

Synthesis, Characterization, and Processing of Aromatic Copolymers with Different Monomer Sequences

S. MAKHIJA* and M. JAFFE

Hoechst Celanese, 86 Morris Avenue, Summit, New Jersey 07901

SYNOPSIS

Two aromatic copolyester compositions were prepared from *p*-hydroxybenzoic acid, hydroquinone, and isophthalic acid with compositions 2 : 1 : 1 (HIQ50) and 1 : 1 : 1 (HIQ33). For each of these compositions, one random copolyester and one known sequence copolymer was prepared. The random compositions were prepared by melt condensation, whereas controlled sequence polymers were prepared by low-temperature solution polymerization. For the 1 : 1 : 1 composition, the controlled sequence polymer had higher crystallinity than that of the random, whereas the 2 : 1 : 1 composition random copolymer had higher crystallinity. The difference in crystallinity is attributed to the sequence distributions in the copolymers. All compositions were thermotropic in nature. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Understanding and reconciling the solid-state order in thermotropic copolymers with the random organization of the mers in the chain backbone has been of interest to us and several other research groups around the world.^{1–8} Although models and assumptions differ, all these models agree on the importance of sequence distribution in defining the level and perfection of the solid-state structure, which, in turn, exerts a profound impact on solid-state properties. In the present work, the concept of controlled sequence copolymers was explored through computer simulation and experimental investigation of a model liquid crystalline polymer system (HIQ), the copolymer of *p*-hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ). The suffix after HIQ in this paper refers to the mol % of HBA in the terpolymer. Therefore, the 1 : 1 : 1 composition of HBA : IA : HQ is referred to as HIQ33 and the 2 : 1 : 1 composition is referred to as HIQ50. The results of molecular simulation are described in a separate publication.⁹ HIQ is a liquid crystalline polymer in the composition range between 20 and 50% of HBA. HIQ can be made by several different routes: In the acidolysis route, ace-

toxy benzoic acid is reacted with hydroquinone diacetate and IA with acetic acid released as a by-product. In the phenyl ester route, phenyl *p*-hydroxybenzoate is reacted with diphenyl isophthalate and hydroquinone and phenol is released as a by-product. During the course of our study, it was found that same composition of HIQ made by these two different routes had subtly different properties. Careful study of the microstructure of these polymers made by different routes led to the hypothesis that the differences in properties was due to the primary backbone architecture of the polymers. Indications of small differences in sequences were observed by triad analysis of the random copolymer and by 500 MHz NMR. No differences in structures were observed at the diad level with 200 MHz NMR.¹⁰ This led us to synthesize known sequence copolymer and study the effect of sequence distribution on the properties of the copolymers. References 12–32 contain other information related to the sequences and morphology of the polymer.

EXPERIMENTAL

Synthesis

Synthesis of Di(p-caboxyphenyl)isophthalate (Trimer Hydroxide)

A 3 L three-necked flask equipped with a nitrogen inlet and outlet, condenser, and thermometer was

* To whom correspondence should be addressed.

charged with 18.0 g (0.44 mol) of sodium hydroxide, 29.0 g (0.21 mol) of HBA, and 300 mL of distilled water. Isophthaloyl dichloride, 20.3 g (0.12 mol), was dissolved in 300 mL methylene chloride. The acid chloride solution was added to the reaction flask. The resulting mixture was stirred at room temperature for 1 h, and the disodium salt of the product was filtered, washed with water, and then acidified with dilute hydrochloride solution. The crude product was filtered, washed three times with distilled water, and dried at 100°C. The product had a melting point of 290–300°C.

**Preparation of
Di(*p*-chlorocarbonylphenyl)isophthalate**

In a 1 L three-necked flask equipped with a nitrogen inlet and outlet, thermometer, condenser, scrubber containing sodium hydroxide solution, and mechanical stirrer were placed 20 g of di(*p*-carboxyphenyl)isophthalate, 300 g of thionyl chloride, and 1 mL of *N,N*-dimethylformamide. The resulting mixture was reacted overnight at about 90°C. The solution was cooled and filtered, washed with hexane, and dried. The crude acid chloride was recrystallized from toluene solution and dried at 100°C overnight under vacuum. The product had melting point of 206°C.

**Synthesis of Controlled HIQ50
(HBA-IA-HBA-HQ)**

The controlled sequence HIQ50 was made by a synthetic procedure developed by us.³³ In a 3 L three-

necked flask were placed 2.22 g (0.005 mol) of di(*p*-chlorocarbonylphenyl) isophthalate and 400 mL of methylene chloride. Hydroquinone (0.55 g, 0.005 mol) and 0.44 g of sodium hydroxide were dissolved in 33 mL of distilled water (see Fig. 1).

This solution was added to the flask, along with an aqueous solution (5 mL) containing 0.07 g of 40% benzyltrimethylammonium hydroxide solution in water. The reaction mixture was stirred overnight at high speed. Methylene chloride was decanted. The solid polymer was filtered, washed twice with water, and air-dried. The polymer had an inherent viscosity (IV) of 0.9 in 0.1% concentration in HFIP/PFP 50/50 by volume at 25°C.

Fibers of Controlled Sequence HIQ50

Fibers were spun from a solution of HIQ50 polymer in PFP/HPIP (50/50). The polymer formed a clear dope but the viscosity of the dope was high. All the dopes were made at about 5% concentration. Fibers were spun through a die at a hole diameter ranging from 5 to 150 μ m; single- as well as multiple-hole spinnerettes were used. The pressure ranged from 10 to 50 psi. The coagulant mediums used were water and methanol. The fibers of reasonable quality were obtained from a single-hole 150 μ m die with pressure ranging from 30 to 45 psig with methanol as the nonsolvent. The fibers were analyzed using DSC and X-ray. The fibers were heat-treated at 250°C for 3 h to develop crystallinity.

