

Synthesis and characterization of segmented copolymers of aromatic polyether sulfone and thermotropic liquid crystalline poly(oxy-1,4-phenylenecarbonyl-co-oxy-2,6-naphthaloyl)

Yu-Ming Chang^a, Chain-Shu Hsu^{a,*}, Min-Chi Liu^b

^aDepartment of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC

^bNankai Junior College of Technology and Commerce, Nantou 54210, Taiwan, ROC

Received 18 January 1995; accepted 13 July 1995

Abstract

The synthesis of segmented copolymers of aromatic polyether sulfone and thermotropic liquid crystalline poly(oxy-1,4-phenylenecarbonyl-co-oxy-2,6-naphthaloyl) is presented. The segmented copolymers were prepared by solution polycondensation of hydroxy-terminated polyether sulfone with 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid in a mixture of triphenylphosphine, pyridine and hexachloroethane. The obtained polymers were fractionated to isolate the pure segmented copolymers. All of the segmented copolymers reveal two glass transitions. The first glass transition at about 75 °C belongs to the segmental motions of liquid crystalline polyester blocks. The second glass transition at about 140 °C belongs to the segmental motions of polyether sulfone blocks. Optical polarizing microscopy and X-ray diffraction measurements verify the presence of a nematic liquid crystalline phase for the segment copolymers. The experimental results indicate that the segmental copolymers have a microphase-separated morphology, i.e., both amorphous and liquid crystalline properties are shown by the polyether sulfone and liquid crystalline polyester segments, respectively.

Keywords: Segmented copolymers; Aromatic polyether sulfones; Thermotropic liquid crystals

1. Introduction

In recent years the synthesis of block copolymers containing thermotropic liquid crystalline polymer (LCP) segments has attracted increasing interest owing to their ability to form microphase-separated systems [1–11]. This class of polymers includes AB block copolymers consisting of amorphous side-chain liquid crystalline [1–6] and amorphous/main-chain liquid crystalline blocks [7–11]. An important application of these block copolymers is in the field of compatibilizing polymer blends [12,13].

Polyether sulfone (PES) is a versatile engineering thermoplastic polymer with some unique properties. Improvement of the mechanical properties using blends of polyether sulfone with LCPs has been reported

[14]. Auman and Percec and our laboratory have reported the synthesis of segmented copolymers of aromatic PES and thermotropic LCPs using a melt copolycondensation method [7,10]. Unfortunately, the resulting copolymers were found to be largely blends of amorphous PES chains extended to a high degree of short LCP segments, and LCP homopolymer, using the melt copolycondensation method. The separation between the segmented copolymers and LCP homopolymer was found to be very difficult.

In this study, segmented copolymers of PES and LCP have been prepared by solution polycondensation of hydroxy-terminated PES with 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) in a mixture of triphenylphosphine, hexachloroethane and pyridine. The segmented copolymers obtained have been well separated and characterized by differential scanning calorimetry (DSC), optical polarizing microscopy, viscometer and X-ray diffraction.

* Corresponding author.

2. Experimental

2.1. Materials

p-Hydroxybenzoic acid (HBA) was obtained from San-Fu Chemical, Hsinchu, Taiwan. 2-Hydroxy-6-naphtholic acid was kindly provided by Hoechst-Celanese Co., Summit, NJ, USA. Triphenylphosphine, bisphenol A (BPA), and 4,4'-dichlorodiphenylsulfone (DCDPS) were purchased from Fluka, Switzerland. All these compounds were recrystallized before use. Pyridine and hexachloroethane (from Aldrich) used as polymerization solvents in this study were distilled before use.

