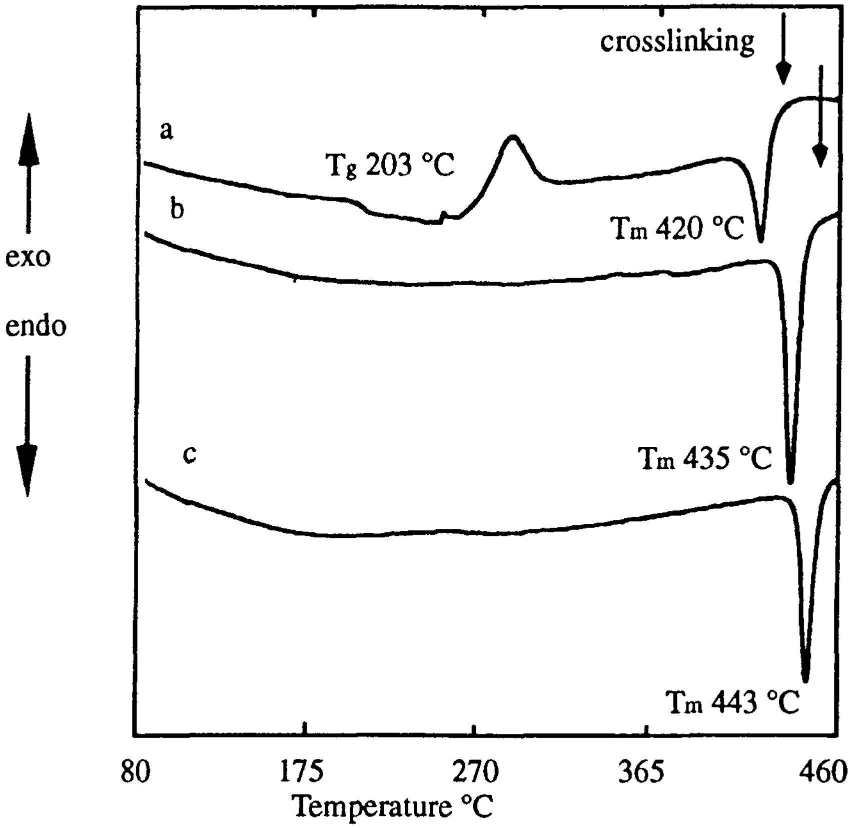


FIG. 6. DSC traces of cured PEϕ5 samples (heating rate: 20°C/min), 5 mol% of functional comonomer: (a) sample as made; (b) cured at 380°C for 2 hours; (c) cured at 420°C for 1 hour.

transition in these curing treatments might be attributed to both crystallization and crosslink formation in the systems.

By incorporating 10 mol% of phenylethynyl-substituted monomer into P_3O, the resultant polymer, PEϕ10, is largely amorphous. This is indicated by the DSC scan which shows a small and wide exotherm peak, indicating a very limited amount of crystallization (Fig. 7, Curve a). The crosslinking reaction commences at 379°C (T_{onset}) and reaches a maximum at 420°C. Both curing at 380°C for 2 hours (Curve b) and 420°C for 1 hour (Curve c) gave similar DSC curves with no evident glass transition but ill-defined transitions over a wide temperature range at a higher temperature. In this case the higher curing temperature apparently results in a relatively high crosslink density in the system, which leads to no evident glass transition in the DSC scan. Since no crystallization is involved in this system, as indicated by the absence of both crystallization exotherm and melting endotherm, the crosslinking reaction appears to be the only process occurring upon thermal treatment under the above curing conditions.