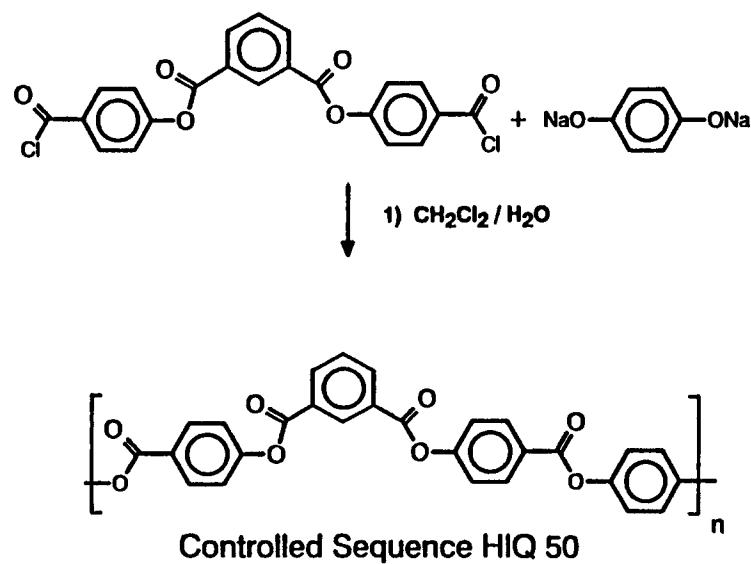


Figure 1 Synthesis of controlled sequence HIQ50.

Synthesis of Preferred Sequence HIQ33

Strictly ordered HIQ50 can be made because HBA-IA-HBA is a symmetrical trimer and, hence, it can be reacted with HQ to form the controlled sequence HBA-IA-HBA-HQ.³³ In the case of controlled HIQ33, the dimer HBA-IA was reacted with HQ. Since HBA-IA is not a symmetrical dimer, the resulting polymer does not have a unique ordered monomer sequence. Therefore, this polymer is referred to as preferred HIQ33 rather than as controlled HIQ33. This polymer cannot have HBA-HBA sequences. However, in this polymer, it is possible to have IA-HQ sequences. This is different from controlled HIQ50, which did not have HBA-HBA or IA-HQ linkages. The preparation of this HIQ33 copolymer is two step and described below.

The first dimer HBA-IA was prepared by reacting 1 mol of hydroxybenzoic acid with 1 mol of isophthaloyl acid chloride in ether solution in the presence of sodium carbonate. The product after filtration and separation was purified. Even after purification, the product had small quantities of the HBA-IA-HBA trimer as seen by NMR. The pres-

ence of the small amount of trimer reduces the molecular weight of the polymer; however, it does not change the premise that this polymer does not have HBA-HBA linkages. The dimer was then reacted with hydroquinone in the presence of mixed solvent pyridine and 1,1,2,2-tetrachloroethane and in the presence of diphenylchlorophosphosphate at 100°C in a N₂ atmosphere (Fig. 2). The polymer was filtered, washed with distilled water twice, and dried in a vacuum oven overnight. The synthesis of this polymer is described in Figure 2. Random HIQ50 and HIQ33 were made by a standard melt transesterification method using the acidolysis route.³

Characterization

Wide-angle X-ray diffraction (WAXS) measurements were done using a Philips APD3720 powder diffractometer equipped with a graphite analyzing crystal operating in the reflection mode. The radiation was CuK α (wavelength = 1.54 Å). A Perkin-Elmer DSC7 and TA Instrument 2100/910 were used to determine the thermal properties of the polymers. The samples were heated to 250°C to erase

SYNTHESIS OF PREFERRED SEQUENCE HIQ33 POLYMER

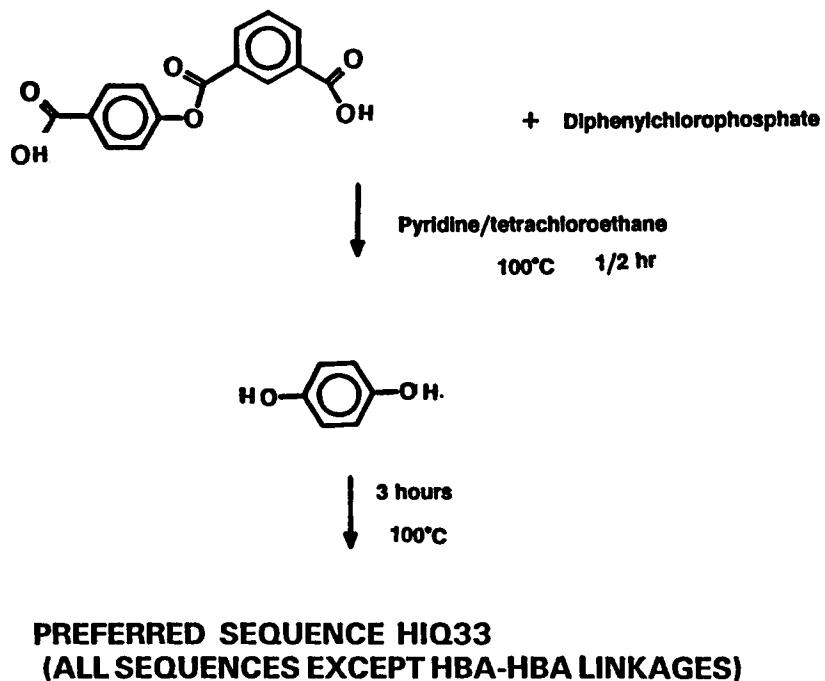


Figure 2 Preferred sequence HIQ33 (all sequences except HBA-HBA linkages).

previous thermal history. Samples were then heated at a 20°C/min rate in a nitrogen atmosphere to measure the glass transition and melting temperatures. IVs were measured in PFP/HFIP solvent at 25°C.

RESULTS AND DISCUSSION

Characterization of Controlled HIQ50

The microstructure of the controlled HIQ50 was confirmed using NMR. In Figure 3, in the carbonyl region, two diads corresponding to HBA-IA and HBA-HQ are observed. In the case of random HIQ50, four carbonyl diads corresponding to HBA-IA, HBA-HQ, HBA-HBA, and IA-HQ are observed (see Fig. 4).

Recently, an infrared method has been developed in our laboratory to study sequences in wholly aromatic copolymers based upon this controlled HIQ50. Infrared bands related to C—O motion have been calibrated against this structure. The details of this are described elsewhere.¹¹

Thermal transitions of controlled sequence copolymer were higher than those of the random HIQ50 polymer. The glass transition temperature is about 144°C compared to 133°C for the random copolymer. The crystal-to-nematic transition is about 390°C compared to 345°C for the random HIQ50. The nematic-to-isotropic temperatures and the decomposition temperatures are in the same range for controlled and random copolymers (460–490°C).

