

Thermotropic polyesters. 2: Synthesis, characterization and thermal transitions of copolyesters containing 4,4'-bis (ω -alkyloxy) biphenyl isophthalate units

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Abstract

Thermotropic copolyesters containing an isophthalate unit and mesogenic 4, 4'-bis (ω -hydroxyalkyloxy) biphenyls ($n = 3, 4, 6$) with different numbers of methylene units have been synthesized by melt polymerization. The number-average molar mass (M_n) was estimated from end group analysis by ^1H NMR. The copolymer compositions were also obtained from ^1H NMR. The thermal behavior of the copolymers containing even–even ($n = 4, 6$) and odd–even ($n = 3, 4$) pairings has been investigated and is also compared with that of the analogous homopolymers. The copolymers exhibit reduced melting point and extending liquid crystalline range identified using polarizing microscopy and DSC. All of the obtained compounds were characterized by conventional spectroscopic methods.

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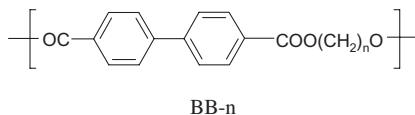
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1. Introduction

Main chain thermotropic polyesters have generated much interest in recent years both because of the challenge of understanding such systems and because of their many industrial and commercial applications [1–6]. However, the necessity for rigid structure of the mesogen usually leads to high melting point and a much

reduced solubility of these polyesters. In order to improve the solubility and to modulate the thermal properties of such stiff polymers, several structural modifications have been performed, such as the insertion of flexible spacers [7–9]; the addition of bulky or non-symmetrical substituents [10,11]; the inclusion of non-linear or bent monomers [12–14]; and copolymerization of different monomers [15–18]. Route of copolymerization provides versatile ways to prepare new thermotropic copolyesters of low T_m and extending liquid crystal (LC) range. This effect was applied to poly(alkylene-4,4'-bibenzoate)s, designated as BB- n (n : carbon number of the methylene spacer) [8].

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The mesomorphic properties of random copolymers, BB-*m-n*; where *m* and *n* are the numbers of methylene units in the two diols, were indicated that incorporation of a second repeating unit of different length does not significantly disrupt the structure of the mesophase if the difference in length between the two units is small [19].

Fischer et al. [20] originally reported the mesophase behavior of polyesters made from the condensation of 4,4'-bis (6-hydroxyhexyloxy) biphenyl and isophthalic acid (IA). However, Khan et al. [21,22] corroborated that the IA polyester did form a biphasic nematic–smectic A phase. In our previous paper, liquid crystalline polyesters containing isophthalate unit and mesogenic diols 4,4'-bis (ω-hydroxyalkyloxy) biphenyl with different lengths spacers were described [23]. The aim of this paper is the synthesis, characterization and thermal properties investigation of a series of random copolyesters containing isophthalate and the same mesogenic diols, 4,4'-bis (ω-hydroxyalkyloxy) biphenyl, with even and odd numbers of methylene units. These mesogenic diols were selected for this study because the mesophase behavior of the IA homopolymers is well characterized in our previous work [23].

2. Experimental

2.1. Materials

The purifying or drying of compounds and solvents has been performed according to the common procedure. Isophthaloyl chloride, terephthaloyl chloride purchased from Merck. The chemical structures of the homopolymers and copolymers are shown in Fig. 1.

2.1.1. Polyesters of 4,4'-bis (ω-hydroxyalkyloxy) biphenyls and isophthaloyl chloride

The synthetic route for the synthesis of the monomers and IA homopolymers are shown in Schemes 1 and 2. The exact synthetic procedure and characterization of the monomers and IA homopolymers were presented in earlier work [23].

2.1.2. Copolyesters—general experimental procedure

The different mole ratio of monomers (0.01 mol) and isophthaloyl chloride (2.1 g, 0.01 mol) were placed in a polymerization flask equipped with a magnetic stirrer, a gas inlet outlet, and a vacuum inlet. The polymerization 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 of 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 about 3.5 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 dichloromethane, filtering, and reprecipitating with acetone purified the polymer further.

