

Thermotropic Polyesters (Part 3): Synthesis, Characterization and Thermal Transition of Random Copolyesters Containing Terephthalate and Isophthalate Units

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ABSTRACT

Thermotropic copolyesters containing an isophthalate unit and mesogenic 4,4'-bis (ω -hydroxyalkoxy) biphenyls with different numbers of methylene units have been synthesized by melt polymerization. The effect of monomer structure and copolymer composition on liquid crystallinity has been studied on the prepared copolymers from isophthaloyl chloride, terephthaloyl chloride, and mesogenic 4,4'-bis (ω -hydroxyalkoxy) biphenyl ($n=4,6$) and it is compared with that of the analogous homopolymers. Our finding shows that high contents of terephthalic acid depend on spacer type have deleterious effects on liquid crystallinity. All of the obtained compounds were characterized by conventional spectroscopic methods.

Key Words:

thermotropic copolyesters;
optical texture; DSC;
terephthalate;
isophthalate.

INTRODUCTION

Main chain thermotropic liquid crystalline polymers have been intensively studied during the past two decades [1]. In the last decade several synthetic strategies for improving the solubility and lowering the melting transitions of ther-

motropic liquid crystalline polymers (TLCP) have been developed and are commonly employed in TLCP design [2]. In order to improve the solubility and to modulate the thermal properties of such stiff polymers, several structural

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modifications have been performed, such as the insertion of flexible spacers [3,4]; the addition of bulky or non-symmetrical substituents [5]; the inclusion of non-linear or bent monomers [6-8]; and copolymerization of different monomers [9-11]. The non-linear (bent) monomers such as resorcinol, isophthalic acid, and *m*-hydroxybenzoic acid are generally used for the preparation of thermotropic copolyesters in order to decrease their crystal-to-nematic transitions, T_m , to a convenient level [12]. In general, the incorporation of each of these monomers is limited to a certain critical amount beyond which the liquid crystallinity of thermotropic copolyester is destroyed. The critical amount for a non-linear monomer in thermotropic copolyester is determined not only by its chemical structure but also by the chemical structures of other mesogenic monomers.

Fischer et al. [13] originally reported the mesophase behaviour of polyesters and polyurethanes containing 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHBB). They claimed that the polyesters of BHBB and isophthalic acid (IA), as well as BHBB and terephthalic acid (TA), formed liquid crystalline mesophase of the smectic type. However, Khan et al. [14, 15] corroborated that the IA polyester did form a biphasic nematic-smectic A phase, but TA polyester crystallized directly on cooling the melt, without forming a mesophase. The IA polyester has a monotropic liquid crystal phase as the mesophase is only observed on cooling.

In our previous paper, liquid crystalline polyesters containing isophthalate unit and mesogenic diols 4,4'-bis (ω -hydroxyalkyloxy) biphenyl with different spacer lengths were prepared [8]. The presence of non-linear moiety (IA unit) substituted with different spacer lengths led to a reduced rigidity of polymers and increased solubility in common organic solvents. In this work, in order to study the effect of terephthaloyl moieties on liquid crystallinity of a semiflexible copolyester, we prepared copolyesters containing 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHBB) and 4,4'-bis (6-hydroxybutyloxy) biphenyl (BHBB) with isophthalate and terephthalate units with different molar percentages. These mesogenic diols were selected for this study because the mesophase behaviour of the IA homopolymers is well characterized in our previous work [8].

EXPERIMENTAL

Materials

The purification or drying of compounds and solvents have been performed according to the common procedure. Isophthaloyl chloride, terephthaloyl chloride purchased from Merck.

Methods

Spectroscopic characterization utilized the following instrumentation: Melting points were recorded with an electrothermal apparatus. FTIR Spectra were recorded on a Bruker spectrometer. ^1H NMR Spectra were taken on a 400 MHz Bruker versus, TMS in CDCl_3 . The inherent viscosities of the samples were determined by an Ubbelohde viscosimeter at 25 C in chloroform. A differential scanning calorimeter STA 625 was used to determine phase transition temperatures at the heating and cooling rates of 10 C/min. An optical Zeiss polarizing microscope equipped with long working distance objectives was also used to observe phase transitions. The samples were heated and cooled with a THMSE 600 hot stage and associated temperature controller. Very small powdered fragments of polymers were placed on the glass slide and heated to about 20 C above the isotropization temperature. The melt was quite viscous and did not form a thin layer spontaneously. Hence, it was sheared between the glass plates in the isotropic state [8]. All of polymers were stable in this condition and textural features appeared to be generally reproducible on several heat-cool cycles with the same specimen.