WAXS scattering of controlled HIQ50 showed it to be more crystalline than is random HIQ50 (Fig. 5). WAXS of controlled HIQ50 showed a number of crystalline peaks, whereas the WAXS of random HIQ50 showed only one pronounced peak at 4.4 Å, which is attributed to the average spacing between the chains in the liquid crystalline state. Annealing of controlled HIQ50 at 200°C for 3 h increased the crystallinity without changing the sequences in the chain backbone. When controlled HIQ50 was annealed at 340°C for 30 min, the backbone sequences randomized and the resulting WAXS was similar to a random HIQ50. From IR data, it is known that the kinetics of randomization at 340°C is fast enough so that in 30 min it is completely randomized.¹⁰

Characterization of Fibers of Controlled HIQ50

As-prepared fibers of controlled sequence HIQ50 were characterized using DSC and WAXS. The DSC traces were similar to those of HIQ50 powder. The X-ray showed that the “as-spun” fiber samples show only a weak meridional reflection with a *d* spacing around 3.7 Å. Since the equatorial pattern of the fibers is different from the meridional pattern, we conclude that “as-spun” fibers are partially oriented but lack crystalline order. The fibers were then annealed at 250°C for 3 h in the oven under the flow of nitrogen gas. FTIR studies indicated that the transesterification rate at this temperature is negligible¹¹; therefore, no change in the backbone sequences of the copolymer is expected. The annealed fibers showed diffraction patterns consistent with crystalline regions embedded in the liquid

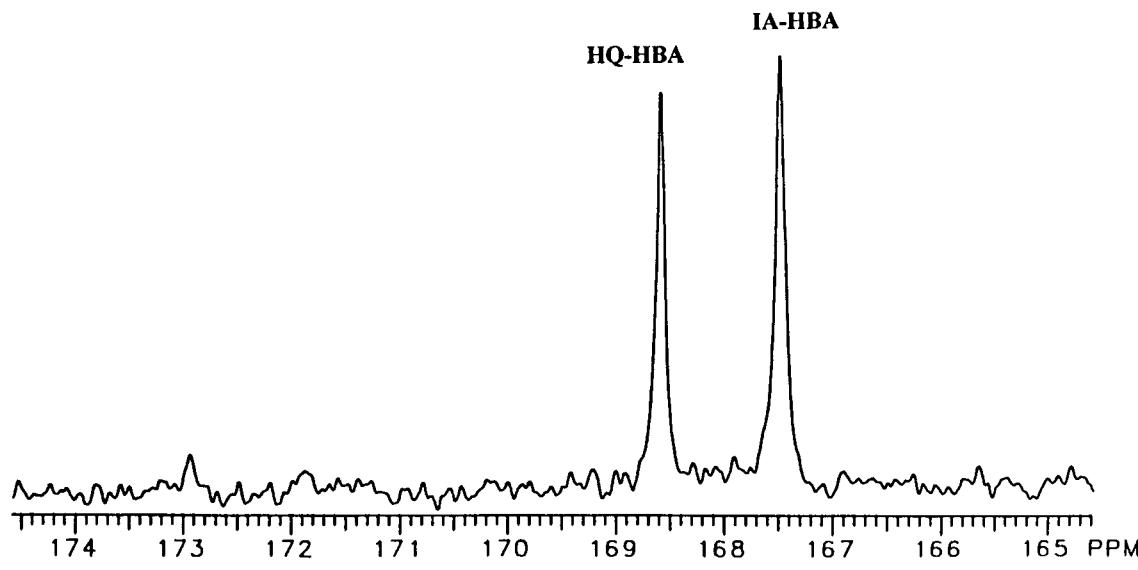


Figure 3 Carbonyl region of ^{13}C -NMR of controlled HIQ50.

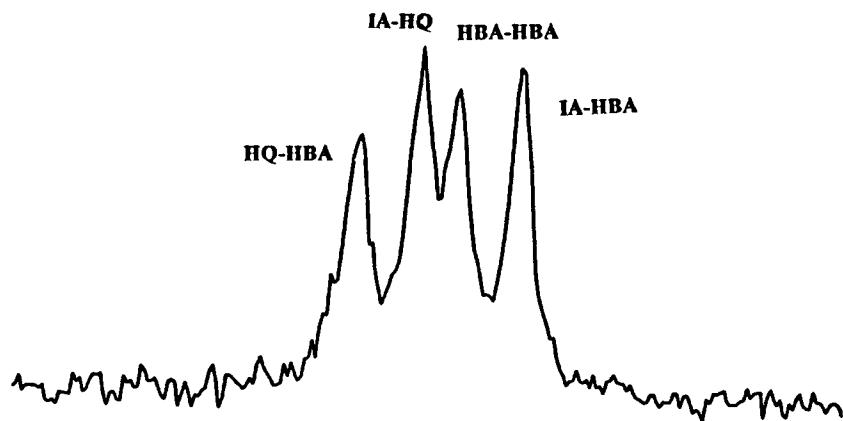


Figure 4 Carbonyl region of ^{13}C -NMR of random HIQ50C.

