Macromolecules **1996,** *29,* 4449−4452

Synthesis and Properties of Poly(*p*-benzamide-*b*-propylene oxide)

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Received December 12, 1995
Revised Manuscript Received March 4, 1996

Introduction

Considerable effort has gone into the preparation and characterization of aromatic polymers for applications requiring properties such as high thermal stability and high tensile properties. Depending on the applications, some of the characteristics of these polymers may be advantageous while others may be disadvantageous. Thus, a high thermal stability implies a high temperature for the processing of such polymers, and materials with a high modulus may show an excessive rigidty.[1,2] To avoid these disadvantages and to improve the properties, block copolymers have been synthesized[3,4] combining a rigid block with another block that is flexible. A rigid block polymer that may be used is based on poly(*p*-benzamide) (PBA), a polymer that shows high thermal stability and can be processed *via* a lyotropic solution[5−7] to yield fibers having ultrahigh-strength/high modulus.[7−9]

This paper reports the synthesis of PBA by the direct polycondensation of *p*-aminobenzoic acid according to the procedure of Yamasaki,[10] the end-capping (referred to below as “activation”) of poly(propylene oxide) with terephthaloyl chloride, and the coupling between these polymers to yield di- and triblock copolymers. All of these materials were characterized by FTIR spectroscopy and thermal analyses. Earlier, block copolymers combining stiff (but not rigid) units of poly(*m*-phenyleneisophthalamide) with flexible units of poly(ethylene oxide) were reported.[11]

Experimental Section

Reagents. 1-Methyl-2-pyrrolidone (NMP) (Fluka, 99%), triphenyl phosphite (TPP) (Aldrich, 97%), and pyridine, PY (J. T. Baker, 99.5%) were purified by distillation. *p*-Aminobenzoic acid (*p*-ABA) (Fluka, 99%) was dried for 1 h at 110 °C under vacuum. Lithium chloride (Merck, 99%) was dried at 325 °C for 12 h. Methanol (Merck, 99.9%) was dried by refluxing with magnesium ribbons and iodine crystals for 1 h. Dimethylacetamide (DMAc) (Fluka, 99.5%) was stirred for 25 h with barium oxide and distilled under nitrogen; the fraction at 164−166 °C was taken as pure solvent. Terephthaloyl chloride (TCl) (Aldrich) was purified by sublimation. Poly(propylene oxide) ($\bar{M}_n = 2000$) was obtained from Aldrich.

Synthesis of PBA. Into a three-neck cone-shaped flask were placed 41.32 g (0.42 mol) of recently distilled NMP, 3.0 mL of Py, 2.55 g (0.06 mol) of LiCl, and 5.74 g (0.042 mol) of *p*-ABA. The mixture was stirred to complete dissolution of the solids, and TPP (13.02 g, 0.047 mol) was added to the stirred flask. The resulting solution was stirred at 100 °C for 2 h, yielding a green paste. The reaction mixture was poured into a blender jar containing methanol, and the polymer was chopped. The product was filtered under vacuum and then extracted in a Soxhlet with dry methanol for 4 h. Yields varied from 90 to 94%. The extracted PBA was characterized by FTIR, TGA, and inherent viscosity.

Activation of Poly(propylene oxide). Poly(propylene oxide) (PPO) of molecular weight 2000 was dried over calcium hydride and then characterized by FTIR and ^{1}H-NMR spectroscopy. The activation procedure, which consisted of reacting the hydroxyl end groups of PPO with TCl, was carried out in a drybox. Thus, 1.77 g (8.7 mmol) of TCl was placed in a flask, stirred, and heated by means of a silicone bath to obtain a melt. To the molten TCl was added slowly 5.0 g (2.5 mmol) of PPO. The reaction was maintained for 20 min following the addition of PPO. The product was a clear viscous liquid which is very unstable toward humidity. Unreacted TCl was separated by distillation under vacuum with a nitrogen bleed.

Coupling Reaction between PBA and Activated PPO. A 1% solution of PBA in DMAc containing 3% dissolved LiCl was prepared in a tightly closed bottle at room temperature by stirring with a magnetic stirring bar over the course of 2−3 h.