2.2. Measurements

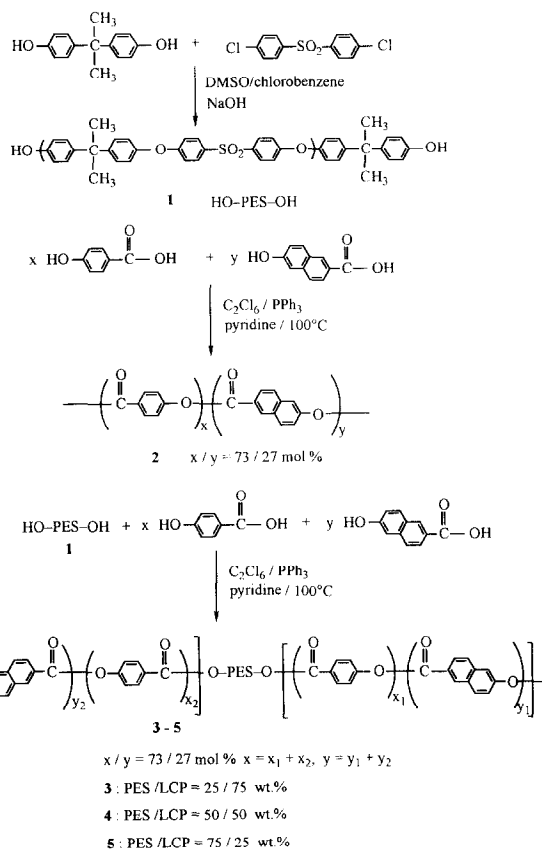
¹H NMR spectra were recorded on a JEOL JNMFX 400 spectrometer. FT-IR spectra were measured on a Nicolet 520 FT-IR spectrometer. Thermal transitions were determined by using a Seiko SSC/5200 differential scanning calorimeter. Heating and cooling rates were 10 °C min⁻¹. Thermogravimetric analysis was performed on a Seiko TG/DTA 200 thermal analyzer. A Carl-Zeiss Axiphot optical polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the anisotropic textures. Gel permeation chromatography (GPC) was run on an Applied Biosystem 400 solvent delivery system equipped with UV and IR detectors. X-ray diffraction measurements were conducted with nickel-filtered Cu K α radiation with a Siemens D5000 powder diffractometer.

2.3. Synthesis of polymers 1 and 2 and segmented copolymers 3–5

The synthetic routes used for the preparation of telechelic polyethersulfone 1, liquid crystalline homopolymer 2 and their segmented copolymers 3–5 are outlined in Scheme 1.

2.4. Synthesis of α,ω -di(hydroxyphenyl)polyether sulfone (1)

In a three-necked flask, BPA (100 g, 0.438 mol) was dissolved in DMSO (200 ml) and chlorobenzene (400 ml). The reaction mixture was heated under a nitrogen atmosphere and 50% NaOH solution (35 ml) was then added. The resulting mixture was further heated to 150 °C to form a clear solution. DCDPS (113.2 g, 0.394 mol) in chlorobenzene (90 ml), which was kept at 120 °C, was added dropwise in 10 min. After the addition was completed, the mixture was allowed to react at 160 °C for 2 h, cooled to room temperature, acidified with acetic acid (80 ml), diluted



Scheme 1. Synthesis of LCP homopolymer 2 and its block copolymers 3–5.

with chloroform (350 ml) and filtered. The product was isolated by precipitation in methanol, filtered, washed with water and methanol, and dried under vacuum to yield 185.5 g (87%). Molecular weights obtained from GPC were: $\bar{M}_n = 9877$, $\bar{M}_w = 21\,280$, $\bar{M}_w/\bar{M}_n = 2.15$.

2.5. Synthesis of a liquid crystalline copolyester (2)

The LC copolyester studied in this work is composed of 73 mol% of the HBA unit and 27 mol% of the HNA unit. HBA (5.95 g, 0.043 mol) and HNA (3.0 g, 0.016 mol) were dissolved by heating to 120 °C in 35 ml of pyridine in a 250 ml three-necked flask equipped with a reflux condenser, a gas inlet and a gas outlet. The reaction mixture was stirred under nitrogen atmosphere. Triphenylphosphine (23.2 g, 0.089 mol) and hexachloroethane (21.0 g, 0.089 mol) were added one after the other. The reaction mixture was heated at 100 °C for 18 h. After cooling, the copolyester was precipitated in 500 ml of methanol, filtered and washed with acetone, methanol and water. The product was dried at 70 °C under vacuum to yield 8.10 g (90.5%).