Synthetic Procedures

Polyesters of 4,4'-bis (ω -hydroxyalkyloxy) Biphenyl and Isophthaloyl Chloride, PI_n ($n=4, 6$)

The exact synthetic procedure and characterization of the monomers and IA homopolymers were presented in earlier work [8].

Polyesters of 4,4'-bis (ω -hydroxyalkyloxy) Biphenyl and Terephthaloyl Chloride, PT_n ($n=4, 6$)

A similar procedure to the previous polymerization was used. Monomer (BHBB or BHBB) (0.01 mol) and terephthaloyl chloride (2.1g, 0.01 mol) were placed in a polymerization flask equipped with a magnetic stirrer, a gas inlet /outlet, and a vacuum inlet. The polymer-

ization flask was evacuated and then filled with nitrogen. This cycle was repeated four times. A slow stream of nitrogen was then maintained in the flask to carry off the hydrogen chloride produced during the polymerization. The flask was heated in an oil bath to 200 C. When it became too viscous to be stirred, vacuum was applied and the temperature was maintained for 3-4 h. The flask was cooled to room temperature under vacuum, and the product was mechanically crashed extracted with acetone, and dried at 50 C. Dissolving in chloroform, filtering, and reprecipitating with acetone purified polymer further. Polyester of BHBB with terephthaloyl chloride (PT₄): FTIR (KBr): 3520 (OH), 2956 and 2860 (CH₂), 1730 (C=O), 1470 (aromatics), 1258 and 1160 (C-O-C) cm⁻¹; ¹H NMR (CDCl₃): δ 10 (s, -OH, carboxylic acid), 8.08 s, 4H aromatic, phenyl), 7.44 (d, 2H aromatic, *ortho* to O), 6.93 (d, 2H aromatic, *meta* to O), 4.42 (t, CH₂, α to -O-C=O), 4.04 (t, CH₂, α to -OAr), 3.88 (b, -OH), 3.62 (t, CH₂, α to terminal -OAr), 1.99 (b, CH₂, β to -O-C=O and -OAr), 1.26 (m, CH₂, β and α to -OH).

Polyester of BHBB with terephthaloyl chloride (PT₆): FTIR (KBr): 3520 (OH), 2958 and 2860 (CH₂), 1729 (C=O), 1470 (aromatics), 1260 and 1160 (C-O-C) cm⁻¹; ¹H NMR (CDCl₃): δ 10 (s, -OH, carboxylic acid), 8.09 s, 4H aromatic, phenyl), 7.44 (d, 2H aromatic, *ortho* to O), 6.92 (d, 2H aromatic, *meta* to O), 4.36 (t, CH₂, α to -O-C=O), 3.96 (t, CH₂, α to -OAr), 3.89 (t, -OH), 3.55 (t, CH₂, α to -OH), 1.81 (b, CH₂, β to -O-C=O and -OH and γ to -O-C=O), 1.54-1.55 (b, the rest CH₂ protons).

Copolyesters (PI_n-co-PT_n)

A similar polymerization procedure to the homopolymers was used for the synthesis of all copolyesters. Isophthaloyl chloride and terephthaloyl chloride with different mole ratios (0.01 mol) and monomer (BHBB or BHBB) (0.01 mol) were used. Dissolving in dichloromethane, filtering, and reprecipitating with acetone purified the polymers.