To a three-neck cone-shaped flask was added 5 g (2.5 mmol) of activated PPO (*act*-PPO), which was then cooled to −22 °C with stirring under nitrogen. Next, 1.4 g (16.7 mmol) of PBA in 140 mL of the 1% PBA solution (above) was added slowly over ca. 1 h, followed by an increase in the stirring rate and the rate of nitrogen flow. The reaction mixture was kept for 13 h at −22 °C before it was precipitated into dry methanol. The product was washed with water, extracted in a Soxhlet with dry methanol for 4 h, and then dried. Yield: 84.4%; inherent viscosity, 2.33 dL/g.

Measurements. Inherent viscosities of PBA were measured with an Ostwald viscometer at 30 °C in concentrated sulfuric acid (98%) and at 25 °C in DMAc/3% LiCl. FTIR and ^{1}H-NMR spectra were recorded on a Magna Nicolet 550 spectrophotometer and Bruker AC 250 spectrometer, respectively. Thermograms were recorded on a Perkin-Elmer TGA-7 thermobalance under nitrogen. Samples (1.8−2.0 mg) were heated in a platinum sample holder between 20 and 500 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Electron micrographs were obtained by using a scanning electron microscope (ETEC Autoscan U-1). The surface of the resin was coated with gold for 2 min to obtain a 150 Å thickness using an Edwards 150 sputter coater.

Results and Discussion

To obtain a block copolymer containing a rigid and a flexible block, the coupling reaction of a rigid aromatic polyamide, poly(*p*-benzamide) (PBA), and a low molecular weight flexible block of poly(propylene oxide) (PPO) was employed. Each of these polymers was characterized separately before the coupling was carried out, and the coupled product was then characterized.

Characterization of PBA. PBA was synthesized following the method of Yamazaki *et al.*[10] in which *p*-aminobenzoic acid is employed as monomer.

(1)

A FTIR spectrum of PBA (Figure 1) showed, among other things, the following typical absorption signals: at 3341.9 cm^{-1} ν_{N-H}(amide), at 1657.0 cm^{-1} $\nu_{C=O}$(amide), at 1499 cm^{-1} $\nu_{C=C}$(aromatic), at 1590 and 1398 cm^{-1} ν_{O-C-O}(carboxylate), at 1313 cm^{-1} ν_{C-N}(amide). The FTIR spectrum of PBA did not show the signals corresponding to O−H and C═O from carboxylic acid which are present in a *p*-aminobenzoic acid spectrum.

Pure PBA shows high thermal stability without any significant weight loss up to 500 °C. However, thermo-

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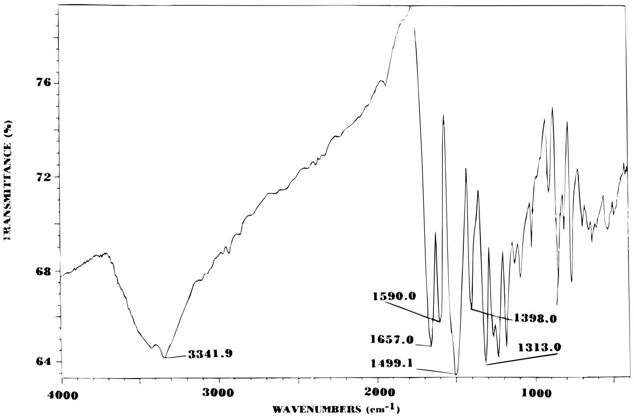


Figure 1. FTIR spectrum of poly(*p*-benzamide) (PBA).

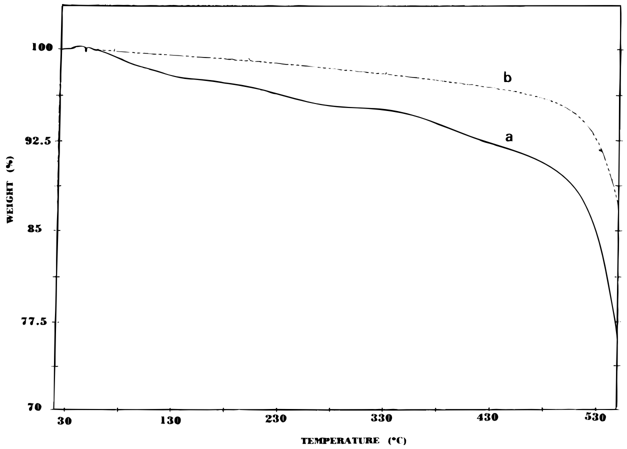


Figure 2. Thermal stability of poly(*p*-benzamide) (PBA) of η_{inh} = 1.65 dL/g: (a) without Soxhlet extraction; (b) with Soxhlet extraction (methanol). (Sample weight: 1.0−2.1 mg; heating rate = 10 °C/min.)