Table 1
Yields and composition of segmented copolymers 3–5 prepared by condensation of PES with HBA and HNA

| Copolymer | Feeding wt.% of PES | Yield (%) | Composition (wt.%) | | |
|-----------|---------------------|-----------|--------------------|------------|------------|
| | | | Fraction a | Fraction b | Fraction c |
| 3 | 25 | 87.2 | 25.3 | 15.0 | 59.7 |
| 4 | 50 | 88.4 | 50.0 | 31.4 | 18.6 |
| 5 | 75 | 86.6 | 84.6 | 7.1 | 8.3 |

2.6. Synthesis of segmented copolymers 3–5 of PES and LCP

The three copolymers 3–5 were prepared by a method similar to that used for copolymer 2 described in the previous section. In these cases, the LCP monomers were partially replaced by an appropriate amount of PES (1). The mole ratio of HBA/HNA was kept at 73:27. The overall weight percent of PES in the copolymers was varied between 25 and 75%, as noted in Table 1. An example is given as follows.

Triphenylphosphine (26.72 g, 0.102 mol) and hexachloroethane (24.20 g, 0.102 mol) were dissolved in 30 ml of pyridine under nitrogen atmosphere. PES (10.0 g) was then added and the resulting solution was heated to 120 °C to form a clear solution. A mixture of HBA (6.65 g, 0.048 mol) and HNA (3.35 g, 0.018 mol) in pyridine (40 ml) was added dropwise over 3 h. After the addition was completed, the solution was stirred at 120 °C for 18 h. After cooling, the copolymer was precipitated in 700 ml methanol, filtered and washed with acetone, methanol and water. The product was dried at 70 °C under vacuum to yield 17.3 g (86.6%).

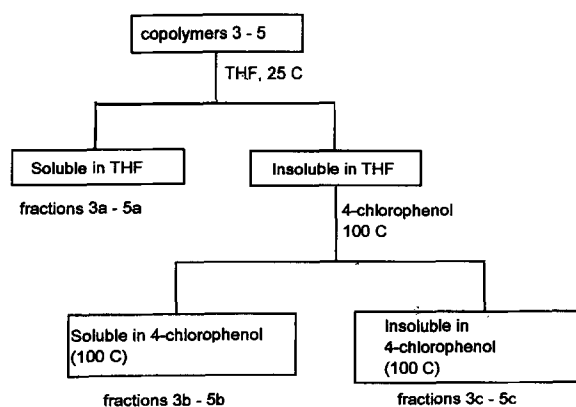
The products were further fractionated according to Scheme 2.

The polymer obtained was put in 200 ml of THF and stirred at room temperature for 24 h and filtered. The dissolved polymer was isolated by reprecipitation in methanol and dried at 70 °C under vacuum, and is

called fraction a. The solid fraction was put in 200 ml of *p*-chlorophenol and stirred at 100 °C for 24 h and then filtered. The solid obtained was washed with acetone and methanol and dried at 70 °C under vacuum, and is called fraction c. The dissolved polymer was isolated by reprecipitation in methanol and dried at 70 °C under vacuum and is called fraction b. The fractionated results are summarized in Table 1.

3. Results and discussion

The synthetic routes used for the preparation of PES and its segmented copolymers with LCP are outlined in Scheme 1. α,ω -di(hydroxyphenyl)polyether sulfone (PES) was prepared in the conventional manner by condensing excess sodium salt of BPA with DCDPS in a mixed solvent of DMSO and chlorobenzene [15]. Only phenol-terminated telechelics were obtained when BPA was used in excess versus DCDPS. The molecular weight of PES was controlled by choosing the suitable BPA/DCDPS ratio and reaction time. Its number average molecular weight (\bar{M}_n) obtained from GPC measurement based on polystyrene standards was 9877 and has only relative meaning. The more reasonable \bar{M}_n



Scheme 2. Separation procedures for copolymers 3–5.