Polyesters of (PI₄-co-PT₄)

Random copolymers with 75:25 and 50:50 ratio of isophthaloyl chloride: terephthaloyl chloride (0.01 mol) and monomer BHBB (3.3 g. 0.01 mol) were used. For copolymer PI₄-co-PT₄ (Z=50%): FTIR (KBr): 3422 (OH), 2950 and 2870 (CH₂), 1717 (C=O), 1606 and 1567 (aromatics), 1271 and 1101 (C-O-C)

cm⁻¹. ¹H NMR (CDCl₃): δ 10 (S, -OH, carboxylic acid), 8.69 (S, 1H aromatic, between the -C=O), 8.21 (d, 2H aromatic, *ortho* to O), 8.09 (S, 4H aromatic, phenyl), 7.51 (t, 1H aromatic, *meta* to each -C=O), 7.43 (d, 2H aromatic, *ortho* to O), 6.93 (d, 2H aromatic, *meta* to O), 4.43 (t, CH₂, α to -O-C=O), 4.05 (t, CH₂, α to -OAr), 3.72 (t, -OH), 3.62 (t, CH₂, α to -OH), 1.98 (b, CH₂, β to -O-C=O and -OAr), 1.26 (m, CH₂, β and γ to -OH).

Polyesters of (PI₆-co-PT₆)

Random copolymers with 75:25, 50:50 and 25:75 ratio of isophthaloyl chloride: terephthaloyl chloride (0.01 mol) and monomer BHBB (3.82 g. 0.01 mol) were used. For copolymer PI₆-co-PT₆ (50:50): FTIR (KBr): 3447 (OH), 2937 and 2862 (CH₂), 1718 (C=O), 1607 and 1500 (aromatics), 1271 and 1173 (C-O-C) cm⁻¹. ¹H NMR (CDCl₃): δ 10 (S, -OH, carboxylic acid), 8.69 (S, 1H aromatic, between the -C=O), 8.21 (d, 2H aromatic, *ortho* to O), 8.09 (S, 4H aromatic, phenyl), 7.51 (t, 1H aromatic, *meta* to each -C=O), 7.43 (d, 2H aromatic, *ortho* to O), 6.93 (d, 2H aromatic, *meta* to O), 4.36 (t, CH₂, α -O-C=O), 3.98 (t, CH₂, α to -OAr), 3.82 (t, -OH), 3.55 (t, CH₂, α to -OH), 1.83 (m, CH₂, β to -O-C=O and γ to -O-C=O), 1.52 (b, the rest CH₂ protons).