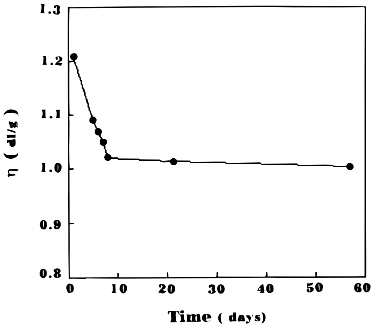


Figure 3. Variation of inherent viscosity with time for poly(*p*-benzamide).

grams for PBA that has not been extracted with methanol in a Soxhlet for 1 day show a lower thermal stability (Figure 2) due to residual solvent which strongly hydrogen bonds to the amide bonds of PBA and most likely also due to the presence of phosphorus byproducts from TPP (the latter possibly could interfere with the coupling of PBA and PPO). There is not a significant effect of molecular weight on thermal stability when PBAs with inherent viscosities of 1.210 and 1.654 dl/g are compared. (Note: according to the relationship of viscosity to molecular weight found by Schaefgen,[12] PBA of inherent viscosity 1.21 dL/g has a molecular weight of less than 10 000.)

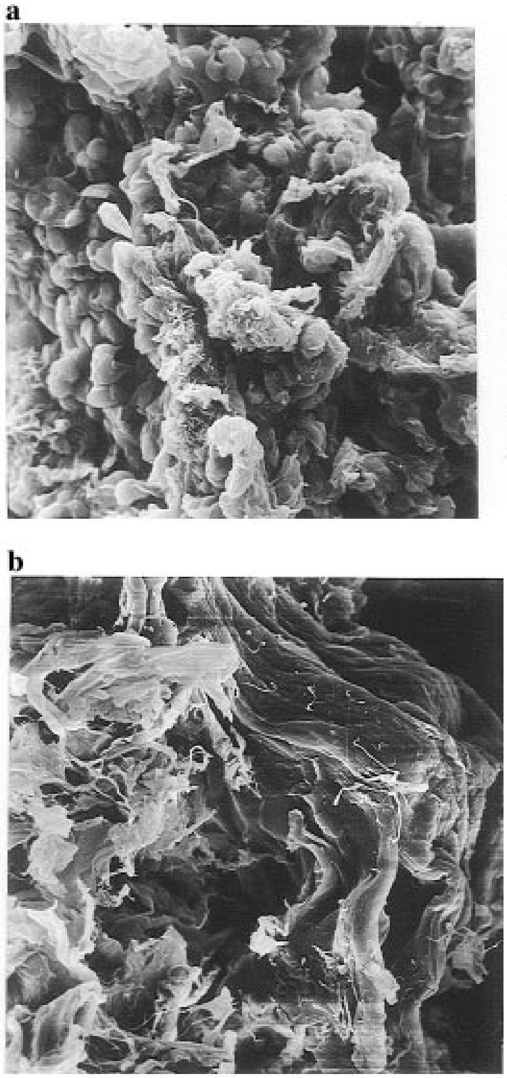
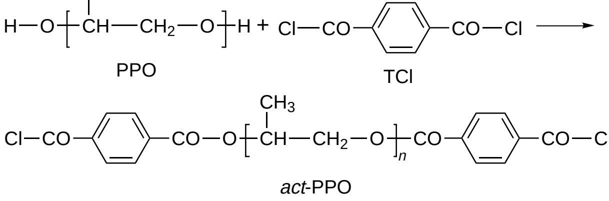


Figure 4. Scanning electron micrographs (800×) of poly(*p*-benzamide): (a) η_{inh} = 1.65 dL/g; (b) η_{inh} = 1.21 dL/g.

The chemical stability of PBA in concentrated sulfuric acid (98%) was studied using PBA of η_{inh} = 1.210 dL/g at a concentration of 0.5 g/dL. The study was carried out at 30 °C for 7 days using a fresh sample for each point. During the first week, the η_{inh} value decreased about 20% but following this initial drop, it remained constant for over 2 months (Figure 3).

The SEM micrographs of PBA showed a smooth surface without holes. The morphologies (Figure 4) of the PBA samples differed depending on their inherent viscosities.

Characterization of Activated PPO. Because the hydroxyl end groups of PPO are not very reactive toward the end groups of PBA, the hydroxyl end groups were end-capped with acid chloride groups derived from terephthaloyl chloride. In this manner, an activated PPO was obtained.