2.1.2.1. Polyesters of (PI3-co-PI4). Random copolymers with 75:25, 50:50 and 25:75 mole ratio of monomers BHPRB:BHBB (0.01 mol) and isophthaloyl chloride (2.1 g, 0.01 mol) were used. For copolymer PI3-co-PI4 (P:X = 50:50): FT-IR (KBr): 3421 (OH), 2953 and 2871 (CH₂), 1718 (C=O), 1607 and 1500 (aromatics), 1235 and 1093 (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 each –C=O), 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), 4.56 (t, CH₂, α to –O–C=O), 4.43 (t, CH₂, α to –O–C=O), 4.15 (t, CH₂, α to –OAr), 4.05 (t, CH₂, α to –OAr), 3.88 and 3.74 (t, –OH), 3.63 and 3.51 (m, CH₂, β to –OH), 2.28 (m,

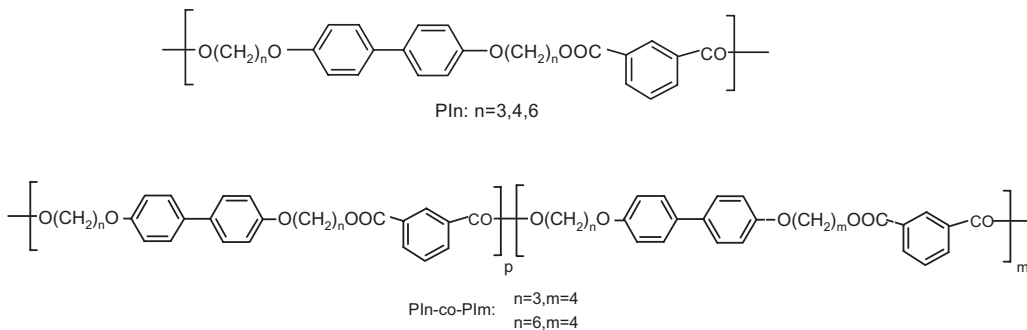
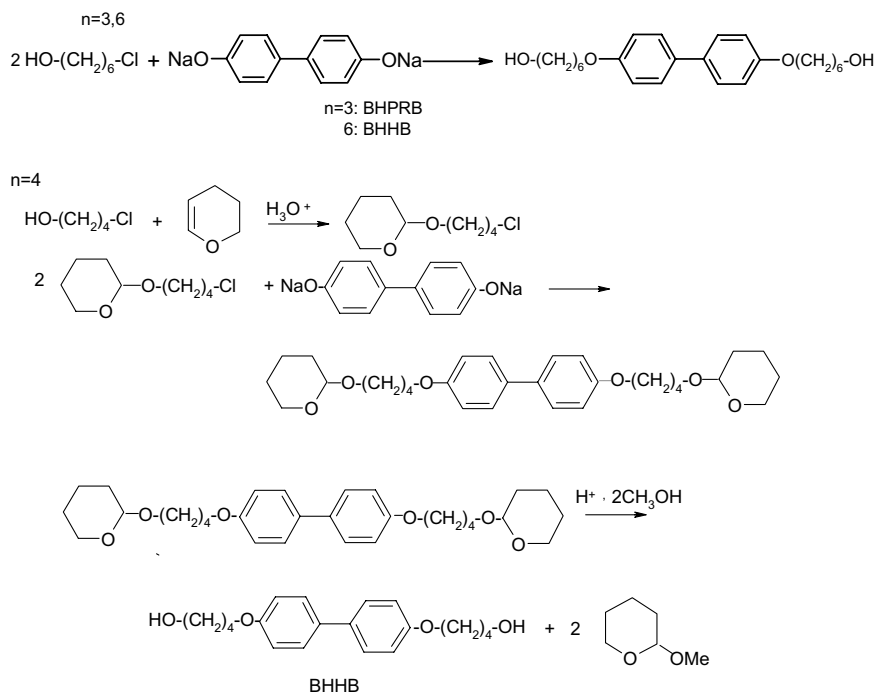
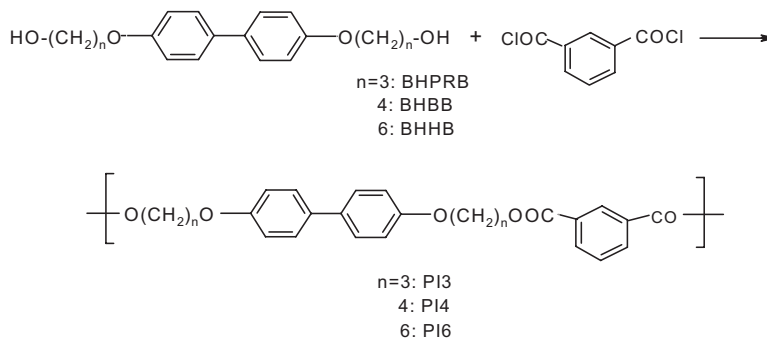