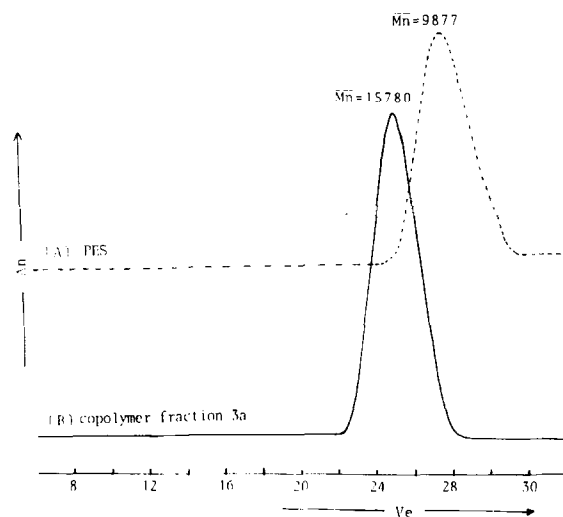


Fig. 1. GPC chromatograms: (A) PES; (B) fraction 3a.

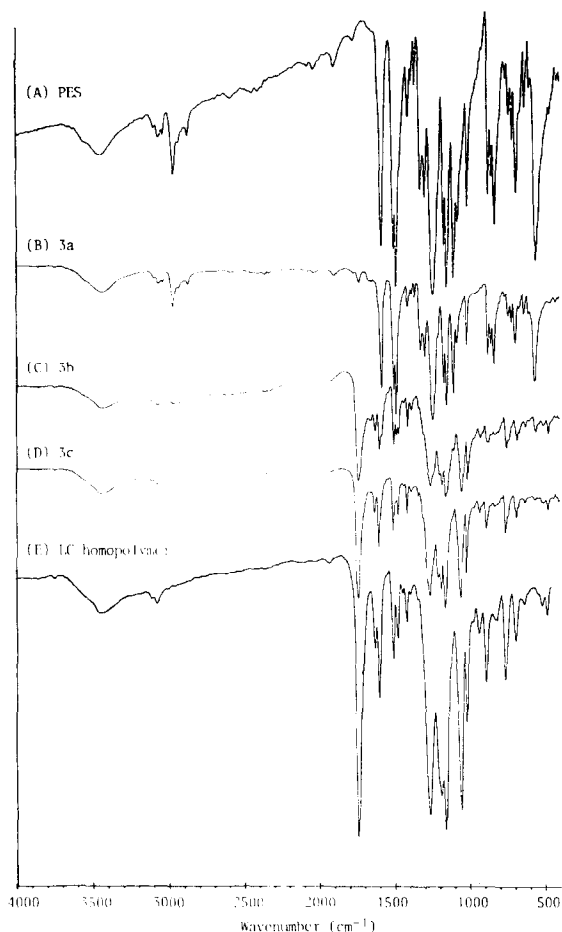


Fig. 2. FT-IR spectra: (A) PES; (B) fraction 3a; (C) fraction 3b; (D) fraction 3c; (E) LC homopolymer, 2.

value calculated from the NMR spectrum by the end group analysis method was 9510 [7].

The prepared PES was subjected to solution condensation with HBA and HNA in pyridine using triphenylphosphine dichloride as a condensing agent [12,16]. The triphenylphosphine dichloride was quantitatively formed by treating triphenylphosphine with hexachloroethane [16]. Although melt acidolysis has been the most versatile method for the preparation of block copolymers of PES and LCP [7,10], we found in our previous study [10] that a large amount of LC homopolymer instead of block copolymer of PES and LCP was formed by the melt acidolysis of telechelic PES with LC monomers. The reason could be that all the LC monomers were added simultaneously with telechelic PES during the melt acidolysis procedure and the relative amount of reactive chain ends of PES was much smaller than that of the LC monomers. Therefore, the resulting copolymers were found to be largely a blend of LC homopolymers and PES chains extended to a high degree by short LCP segments. In this study, solution condensation was used and the HBA and