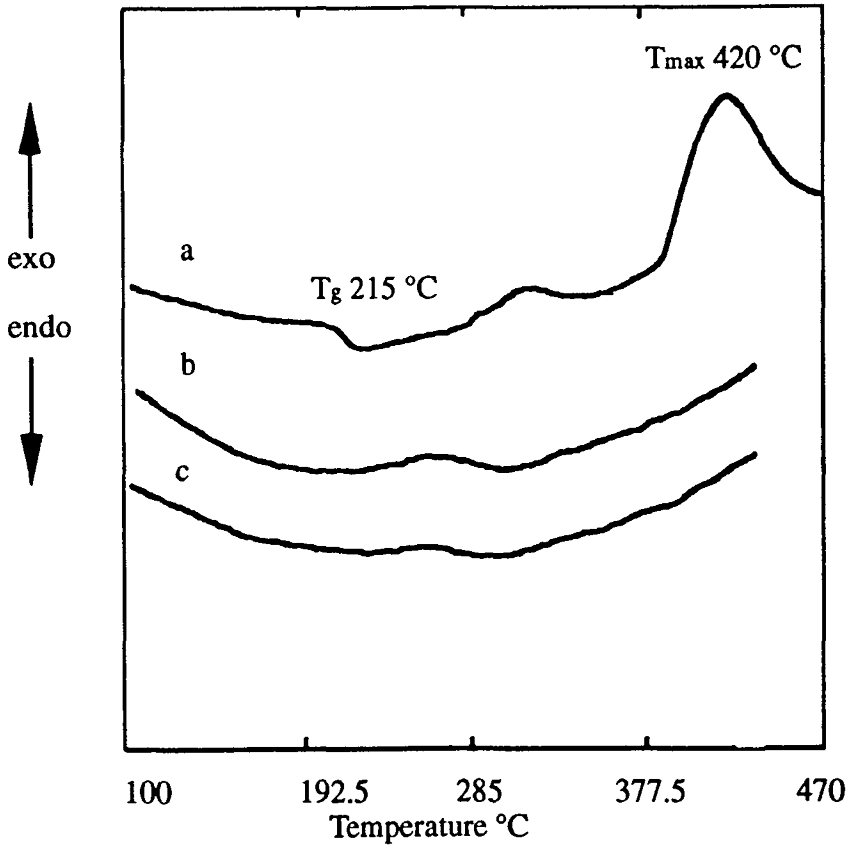


FIG. 7. DSC traces of cured PEϕ10 samples (heating rate: 20°C/min), 10 mol% of functional comonomer: (a) sample as made; (b) cured at 380°C for 2 hours; (c) cured at 400°C for 1 hour.

Solubility and TGA Profiles

As expected for crosslinked polymers, the cured acetylene-containing P_3O polymers were significantly more solvent resistant than the uncured polymers. Pellets of the polymers were prepared in a KBr press (4 tons pressure/1.25″ die). PE5 and PE10 were cured in the DSC at 350°C for 1 hour. PEϕ5, PEϕ10, and P_3O were cured at 400°C for 1 hour. The cured polymers PE5, PE10, PEϕ5, PEϕ10, and P_3O were placed in chloroform at room temperature for 24 hours. The acetylene-containing polymers, which before curing are readily soluble in chloroform, show no observable swelling over 24 hours in chloroform. P_3O, which has crystallized under these conditions, remains soluble. A TGA and DTG profile comparison between the acetylene-substituted polymers and P_3O is shown in Fig. 8. A P_3O sample and the acetylene-substituted polymers PE10 and PEϕ10 were treated identically by heating at 400°C for 30 minutes. Under these conditions the P_3O sample will develop significant amount of crystallinity based on DSC results while the polymers bearing the cure sites, which are largely amorphous in nature, will generate