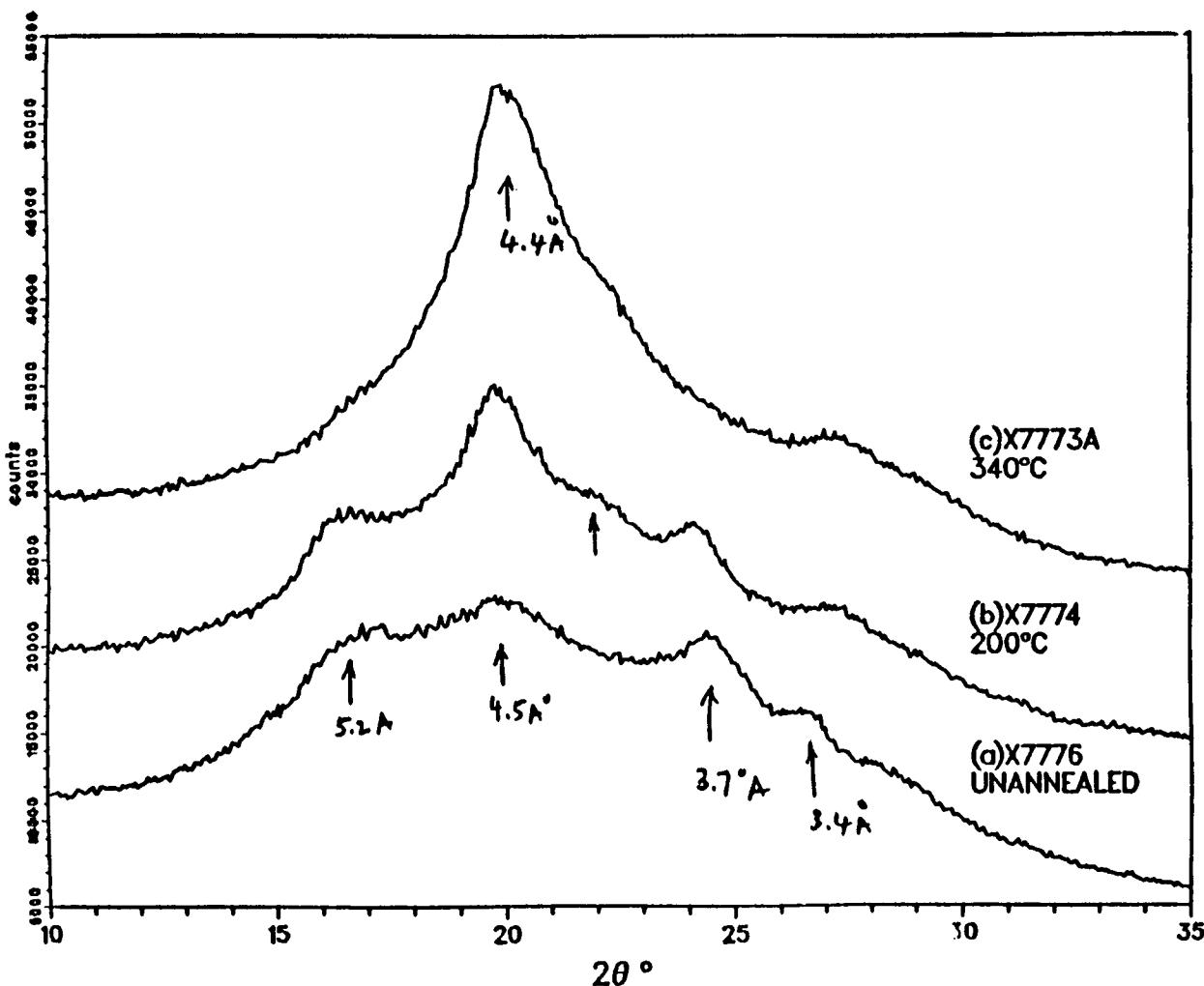
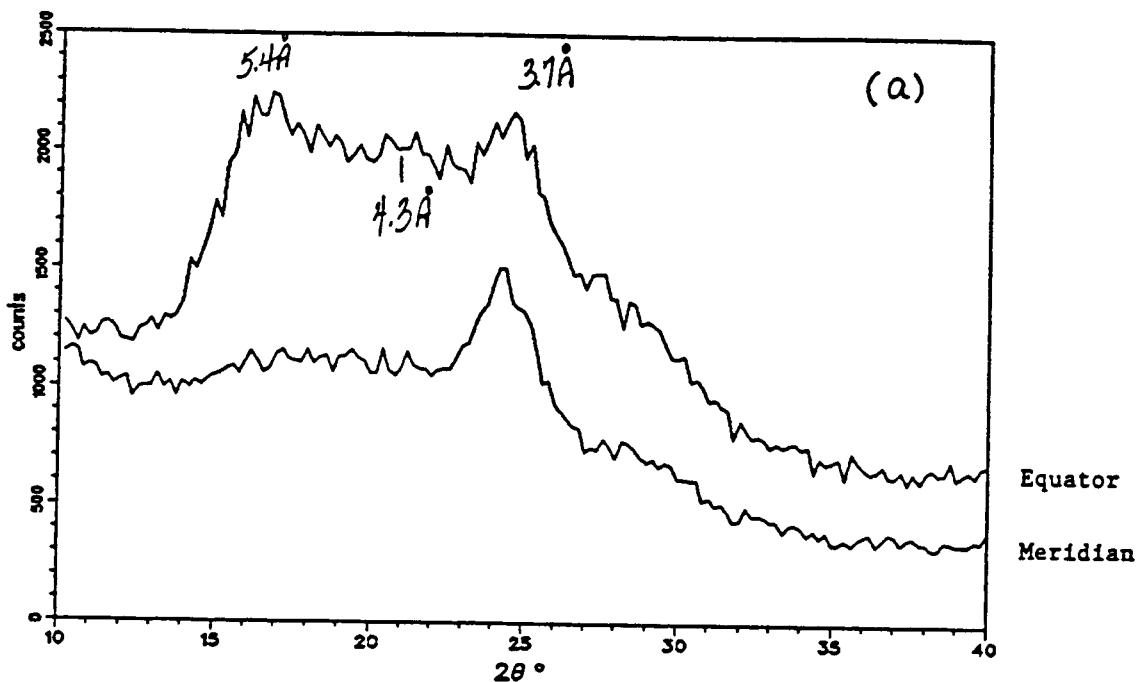


Figure 5 WAXS patterns of controlled HIQ50: (a) unannealed; (b) annealed at 200°C for 3 h; (c) annealed at 340°C for 30 min.