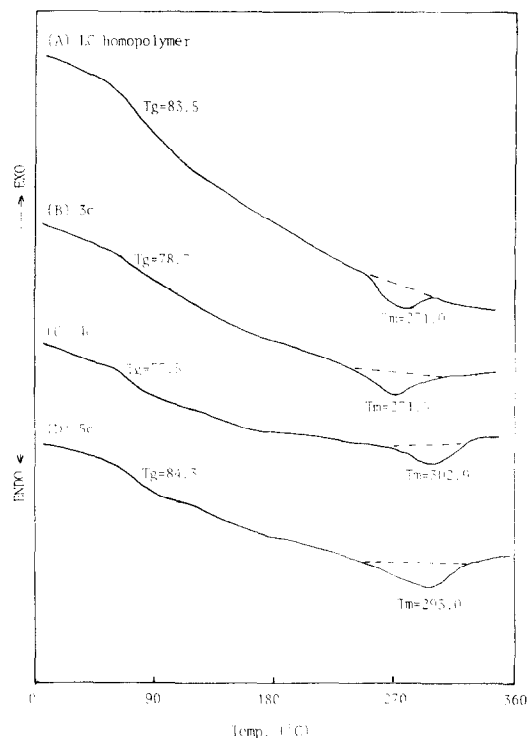


Fig. 3. DSC heating thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$): (A) LC homopolymer, 2; (B) fraction 3c; (C) fraction 4c; (D) fraction 5c.

HNA were added dropwise to the solution of telechelic PES in pyridine in the presence of triphenylphosphine and hexachloroethane. Since telechelic PES was in large excess with respect to HBA and HNA at the beginning of the reaction, it had more opportunity to form the segmented copolymers of PES and LCP. It should be

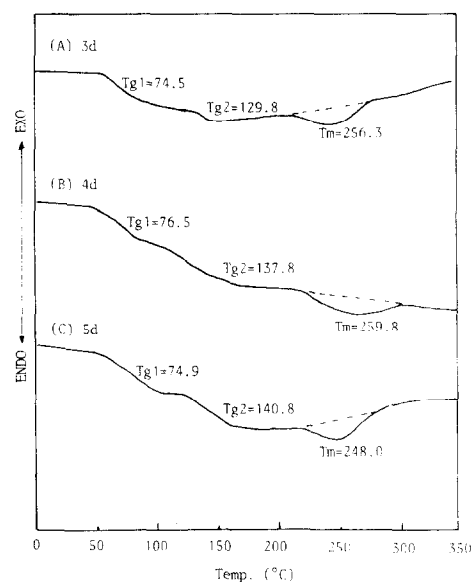


Fig. 4. DSC heating thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$): (A) fraction 3b; (B) fraction 4b; (C) fraction 5b.

Table 2
Characterization of polymers 1 and 3a–5a

| Polymer | \bar{M}_n^a | T_g | T_d^b |
|---------|---------------|-------|---------|
| 1 | 9877 | 170 | |
| 3a | 15780 | 154.4 | 427.6 |
| 4a | 13916 | 168.6 | 424.7 |
| 5a | 14448 | 169.4 | 437.0 |

^a Number average molecular weight obtained from GPC measurements based on polystyrene standards.

^b T_d = decomposition temperature obtained from TG measurements.

noted that the copolymerization system was non-stoichiometric. Since the number average molecule of PES was as high as 9510, the calculated maximum degree of polymerization was about 190, 64 and 22 for copolymers 3, 4 and 5, respectively. We expected that polymerization could not reach such a high molecular weight by solution condensation due to the limitation of the solubility of the polymers obtained.