Fig. 1. Chemical structures of polyesters and copolyesters.



Scheme 1. Synthesis of 4,4'-bis (ω-hydroxyalkyloxy) biphenyl.



Scheme 2. Synthesis of polyesters of 4,4'-bis (ω-hydroxyalkyloxy) biphenyl and isophthaloyl chloride.

CH_2 , β to $-\text{O}-\text{C}=\text{O}$ and $-\text{OAr}$), 1.99 (b, CH_2 β to $-\text{O}-\text{C}=\text{O}$ and $-\text{OAr}$).

2.1.2.2. Polyesters of (PI4-co-PI6). Random copolymers with 75:25, 50:50 and 25:75 mol ratio of monomers BHBB:BHBB (0.01 mol) and isophthaloyl chloride (2.1 g, 0.01 mol) were used. For copolymer PI3-co-PI4 (P:X = 50:50): FT-IR (KBr): 3421 (OH), 2939 and 2865 (CH_2), 1720 ($\text{C}=\text{O}$), 1607 and 1500 (aromatics), 1238 and 1049 ($\text{C}-\text{O}-\text{C}$) cm^{-1} . ^1H NMR (CDCl_3): δ 10 (s, $-\text{OH}$, carboxylic acid), 8.69 (s, 1H aromatic, between the $-\text{C}=\text{O}$), 8.21 (d, 2H aromatic, *ortho* to each $-\text{C}=\text{O}$), 7.51 (t, 1H aromatic, *meta* to each $-\text{C}=\text{O}$), 7.43 (d, 2H aromatic, *ortho* to O), 6.93 (d, 2H aromatic, *meta* to

O), 4.44 (t, CH_2 , α $-\text{O}-\text{C}=\text{O}$), 4.36 (t, CH_2 , to $-\text{O}-\text{C}=\text{O}$), 4.05 (t, CH_2 , α to $-\text{OAr}$), 3.99 (t, CH_2 , α to $-\text{OAr}$), 3.73 (t, $-\text{OH}$), 3.64 and 3.53 (t, CH_2 , α to $-\text{OH}$), 1.99 (b, CH_2 , β to $-\text{O}-\text{C}=\text{O}$ and $-\text{OAr}$), 1.83 (m, CH_2 , β to $-\text{O}-\text{C}=\text{O}$ and γ to $-\text{O}-\text{C}=\text{O}$), 1.55 (b, the rest CH_2 protons).

2.2. Methods

Spectroscopic characterization utilized the following instrumentation: Melting points were recorded with an electrothermal apparatus. FT-IR spectra were recorded on a PS-15 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 [23]. 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.

3. Results and discussion

3.1. Synthesis and characterization of polyester

The mesogenic monomers 4,4'-bis (3-hydroxypropyloxy) biphenyl (BHPRB), 4,4'-bis (4-hydroxybutyloxy) biphenyl (BHBB) and 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHHB) were synthesized by the standard method [23,24] (Scheme 1). The homopolymers of PI3 [23], PI4 [23] and PI6 [22,23] were prepared by melt poly-

condensation of respective synthesized monomers with isophthaloyl chloride. The polyesters were characterized by FTIR and ¹H NMR.