(2)

The first step in the synthesis of *act*-PPO was to thoroughly dry the starting material, PPO, with calcium hydride. This procedure was apparently quite successful because the intensity of the OH groups was de-

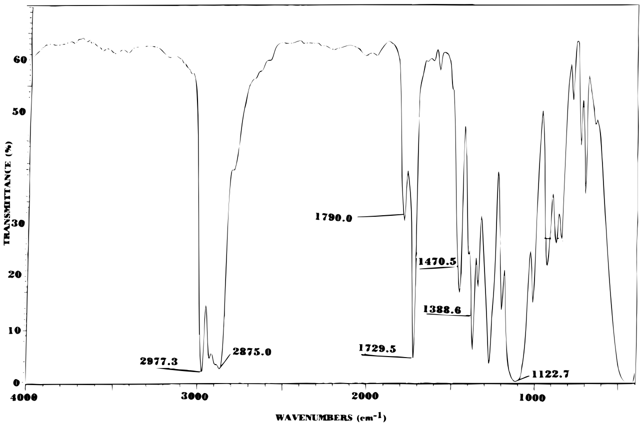


Figure 5. FTIR spectrum of activated poly(propylene oxide) (*act*-PPO).

Table 1. Data for the Coupling Reaction of *act*-PPO with PBA

	mol of *act*-PPO	mol of PBA[b]	molar ratio	η_{inh},[a] dL/g	yield, %
PPO–PBA	2.5×10^{-3}	1.67×10^{-4}	15:1	2.33	84.8[c]
PPO–PBA–PPO	7.5×10^{-3}	1.67×10^{-4}	45:1	3.22	80.8[d]

[a] Determined at 25 °C on a solution of 1 g of polymer in 100 mL of DMAc containing 3% dissolved LiCl. [b] The inherent viscosity of PBA determined at 25 °C on 1 g of polymer in 100 mL of DMAc containing 3% dissolved LiCl was 1.64 dL/g. [c] The yield, if the product were PPO–PBA–PPO, would be 71.7%. [d] The yield, if the product were PPO–PBA, would be 96.31%.

creased about 20% according to ^{1}H-NMR. In order to ensure the activation on both ends of PPO, a feed molar ratio of PPO:TCl of 1:3.5 was used; excess TCl was removed by distillation under vacuum.

The FTIR spectrum (Figure 5) of *act*-PPO did not show signals corresponding to hydroxyl end groups but rather showed absorption bands at 1790 and 1730 cm^{-1}, which can be assigned to $\nu_{C=O}$ from acid chloride and ester, respectively. The structure of *act*-PPO was further confirmed by the fact that the ^{1}H-NMR spectrum (250 MHz, CDCl$_3$, TMS) showed (Figure 6) four assignments from downfield at $\delta = 8.25{-}8.16$ (aromatic protons) derived from the TCl moiety; the other three assignments were at $\delta = 3.61$ ppm (corresponding to CH$_2$O), $\delta = 3.4$ ppm (corresponding to CHO), and $\delta = 1.35$ ppm (corresponding to CH$_3$).

Coupling of the Rigid Block and the Flexible Block. The coupling reaction of the rigid PBA block with the flexible PPO block was carried out under conditions which favored the formation of a diblock rather than a triblock copolymer. (The latter can be formed readily by the reaction of 2 mol of PBA and 1 of *act*-PPO by coupling through amide formation.) Consequently, a large feed molar ratio (15:1) of *act*-PPO to PBA was taken to promote monocoupling.

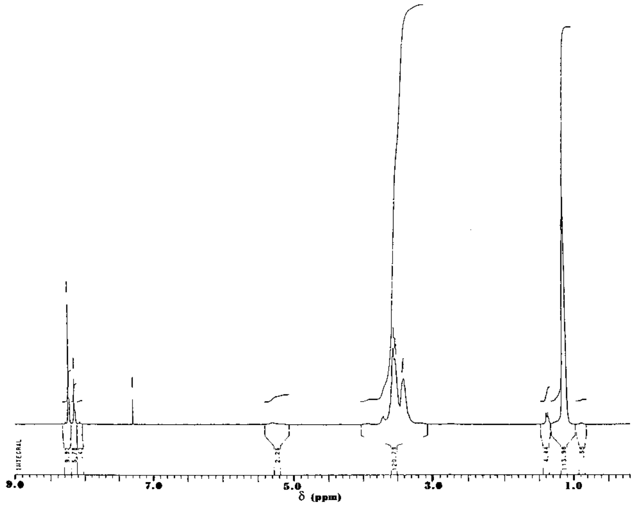


Figure 6. ^{1}H-NMR (250 MHz, CDCl$_3$, TMS) of *act*-PPO.