Table 1 summarizes the copolymerization results. The resulting copolymers have been fractionated into three fractions, i.e., THF soluble fraction, 3a–5a, *p*-chlorophenol soluble fractions, 3b–5b, and *p*-chlorophenol insoluble fractions, 3c–5c. The weight percentage of each fraction in a copolymer sample depends very much on the feeding wt.% of PES. In order to understand the nature of the copolymers produced, the THF-soluble fractions, 3a–5a, were characterized by GPC, IR and DSC. Table 2 summarizes the GPC and DSC results for 3a–5a. Although the molecular weights obtained from GPC have only relative meaning, the results demonstrate that a fairly large amount of chain extension of the PES has occurred. Graphically, this chain extension is illustrated by the GPC traces in Fig. 1. The GPC curve of 3a shifts completely to a higher molecular weight in comparison with that of PES. Fig. 2(A) and 2(B) are the IR spectra of PES and 3a, respectively. Only a small amount of LCP segment is present in the IR spectrum of 3a. DSC measurements of 3a–5a show only a glass transition (T_g) for each sample. The results indicate that they are eventually amorphous polymers. The T_g value of 3a is about 15° lower than that of PES and those of 4a and 5a are very close to that of PES. All these results illustrate that the THF soluble fractions, 3a–5a, belong to the PES chain extended with short LCP segments.

Since the LCP homopolymer 2 was insoluble in *p*-chlorophenol even at 100 °C, the copolymers obtained were further fractionated into *p*-chlorophenol soluble fractions 3b–5b and insoluble fractions 3c–5c. The IR spectrum of 3c (Fig. 2(D)) indicates that the *p*-chlorophenol insoluble fraction contains predominantly



Fig. 5. Nematic Schlieren texture exhibited by fraction 3b.

the LCP homopolymers. Fig. 3 presents the DSC traces of 3c–5c and LC homopolymer 2. A glass transition at about 80 °C and a melting transition in the temperature range 270 to 300 °C are observed for 3c–5c (curves B–D). They are basically very similar to that of the LC homopolymer of HBA and HNA (curve A).

The *p*-chlorophenol soluble fractions 3b–5b belong to the segmented copolymers of PES and LCP. Fig. 2(C) shows the IR spectrum of 3b. Both LCP and PES are presented in the spectrum. Fig. 4 depicts the DSC thermograms of 3b–5b. All these segmented copolymers show distinctly two glass transitions and a melting endotherm on their DSC traces. The first T_g at about 75 °C belongs to the segmental motions of LCP segments and the second T_g at about 140 °C belongs to the segmental motions of PES segments. The double glass transitions indicate a microphase separated morphology for these segmented copolymers. Nevertheless, in comparing these thermal analysis data with those of their corresponding homopolymers, all the glass transitions have shifted to lower temperatures. This indicates that both LCP and PES segments in the copolymers eventually can affect each other in the segmental motions. The

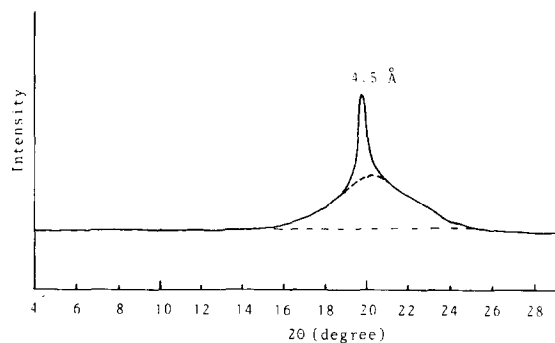


Fig. 6. Powder X-ray diffraction diagram of fraction 4b.

Table 3
Characterization of segmented copolymers **3b–5b**

| Polymer | IV (dl g ⁻¹) ^a | T _{g1} | T _{g2} | T _m | T _d ^b |
|-----------|---------------------------------------|-----------------|-----------------|----------------|-----------------------------|
| 3b | 0.175 | 74.0 | 129.8 | 256.3 | 472.2 |
| 4b | 0.200 | 76.5 | 137.8 | 259.8 | 478.5 |
| 5b | 0.165 | 74.9 | 140.8 | 248.0 | 462.7 |

^a IV = intrinsic viscosity obtained by dissolution of the sample in 4-chlorophenol at 150 °C.

^b T_d = decomposition temperature obtained from TG measurements.

broad endothermic peak covered a temperature range from 230 to 280 °C corresponding to the crystalline to nematic phase transition of LCP segments [17]. Fig. 5 shows the typical nematic texture exhibited by **3b**.