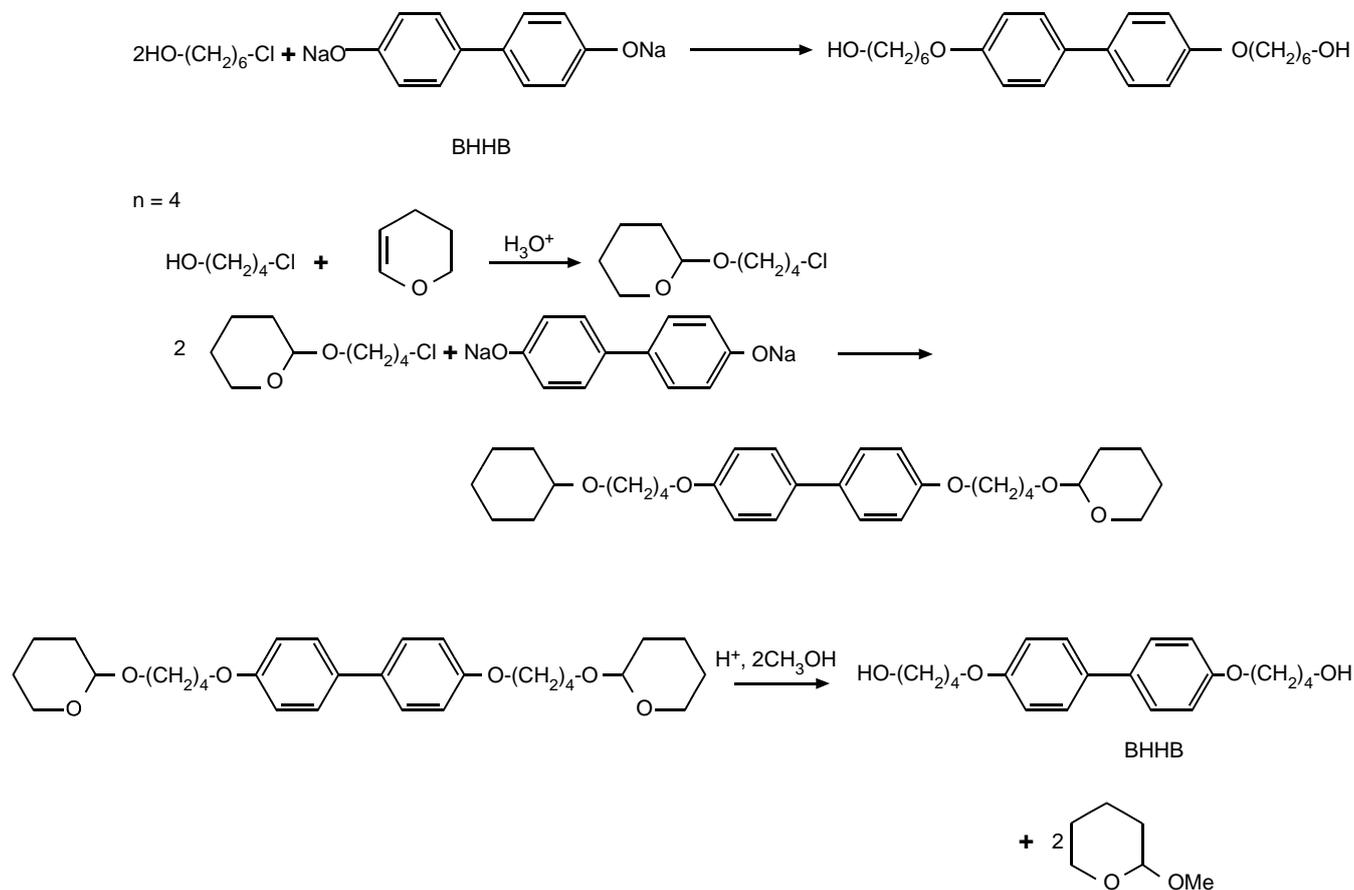
RESULTS AND DISCUSSION

Synthesis and Characterization of Polyester

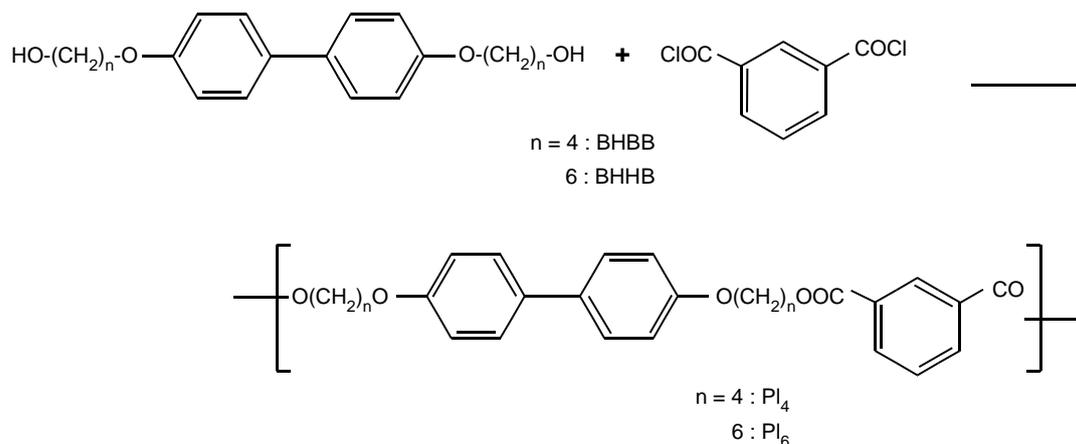
The mesogenic monomers 4,4'-bis (4-hydroxybutyloxy) biphenyl (BHBB) and 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHBB) were synthesized by the standard method [8,16]. The synthetic route for the synthesis of the monomers and IA homopolymers are shown in Schemes I and II.

The homopolymers of PT₄ and PT₆ [15] as well as PI₄ [8] and PI₆ [8, 15] were prepared by melt polycondensation of respective synthesized monomers with terephthaloyl chloride. The reaction scheme for the synthesis of the TA homopolymers is shown in Scheme III. The polyesters were characterized by FTIR and ¹H NMR [15].

A similar polymerization procedure to the polyesters was used for the synthesis of all copolyesters. The chemical structure of copolymers is shown in Scheme IV.