A similar polymerization procedure to the polyesters was used for the synthesis of all copolyesters. The number-average molar mass (M_n) was estimated from end group analysis by ¹H NMR. The intensity of the C–H proton peaks of methylene units in α -position to terminal –OH group were used for the M_n estimation. These peaks were seen at 3.50 ppm and 3.62 ppm for copolymer PI3-co-PI4 (P:X = 25:75) in Fig. 2. Composition of copolymers was also obtained from ¹H NMR spectrum. For example, the intensity of the peaks at 4.56 ppm and 4.44 ppm of copolymer PI3-co-PI4 (P:X = 25:75) due to the α methylene units to the ester bond in the spacer of BHPRB and BHHB monomers were definitely used for this purpose (Fig. 2).

The molar masses, average degree of polymerization (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. The monomer ratio in the feed was similar to the ratio of the two monomeric.

3.2. Thermal transition of PIn-co-PI_m polyesters

In order to confirm the existence of the liquid crystalline phase for the copolymers sample, DSC measurements and polarizing optical microscopic observations

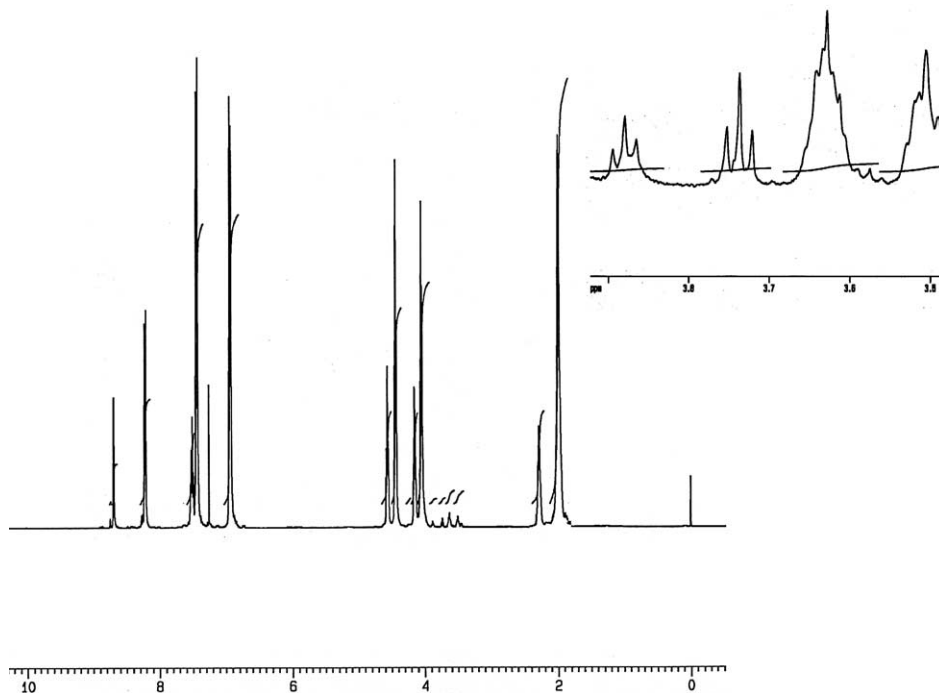


Fig. 2. ¹H NMR spectra of copolymer PI3-co-PI4 (P:X = 25:75) in CDCl₃.

Table 1
Copolymerization of 4,4'-bis (ω -hydroxyalkoxy) biphenyls ($n = 3, 4$ or $4, 6$) with isophthaloyl chloride

Polyester	Composition (P:X)		M_n^a (g/mol)	η^b (dl/g)	Yield (%)
	In fed	In copolymer			
PI3-co-PI4	100:0	100:0	22,000	0.25	94
PI3-co-PI4	75:25	71:29	11,000	0.16	80
PI3-co-PI4	50:50	48:52	11,000	0.15	85
PI3-co-PI4	25:75	30:70	4000	0.05	85
PI4-co-PI6	0:100	0:100	10,000	0.13	90
PI4-co-PI6	75:25	70:30	8500	0.08	88
PI4-co-PI6	50:50	53:47	10,000	0.14	85
PI4-co-PI6	25:75	26:74	15,500	0.17	88
PI4-co-PI6	0:100	0:100	19,500	0.19	96

^a Estimated from end group analysis by ^1H NMR.