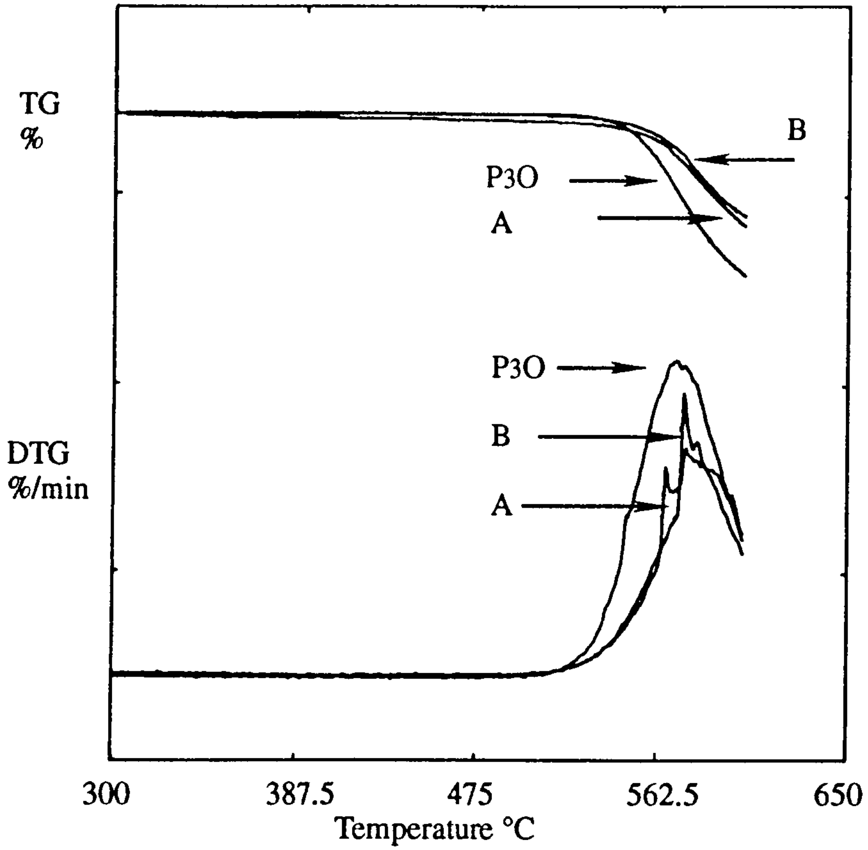


FIG. 8. TGA and DTG profiles of P_3O and crosslinked P_3O samples after heating at 400°C for 30 minutes. A, PEϕ10; B, PE10.

crosslinks in the polymer matrix. The crosslinked polymers show somewhat higher thermal stability than the parent polymer P_3O. In Fig. 8, samples PE10 and PEϕ10 show only slightly lower decomposition rates and slightly higher decomposition temperatures than P_3O as indicated in the DTG profiles. Hence, the crosslinks introduced into P_3O do not introduce any thermally unstable groups into the polymer but do enhance the thermal stability.

CONCLUSIONS

We have designed a system capable of crosslinking P_3O under curing. By making copolymers utilizing acetylene-containing monomers, systems are formed which are capable of undergoing thermal curing over a wide temperature range. This provides the possibility that the modified P_3O could be processed from both solution and melt. By starting with preformed high molecular weight copolymers with a relatively low density of reactive sites on the polymer, the brittleness associated with intensive crosslinking of oligomers is avoided.

REFERENCES

[1] A. S. Hay, *Macromolecules,* 2, 107 (1969); U.S. Patent, 3,432,466 (1969).

[2] W. Wrasidlo, *Macromolecules, 4,* 642 (1971).

[3] J. Vermeer, W. Boone, J. Bussink, and H. Breakel, *1970 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena,*NAS Publication p52; *Chem. Abstr. 75,* 153114p (1971).

[4] Technical Bulletin 24, Applied Science Laboratories, State College, Pennsylvania, 16801.

[5] A. S. Hay and D. E. Dana, *J. Polym. Sci., Polym. Chem. Ed., 27,* 873 (1989).

[6] H. Yang and A. S. Hay, *Ibid.*, In Press.

[7] P. M. Hergenrother, *Chemistry and Properties of Cross-linked Polymers* (S. S. Labana, Ed.), Academic Press., New York, 1977, p. 107.

[8] S. C. Temin, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys., C22*(1), 131 (1982-83).

[9] F. W. Harris and H. J. Spinelli, *Reactive Oligomers,* Washington, D.C., 1985.

[10] P. M. Hergenrother, *Encyclopedia of Polymer Science and Technology,* Vol. 1, Wiley, New York, 1985, p. 61.

[11] F. W. Harris, S. M. Podaki, and S. Varaprath, *Polym. Prepr., 21*(1), 3 (1980).

[12] G. Lucotte, L. Cormier, and B. Delfort, *J. Polym. Sci., Part A: Polym. Chem., 29,* 897 (1991).

[13] F. L. Hedberg, P. M. Lindley, C. Y.-C. Lee, and I. J. Goldfarb, *J. Polym. Sci., Polym. Chem. Ed.*, 20,3069 (1982).

[14] S. A. Swanson, W. W. Fleming, and D. C. Hofer, *Macromolecules, 25,* 582 (1992).

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

[16] H. Yang and A. S. Hay, *Synthesis,* p. 467 (1992).

Received November 26, 1992
Revision received April 6, 1993