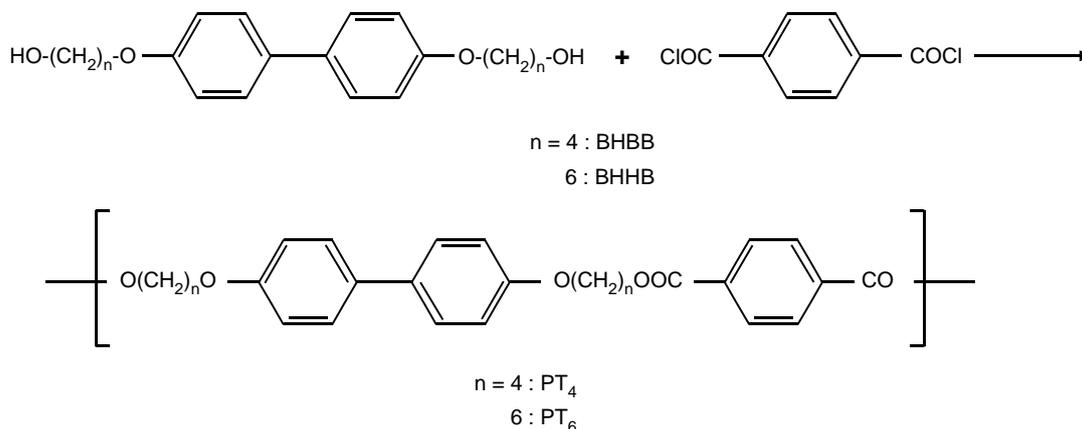
Scheme I. Synthesis of 4,4'-bis(ω -hydroxyalkyloxy) biphenyl.



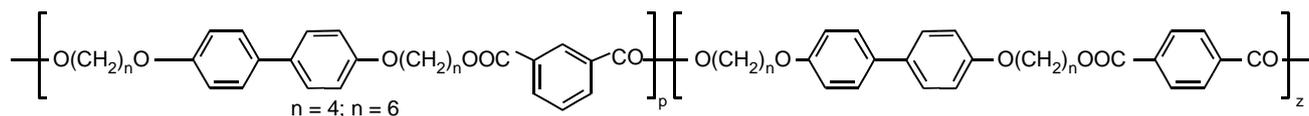
Scheme II. Synthesis of polyesters of 4,4'-bis(ω -hydroxyalkyloxy) biphenyl and isophthaloyl chloride.

^1H NMR Spectra of PI₆-*co*-PT₆ ($Z=50\%$) are shown in Figure 1. The observation of very small peak at 10 ppm in ^1H NMR spectra of polyesters shows that the terminal -COCl group in polyesters hydrolyze to -COOH group during the purification process [8]. The

number-average molecular weight (\bar{M}_n) was estimated from end group analysis by ^1H NMR. The intensity of the C-H proton peak of methylene unit in position to terminal -OH group was used for the \bar{M}_n estimation. This peak was seen at 3.55 ppm for PI₆-*co*-PT₆ ($Z =$



Scheme III. Synthesis of polyesters of 4,4'-bis (ω -hydroxyalkoxy) biphenyl and isophthaloyl chloride.



Scheme IV. Chemical structure of copolyesters.

50%) in Figure 1. Composition of copolymers was also obtained from ^1H NMR spectrum. For example, the intensity of the peaks at 8.21 ppm and 8.09 ppm of PI₆-co-PT₆ (Z = 50%) copolymer due to the aromatic protons of the isophthaloyl and terephthaloyl units respectively, were definitely used for this purpose (Figure 1).