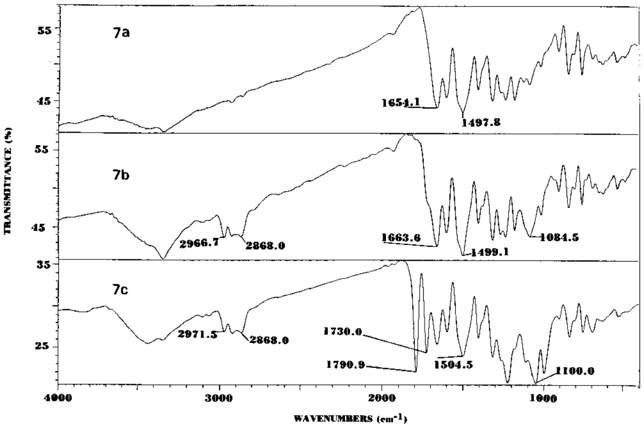
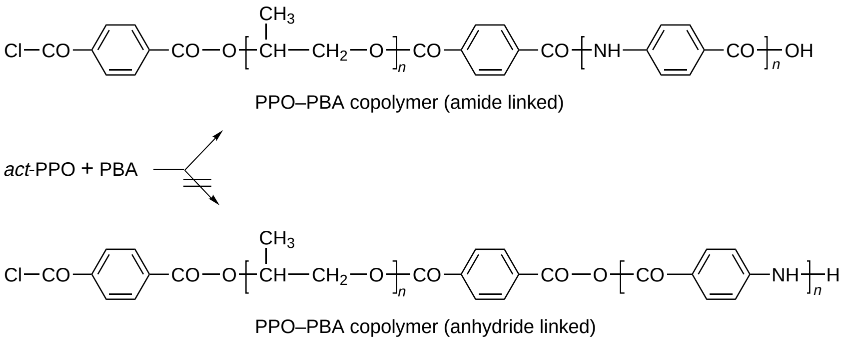


Figure 7. FTIR spectra of poly(*p*-benzamide-*b*-propylene oxide): (a) poly(*p*-benzamide); (b) PPO–PBA from feed molar ratio of PBA to *act*-PPO of 1:15, (c) PPO–PBA–PPO from feed molar ratio of PBA to *act*-PPO of 1:45.

Although it would be possible for the acid chloride group of *act*-PPO to react at either the amino end group or the carboxylic acid end group of PBA, the FTIR evidence indicates that only amide formation occurs. Thus, the FTIR spectrum (Figure 7) of the block copolymer PPO–PBA (Table 1) shows a signal at 1499 cm^{-1}, ν_{N-H}(amide II), which is also present in PBA; there is an absence of a signal at 1790 cm^{-1} characteristic of anhydride formation, further bolstering our conclusion that the blocks are joined only through an amide bond, yielding a diblock copolymer. The evidence for the incorporation of the PPO block is the fact that block copolymer PPO–PBA has signals at 1084 and 2967 cm^{-1} corresponding, respectively, to ν_{C-O-C} from ether and to ν_{CH} from methyl and methylene groups. The latter evidence is necessary because it might be argued that



PPO–PBA copolymer (amide linked)

PPO–PBA copolymer (anhydride linked)

(3)

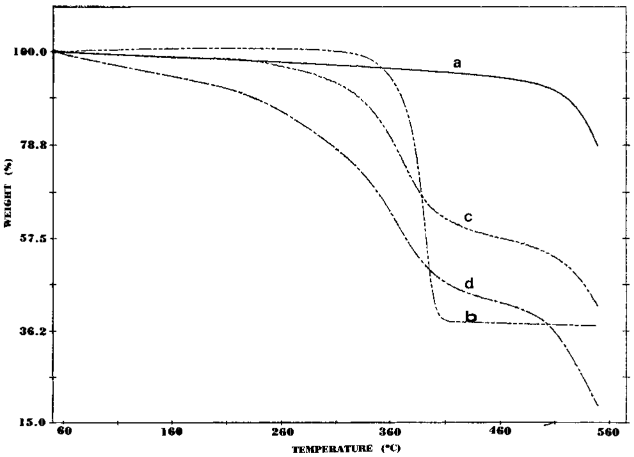


Figure 8. Thermograms of (a) poly(*p*-benzamide), (b) poly(propylene oxide), (c) PPO−PBA, and (d) PPO−PBA−PPO. (Sample weight: 1.8−2.0 mg; heating rate = 10 °C/min under nitrogen.)

residual TCl in *act*-PPO could lead to coupling of two PBA molecules. Any tendency for this to occur was lowered by the use of a large excess of *act*-PPO.