Q7846B: RT CHIQ50 FIBER, 10-27-92



Q7866A: ANNALED CHIQ50, 2SCANS, 11-17-92

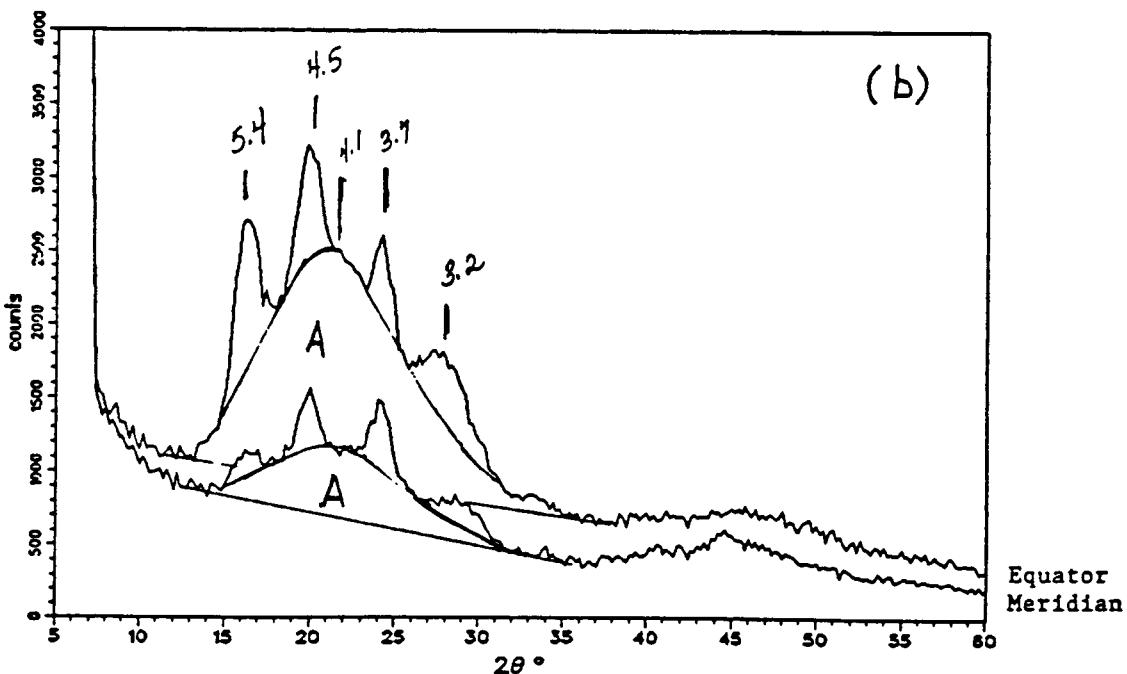


Figure 6 Comparison of the equatorial and meridional scans of the as-made and annealed CHIQ50 fibers.

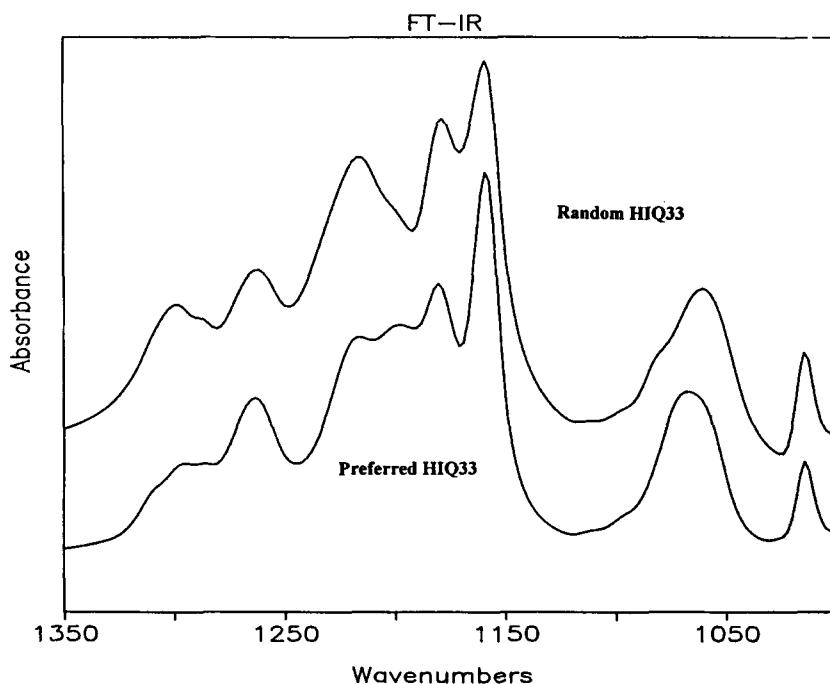


Figure 7 FTIR of preferred and random HIQ33.

crystalline matrix (Fig. 6). The meridian scans had four peaks at 5.4, 4.5, 3.7, and 3.2 Å. Earlier work of Johnson et al.⁹ showed that random HIQ50 annealed fibers had three sharp equatorial reflections at 5.59, 3.92, and 3.22 Å. They assigned these peaks to crystalline regions containing *p*-phenylene isophthalate sequences (IA–HQ). Since controlled HIQ50 does not have IA–HQ sequences in our samples, these peaks cannot arise due to the IA–HQ

sequences. Currently, modeling efforts are underway to understand the conformations of the HBA–IA–HBA–HQ polymer in the fiber form.

Characterization of Preferred HIQ33

Since it was difficult to purify the dimer, a low molecular weight polymer was obtained with an IV of

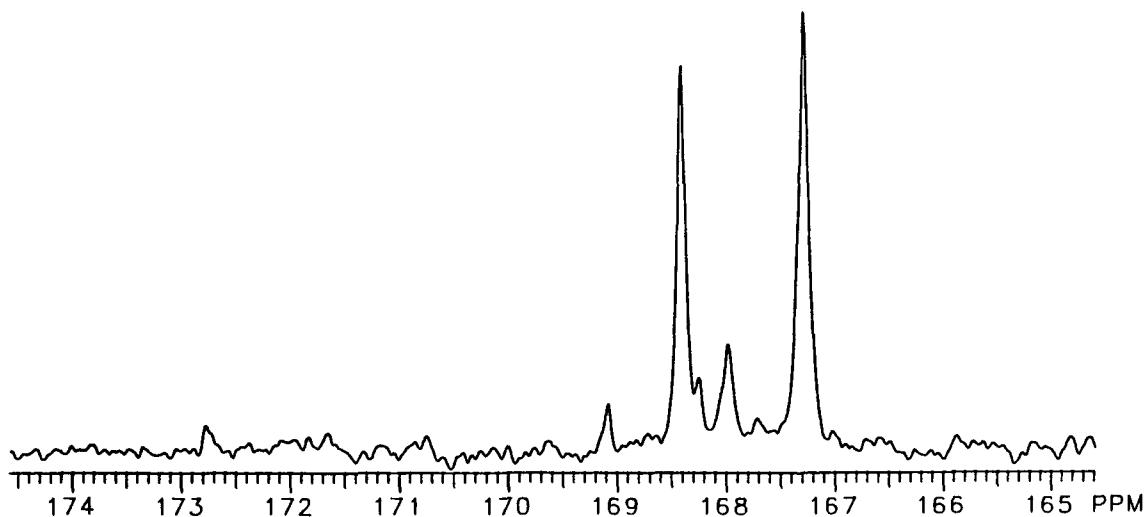


Figure 8 Carbonyl region of ^{13}C -NMR of preferred HIQ33.