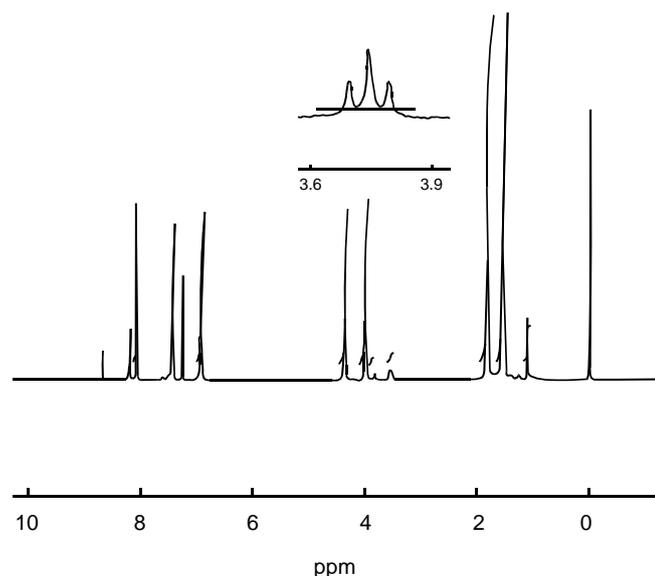


Figure 1. ^1H NMR Spectra of copolymer PI₆-co-PT₆ (Z=50%) in CDCl₃.

The molecular weights, average degree of polymerization (\overline{DP}) and copolymer composition are listed in Table 1. These amounts show that the prepared copolyesters have usually the lower molecular weight in comparison with IA homopolymers. As shown in the

Table 1. Copolymerization of 4,4'-bis (ω -hydroxyalkoxy) biphenyls ($n=4$ or 6) with isophthaloyl chloride and terephthaloyl chloride.

| Polyesters | Composition (P:Z) | | $\overline{M}_n^{(b)}$ (g/mol) | $\eta^{(c)}$ (dL/g) | Yield (%) |
|-------------------------------------|----------------------|-----------------------------|-----------------------------------|------------------------|--------------|
| | In fed | In copolymer ^(a) | | | |
| PI ₄ -co-PT ₄ | 100:0 ^(d) | 100:0 | 10000 | 0.13 | 90 |
| PI ₄ -co-PT ₄ | 75:25 | 70:30 | 19000 | 0.19 | 75 |
| PI ₄ -co-PT ₄ | 50:50 | 49:51 | 11000 | 0.15 | 70 |
| PI ₄ -co-PT ₄ | 0:100 | 0:100 | 9000 | 0.08 | 80 |
| PI ₆ -co-PT ₆ | 100:0 ^(d) | 100:0 | 19500 | 0.19 | 96 |
| PI ₆ -co-PT ₆ | 75:25 | 71:29 | 18500 | 0.18 | 90 |
| PI ₆ -co-PT ₆ | 50:50 | 50:50 | 5500 | 0.07 | 92 |
| PI ₆ -co-PT ₆ | 25:75 | 33:67 | 5000 | 0.06 | 88 |
| PI ₆ -co-PT ₆ | 0:100 | 0:100 | 5000 | 0.06 | 90 |

(a) Obtained by ^1H NMR; (b) Estimated from end group analysis by ^1H NMR;

(c) Concentration of 0.25 g/dL of CHCl₃, at 25°C; (d) Ref. [8].

Table 1 increasing the terephthaloyl unit in copolymer composition leads to a molecular weight decreasing. The monomer ratio in the feed was almost as the ratio of the two monomeric units in all copolymers, because the monomer reactivity ratios are close together.

Thermal Transition of PI_n -*co*- PT_n Polyesters

In order to study the monomer structural effects on liquid crystallinity, we examined thermal properties and mesomorphic behaviour in PI_n -*co*- PT_n ($n=4, 6$) copolymers. It was found that PT_6 prepared from TA and BHBB melts directly to the isotropic liquid phase [15]. The polyesters of PI_n may be modified by the introduction of a rigid terephthaloyl unit in the suitable proportion. Therefore, we investigated how much of the linear terephthalate unit can be tolerated in liquid crystalline polyesters. First, we consider the PI_4 -*co*- PT_4 ($P + Z = 100$) copolymers containing two repeat units, where P is the molar percentage of biphenylene isophthalate and Z is the molar percentage of biphenylene terephthalate units. The phase transition temperatures of copolymers PI_4 -*co*- PT_4 are given in Table 2.

Figure 2 shows a phase diagram of copolymers PI_4 -*co*- PT_4 in which the transition temperatures are plotted against the molar percentage of Z, the biphenylene terephthalate repeat units.