When a very large excess of *act*-PPO is taken relative to PBA, apparently it is possible for the acid chloride group of an *act*-PPO block to react with the carboxylic acid group of PBA (probably on an already formed diblock of PPO−PBA) to give a triblock copolymer, PPO−PBA−PPO (Table 1). The evidence for this is found in the FTIR spectrum of PPO−PBA−PPO, which shows the presence of a signal at 1791 cm^{-1} which can be attributed to $\nu_{\mathrm{CO-O-CO}}$ from an anhydride group. Additionally, there is an increase in signals ν_{CH} coming from the aliphatic groups of PPO (2972−2868 cm^{-1}) and a decrease in the signal at 1504 cm^{-1} corresponding to $\nu_{\mathrm{N-H}}$ of amide II coming from the amide groups of PBA, showing that the relative concentration of PPO is greater in the new polymer while the relative concentration of PBA is less.

The larger inherent viscosity values of the presumedly coupled blocks compared to PBA, using the same solvent, are a strong argument for coupling.

Thermal Stability of Block Copolymers PPO−PBA and PPO−PBA−PPO. Both block copolymers of Table 1 showed a lower thermal stability than either PBA or PPO. It is to be expected that the diblock copolymer of PBA and PPO would be less stable than PBA alone because of the low thermal stability of PPO. That the diblock and triblock coopolymers are less stable than PPO is somewhat surprising. However, increasing the content of PPO in a block copolymer does in fact decrease the thermal stability of the derived copolymer (Figure 8). Thus, as might be expected based on the low thermal stability of PPO, the triblock copolymer, PPO−PBA−PPO, containing a higher proportion of PPO appears to show somewhat lower thermal stabilty than the diblock copolymer PPO−PBA.

Conclusions

Block copolymers containing PBA as the rigid segment and PPO as the flexible one can be synthesized by a relatively simple coupling reaction. Depending on the concentration of one of the segments, it is possible to obtain, preferentially, a diblock or a triblock. Thus, for a molar ratio of PPO:PBA = 15:1, a diblock is formed *via* amide formation. For a much larger molar ratio of PPO:PBA, 45:1, it appears that the initially formed diblock reacts with excess PPO to form a triblock *via* anydride formation. The block copolymers show a decrease in thermal stability with increasing PPO content.

Acknowledgment. The authors wish to acknowledge the support of the Commission of European Communities (Grant CI1*-CT93-0322), the Direccion de Investigacion, Universidad de Concepcion, and the Departamento de Investigaciones Cientificas y Tecnologicas, Universidad de Santiago de Chile. This work also was supported (J.P.) in part by NSF Grant CTS-9402055.

References and Notes

(1) Preston, J.; Hofferbert,W. L., Jr. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 13.
(2) Alfonso, G. C.; Bianchi, E.; Ciferri, A.; Russo S.; Salaris, F.; Valenti, B. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 213.
(3) Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A.; Krigbaum, W. R.; Preston, J. *Polym. J.* **1988**, *20*, 83.
(4) Conio, G.; Tealdi, A.; Marsano, E.; Mariani, A.; Ponomarev, I. *Polymer* **1994**, *35*, 5.
(5) Krigbaum, W. R.; Shufan, Zhang; Preston, J.; Ciferri, A.; Conio, G. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1043.
(6) Takasa, M.; Ciferri, A.; Krigbaum,W. R.; Hacker, H. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1657.
(7) Lin, L.; Sherrington, D. *Adv. Polym. Sci.* **1994**, *111*, 177.
(8) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Macromolecules* **1977**, *10*, 1390.
(9) Preston, J.; Black, W. B.; Hofferbert, W. L., Jr. *J. Macromol. Sci., Chem.* **1973**, *A7* (1), 67.
(10) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373.
(11) Zdrahala, R. J.; Firer, E. M.; Fellers, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 689.
(12) Schaefgen, J. R.; Foldi, K. L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1976**, *17*, 69.

MA9518316