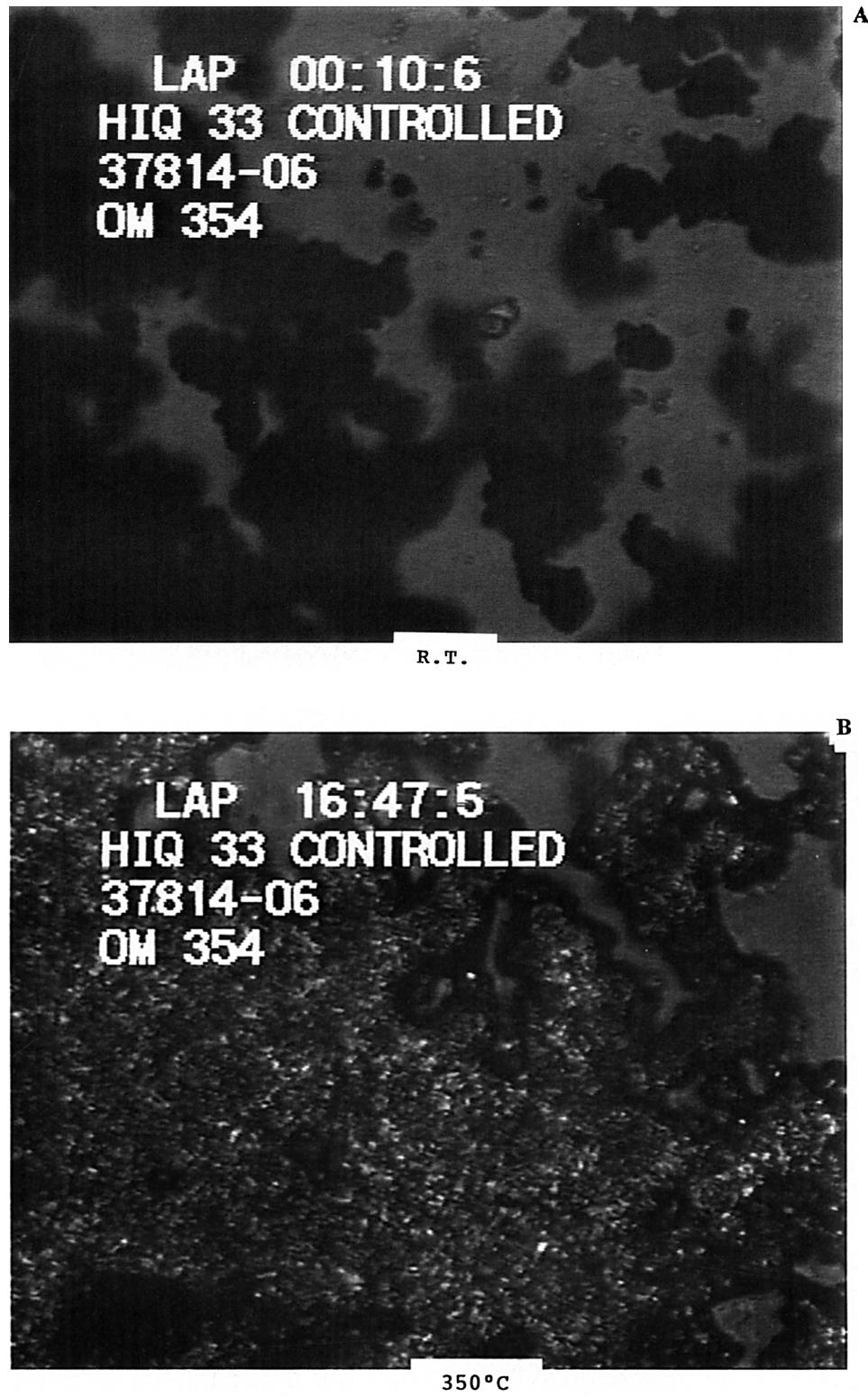
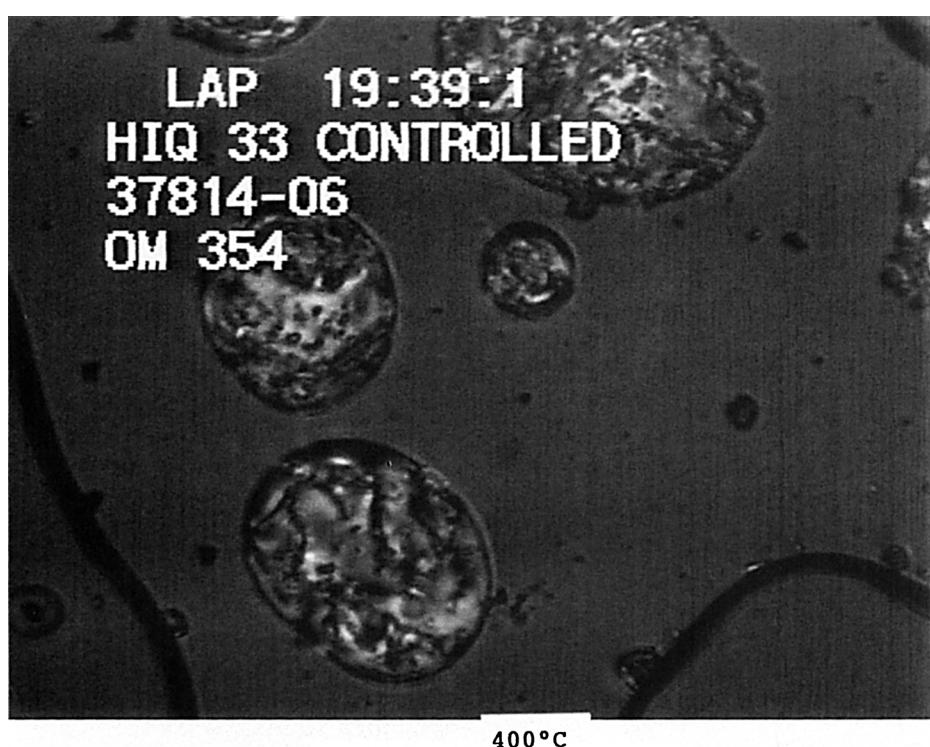


Figure 9 Hot-stage optical microscopy of P-HIQ33.