Copolymers PT_4 ($Z = 100\%$) exhibit a melting temperature of 191 C. As Z decreases, the melting temperature of this polyester decreases rapidly. Similarly, the copolymer PI_4 -*co*- PT_4 ($Z = 75\%$) has a melting temperature form only isotropic melts at 160 C. However, the copolymer PI_4 -*co*- PT_4 with Z ranging from 25 to 0% exhibits a smectic A mesophase. For example, the copolymer PI_4 -*co*- PT_4 ($Z = 25\%$) has a T_m of

Table 2. Phase transition temperatures of the PI_4 -*co*- PT_4 copolymers determined by DSC at scan rate 10°C/min on the first cooling and second heating and microscopy observation.

| PI_4 - <i>co</i> - PT_4 (P:Z) | Cooling (°C) | | Heating (°C) | |
|--------------------------------------|-----------------------|-------------------|-----------------------|-------------------|
| | T _{I-SA} | T _{SA-K} | T _{K-SA} | T _{SA-I} |
| | T _{I-K} *(a) | | T _{K-I} *(a) | |
| 0: 100 | 169* | - | 191* | - |
| 50: 50 | 119* | - | 160* | - |
| 75: 25 | 116.5 | 103 | 120 | 135 |
| 100:0(b) | 121.9 | 113.3 | 116.8 | 127.4 |

(a) Without mesophase forming; (b) Ref. [8].

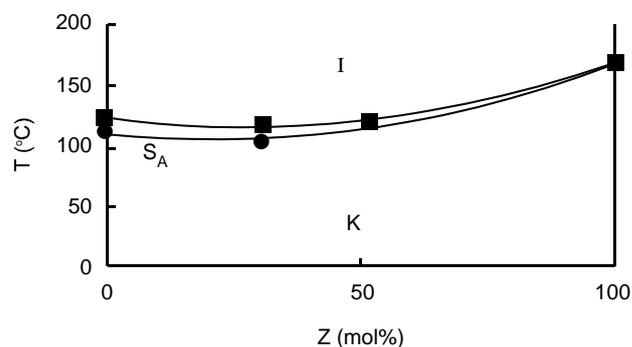


Figure 2. Transition temperatures vs. molar percentage of *p*-biphenylene terephthalate for PI_4 -*co*- PT_4 .

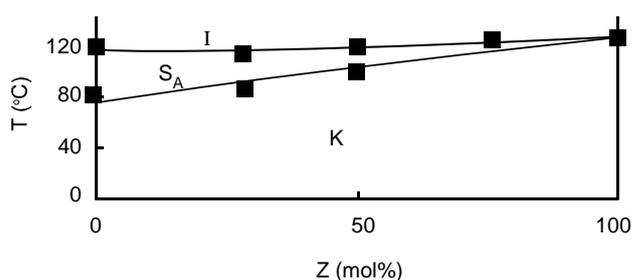


Figure 3. Transition temperatures vs. molar percentage of *p*-biphenylene terephthalate for PI_6 -*co*- PT_6 .

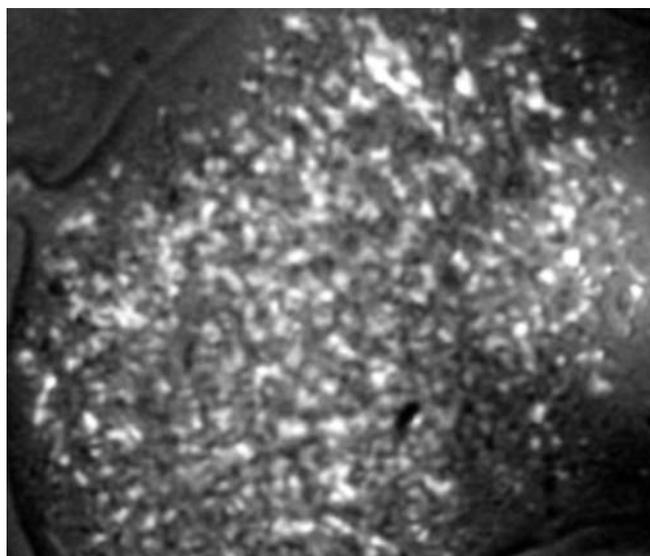
122 C and a mesophase range of 13.5 C. This copolymer exhibits a smectic A phase.