Thermogravimetric analyses of **3b–5b** revealed that all these segmented copolymers were thermally stable up to 470 °C under nitrogen atmosphere. The thermal analysis data of **3b–5b** together with their intrinsic viscosity (IV) values, which have been measured by dissolution of the segmented copolymers in *p*-chlorophenol at 150 °C, are summarized in Table 3. The IV values of **3b–5b** range from 0.165 to 0.200. The powder X-ray diffraction of **4b** is shown in Fig. 6. It shows sharp wide angle diffraction with a *d*-spacing of 4.5 Å corresponding to the amorphous structure of the PES segments. The X-ray diffraction results agree very well with the phase assignment obtained from DSC thermograms and optical microscopic textures.

Finally, let us reexamine the compositions of all fractions in the copolymers prepared (see Table 1). When the feeding wt.% of PES is as low as 25%, the product obtained contains predominantly the LC homopolymer. On the other hand, the feeding wt.% of PES is as high as 75%, the product obtained consists predominantly of the PES chain extended with short LCP segments. Only when both the feeding wt.% of PES and LC monomers is equal can a higher amount of the segmented copolymer be formed.

4. Conclusions

Segmented copolymers of PES and LCP have been prepared by solution condensation of telechelic PES with HNA and HBA monomers. The products obtained have been fractionated to isolate the pure segmented copolymers. The segmented copolymers reveal a microphase-separated morphology, i.e., both amorphous and liquid crystalline properties are presented by the PES and LCP segments, respectively. Optical microscopy and X-ray diffraction verified the presence of a nematic liquid crystalline phase. The segmented copolymers have potential applications in the field of compatibilizing polymer blends.

References

- [1] A. Gattschalk and H.W. Schmidt, *Liq. Cryst.*, 5 (1989) 1619.
- [2] J. Adams and W. Gronski, *Makromol. Chem., Rapid Commun.*, 10 (1989) 533.
- [3] M. Heftt and J. Springer, *Makromol. Chem., Rapid Commun.*, 11 (1990) 397.
- [4] B. Zschke, W. Frank, H. Fischer, K. Schmutzler and M. Arnold, *Polym. Bull.*, 27 (1991) 1.
- [5] G. Galli, E. Chiellini, Y. Yagci, E.I. Serhatli, M. Laus, M.C. Bignozzi and A.S. Angeloni, *Makromol. Chem., Rapid Commun.*, 14 (1993) 185.
- [6] A. Gattschalk and H.W. Schmidt, *Polym. Prepr.*, 34 (1993) 188.
- [7] B.C. Auman and V. Percec, *Polymer*, 29 (1988) 938.
- [8] W. Heitz, *Makromol. Chem., Makromol. Symp.*, 26 (1989) 1.
- [9] M. Sato, T. Kobayashi, F. Komatsu and N. Takeno, *Makromol. Chem., Rapid Commun.*, 12 (1991) 269.
- [10] C.S. Hsu and L.B. Chen, *Mater. Chem. Phys.*, 34 (1993) 28.
- [11] E. Chiellini, G. Galli, A.S. Angeloni, M.C. Bignozzi, M. Laus, E.I. Serhatli and Y. Yagci, *Polym. Prepr.*, 34 (1993) 190.
- [12] W. Riess and W. Heitz, *US Patent No. 4 769 423* (Sept. 1988).
- [13] V. Eckhardt, H.R. Dicke and L. Bottenbruch, *Ger. Offen. DE 3 623 319* (1988).
- [14] G. Kiss, *Polym. Eng. Sci.*, 27 (1987) 410.
- [15] R. Viswanathan, B.C. Johnson and J.E. McGrath, *Polymer*, 25 (1984) 1827.
- [16] S. Kitayama, K. Sanui and N. Ogata, *J. Polym. Sci. Polym. Chem.*, 22 (1984) 2705.
- [17] M.Y. Gao and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, 23 (1985) 521.