C



D

Figure 9 (Continued from the previous page)

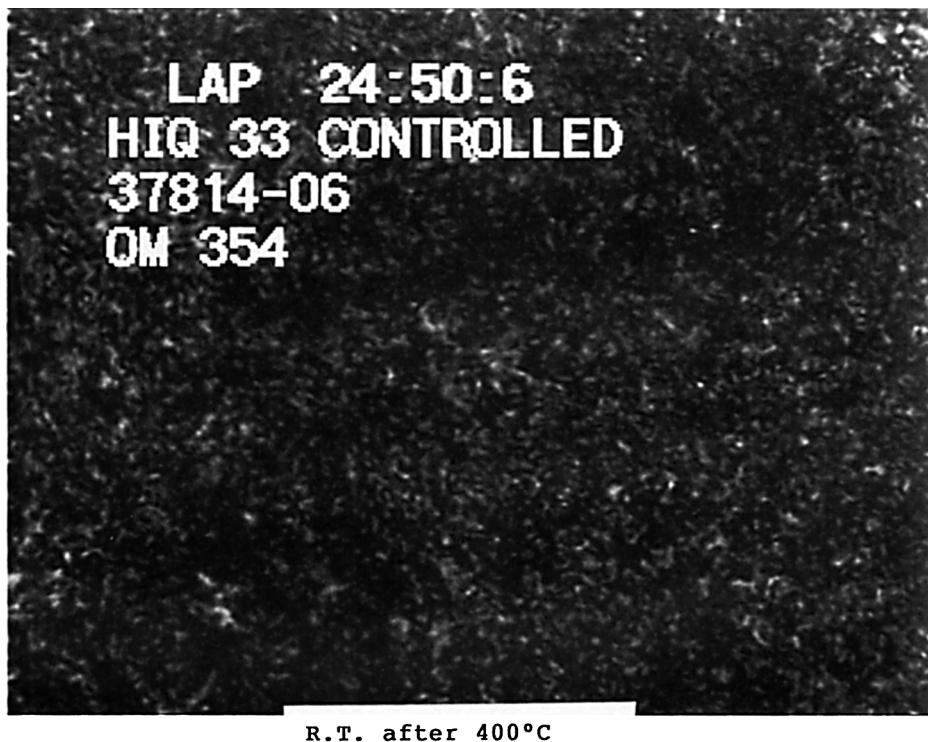


Figure 9 (Continued from the previous page)

about 0.24 and $M_w = 3500$ and $M_n = 2600$. This was not suitable for a mechanical properties study; however, for backbone characterization and studying of sequences, the molecular weight was sufficient. The FTIR spectrum (Fig. 7) was essentially similar to the corresponding random HIQ polymer with shifts in the region 1050 – 1070 cm^{-1} , consistent with expected shifts to higher frequency due to the lack of HBA–HBA linkages. The NMR data (Fig. 8) was consistent with the FTIR and showed three peaks in the carbonyl region, indicating that material did not have HBA–HBA linkages present in the random HIQ33 polymer.

The random HIQ33 shows four peaks in the carbonyl region similar to those shown by random HIQ50. In DSC, one broad transition around 377°C was observed, which may be actually two overlapping peaks: one due to the crystal to nematic transition and the other due to the nematic to isotropic transition. Polarized light optical microscopy (Fig. 9) shows these transitions very clearly. Upon heating on the microscope hot stage, the material undergoes a nematic transition around 350°C and transforms to the isotropic melt around 400°C . Upon cooling

at 375°C , the isotropic phase undergoes a transition back to the nematic phase, and upon cooling to room temperature, the material is nematic. Figure 10 shows WAXS of preferred HIQ33. It has d -spacing corresponding to 5.84 , 4.67 , 4.13 , and 3.39 \AA . The random HIQ33 made by Erdemir et al.² had all the above d -spacings except the 3.79 \AA . This could be due to the fact our preferred HIQ33 does not have HBA–HBA linkage. As expected, heating the polymer in the X-ray up to 270°C does not change the crystal structure.

CONCLUSIONS

Controlled sequence HIQ50 and partially controlled HIQ33 copolymers have been prepared and characterized. The properties of these polymers are different from the corresponding random copolymers. The “as-made” solution-spun fibers of controlled HIQ50 are oriented but lack crystalline order. Annealing the fibers at 250°C for 3 h introduces crystalline order embedded in the liquid crystalline phase.