Encouraged by our finding that PI_4 -*co*- PT_4 copolymers with a low percentage of the biphenylene terephthalate unit exhibit liquid crystallinity, we pursued the possibility of incorporating the longer methylene spacer into these copolymers to alternate monomer sense and

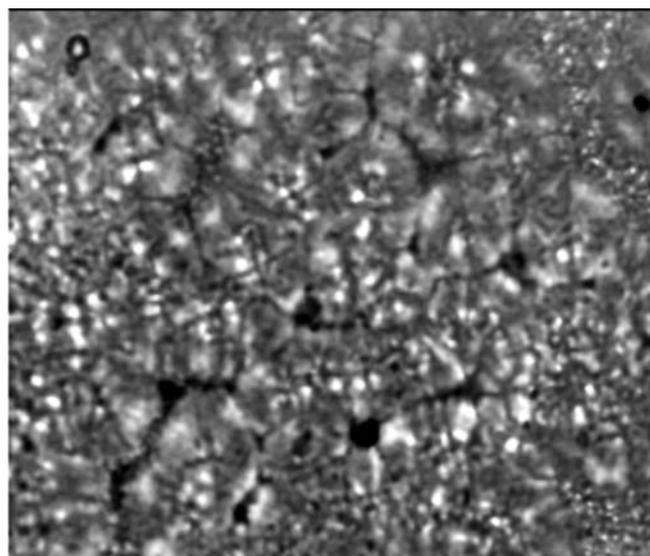
Table 3. Phase transition temperatures of the PI_6 -*co*- PT_6 copolymers determined by microscopy observation and DSC at scan rate of 10°C/min on the first cooling and second heating.

| PI_6 - <i>co</i> - PT_6 (P:Z) | Cooling (°C) | | Heating (°C) | |
|--------------------------------------|-----------------------|-------------------|-----------------------|-------------------|
| | T _{I-SA} | T _{SA-K} | T _{K-SA} | T _{SA-I} |
| | T _{I-K} *(a) | | T _{K-I} *(a) | |
| 0: 100 | 126* | - | 152* | - |
| 25: 75 | 117* | - | 147.7* | - |
| 50: 50 | 116 | 103 | 118 | 138 |
| 75: 25 | 110 | 73 | 99 | 115 |
| 100:0(b) | 115.6 | 68 | 120* | - |

(a) Without mesophase forming; (b) Ref. [8].



(a)



(b)

Figure 4. Optical polarized microphotograph of PI_6 -co- PT_6 (P:Z = 50:50) and a scanning rate of 5 C/min on the second cooling (a) at 114 C and (b) 90 C.

thereby further lower the melting temperature. Table 3 gives the thermal data for the copolyesters PI_6 -co- PT_6 .

Figure 3 shows that the polyester PI_6 -co- PT_6 (Z = 100 %) melts at 152 C. The T_m of the polyester PI_6 -co- PT_6 (Z = 75 %) is fairly constant at about 148 C. Additionally, T_m decreases steeply when Z decreases from 50% to 0%. Optical microscopy shows that polyesters PI_6 -co- PT_6 form a smectic A phase with a 13 and 37 C range, when Z = 50% and 25%, respectively (Figure 4a). As shown in Figure 4b, the crystallization of copolymers leads to a spherulitic texture.

CONCLUSION

The synthesis and characterization of new thermotropic copolyesters based on IA and 4,4'-bis (ω -hydroxyalkoxy) biphenyls with different numbers of methylene units have been reported. The structural modifications have been resulted reducing melting point and extending (LC) range accompanied by LC properties. Also, we have been synthesized and characterized copolyesters formed by condensation of the 4,4'-bis (ω -hydroxyalkoxy) biphenyl smectic monomers with isophthaloyl chloride and terephthaloyl chloride. The presence of non-linear moiety (IA unit) substituted with different length spacers led to a reduced rigidity of polymers. The copolyesters with a low percentage of the p-biphenylene terephthalate unit exhibit liquid crystallinity, while the copolymers with molar percentages of terephthalate unit melt directly to the isotropic liquid phase. These results show the importance of the copolymerization method to modulate the thermal properties of such polyesters.

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