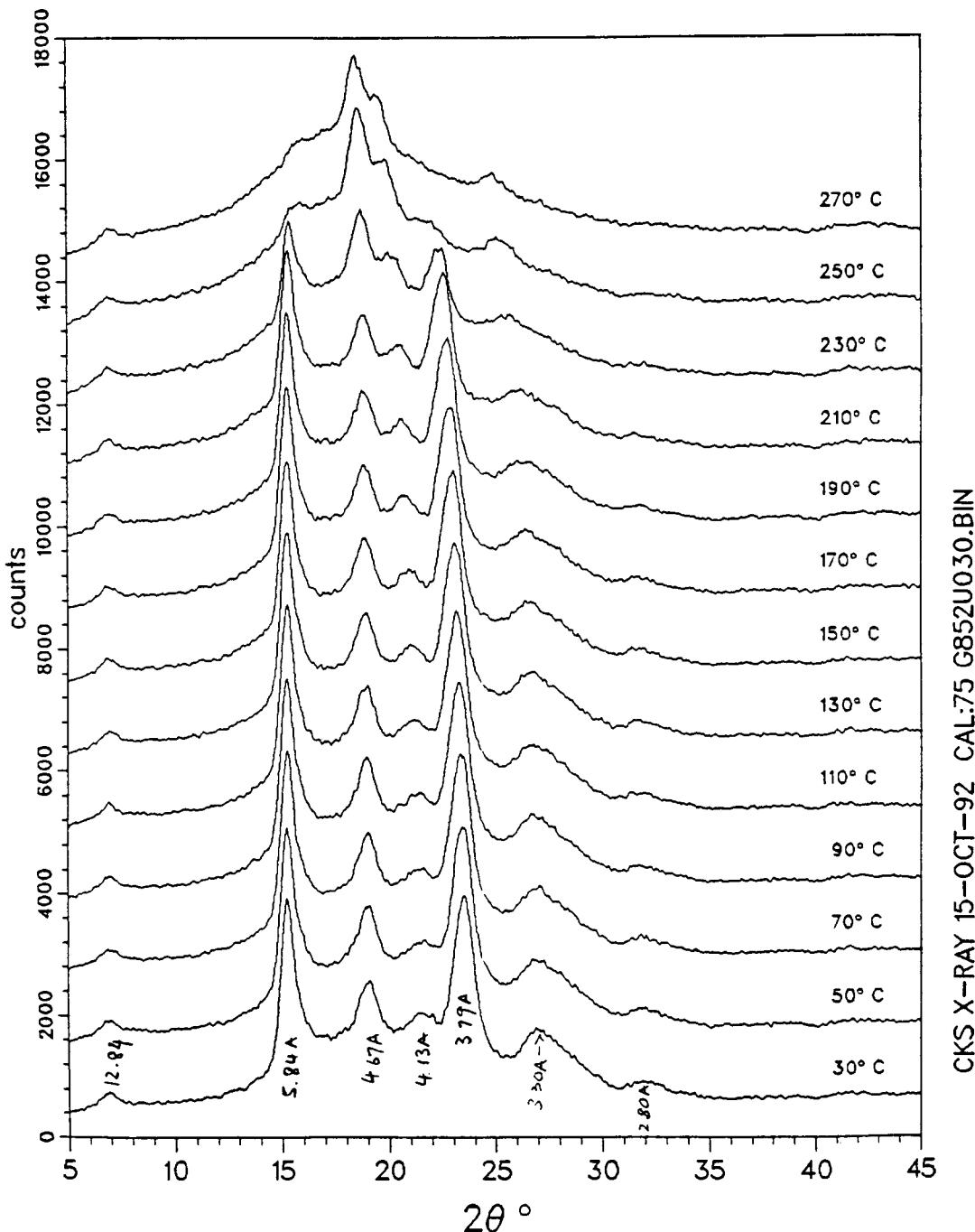


Figure 10 WAXS of preferred HIQ33 as a function of temperature.

The authors would like to acknowledge Dr. C. Saw for the X-ray measurements, Dr. J. Menczel for the DSC measurements, Dr. T. Bruno for the hot-stage microscopy, Dr. M. Borzo for the NMR measurements, Dr. J. Rafalko for the FTIR measurements, and Drs. E. Chenevey, E. Choe, S. Jacobson, and I. Haider for helpful discussions.

REFERENCES

1. D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **32**(13), 2312 (1991).
2. A. B. Erdemir, D. J. Johnson, and J. G. Tomka, *Polymer*, **27**, 441 (1986).

3. A. B. Erdemir, D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **29**, 597 (1988).
4. D. J. Johnson, I. Karacan, and J. G. Tomka, *J. Text. Inst.*, **81**(4), 441 (1990).
5. D. J. Johnson, I. Karacan, and J. G. Tomka, *Polymer*, **31**, 8 (1991).
6. J. I. Jin, J. H. Chang, K. Hatada, K. Ute, and M. Hotta, *Polymer*, **33**(7), 1374 (1992).
7. J. I. Jin and J. H. Chang, *Macromolecules*, **22**, 4402 (1989).
8. J. I. Jin, J. H. Chang, B. W. Jo, K. Y. Sung, and C. S. Kang, *Makromol. Chem. Macromol. Symp.*, **33**, 97 (1990).
9. S. Makhija, S. Jacobson, and M. Jaffe, to appear.
10. M. Jaffe, S. Makhija, E. Chenevey, I. Haider, and S. Jacobson, Paper presented at APS meeting held in Indianapolis, 1992, Vol. 37, No. 1, p. 572.
11. J. J. Rafalko, M. Borzo, W. Choe, and M. Jaffe, Paper presented at ACS meeting, Division of Polymer Chemistry, held in Denver, 1992.
12. A. Staubli, E. Mathiowitz, and R. Langer, *Macromolecules*, **24**, 2291 (1991).
13. J. Devaux, P. Godard, and J. P. Mercier, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1881 (1982).
14. J. Devaux, P. Godard, R. Touilaux, and J. M. Dereppe, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1895 (1982).
15. J. Devaux, P. Godard, R. Touilaux, and J. M. Dereppe, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1875 (1982).
16. R. W. Lenz and S. Go., *J. Polym. Sci. Part A*, **11**, 2927 (1973).
17. R. W. Lenz and S. Go., *J. Polym. Sci. Part A*, **12**, 1 (1974).
18. G. J. Ray, P. E. Johnson, and J. R. Knox, *Macromolecules*, **10**, 773 (1977).
19. J. C. Randall, *Macromolecules*, **11**, 33 (1978).
20. G. J. Ray, J. Spanswick, J. R. Knox, and C. Serres, *Macromolecules*, **14**, 1323 (1981).
21. E. T. Hsieh and J. C. Randall, *Macromolecules*, **15**, 353 (1982).
22. B. Florin-Michel, M. F. Llauro, R. Spitz, and Q. T. Pharm, *Eur. Polym. J.*, **15**, 277 (1979).
23. E. T. Hsieh and J. C. Randall, *Macromolecules*, **15**, 1402 (1982).
24. K. Soga, T. Uozumi, and J. R. Park, *Macromol. Chem.*, **191**, 100 (1990).
25. M. De Pooter et al., *J. Appl. Polym. Sci.*, **42**, 399 (1991).
26. H. N. Cheng, *Polym. Bull.*, **26**, 325 (1991).
27. H. N. Cheng, *Polym. Commun.*, **25**, 99 (1984).
28. K. Kimura, S. Yuasa, and Y. Maru, *Polymer*, **25**, 441 (1984).
29. C. Tosi, *Eur. Polym. J.*, **6**, 161 (1970).
30. C. Wallings and E. R. Briggs, *J. Am. Chem. Soc.*, **67**, 1774 (1945).
31. H. Komber, F. Bohme, K. Grasshoff, M. Ratzsch, and G. Rafler, *Makromol. Chem.*, **190**, 3173 (1989).
32. H. Jancke, F. B. Karin Grabhoff, M. Ratzsch, and G. Rafler, *Makromol. Chem.*, **190**, 3173 (1989).
33. M. Jaffe, M. Borzo, E. Chenevey, E. Choe, I. Haider, and S. Makhija, U.S. Pat. 5256760 (1993).

Received August 11, 1993

Accepted December 8, 1993