^b Concentration of 0.25 g/dl of CHCl_3 , at 25°C.

have been performed. The thermal properties of $\text{PI}n\text{-co-PI}m$ ($n = 3, m = 4$ and $n = 6, m = 4$) copolymers with different molar ratio of monomers (P:X) and PI3, PI4 and

PI6 homopolymers are shown in Tables 2 and 3. Although PI3 had a smectic C phase [23], only PI3-co-PI4 copolymer with higher contents of PI3 unit (P:X = 75:25) exhibited S_C and S_A phases on heating and cooling. It was already reported that the PI4 [23] and PI6 [22,23] polymers had a smectic A phase. Other copolymers only showed a single mesophase which was identified as a S_A phase on the basis of its optical texture when viewed through the polarizing microscope. It is noteworthy that the monotropic PI6 gave enantiotropic PI4-co-PI6 copolymers.

The phase behavior of PI3-co-PI4 and PI4-co-PI6 copolymers is shown in Fig. 3. It can be seen that the isotropization temperature of S_A falls on a smooth curve very nearly corresponding to the arithmetic average of those for the homopolymers. The melting temperatures of the crystals have a clear indication of eutectic behavior when the second component is added. For example, a PI3-co-PI4 (P:X = 50:50) copolymer had a smectic phase from 100 to 130°C (= I). The melting temperature

Table 2
Phase transition temperatures and enthalpies of the copolyesters ($\text{PI}n\text{-co-PI}m$) determined by DSC at scan rate 10°C/min on the first cooling

$\text{PI}n\text{-co-PI}m$ (P:X)	$T_{I-S_A} T_{I-S_C}^*$ (°C)	$T_{S_A-S_C}$ (°C)	$T_{S_C-K}^* T_{S_A-K}$ (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)	ΔH_3 (J/g)
$n = m = 3$	166.7 ^a	—	^{a*}	−25.8	—	^a
$n = m = 4$	121.9	—	113.3	−12.3	—	−2.5
$n = m = 6$	115.6	—	82.5	−11.6	—	n.s. ^b
$n = 3, m = 4$ (25:75)	123.7	—	108	−7.1	—	n.s.
$n = 3, m = 4$ (50:50)	130	—	100	−4.3	—	n.s.
$n = 3, m = 4$ (75:25)	148	^c	115 [*]	−9.7	^c	n.s.
$n = 4, m = 6$ (25:75)	105.7	—	81	−8.8	—	n.s.
$n = 4, m = 6$ (50:50)	116.6	—	101.7	−11.6	—	−2.8
$n = 4, m = 6$ (75:25)	115	—	104.2	−11.1	—	−2.8

* Transitions containing S_C phase.

^a Significant overlapping of the two peaks due to the isotropic phase to smectic C and smectic C to crystal transition.

^b Negligibly small.

^c Significant overlapping of the two peaks due to the isotropic phase to smectic A and smectic A to smectic C transition.

Table 3
Phase transition temperatures and enthalpies of the copolyesters $\text{PI}n\text{-co-PT}n$ determined by DSC at scan rate 10°C/min on the second heating

$\text{PI}n\text{-co-PI}m$ (P:X)	$T_{K-S_A} T_{K-S_C}^*$ (°C)	$T_{S_C-S_A}$ (°C)	$T_{S_C-I}^* T_{S_A-I}$ (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)	ΔH_3 (J/g)
$n = m = 3$	190.8 [*]	—	196.5 [*]	25.4	—	^a
$n = m = 4$	116.8	—	127.4	3.3	—	11.8
$n = m = 6$	—	—	120 ^b	—	—	12.1
$n = 3, m = 4$ (25:75)	104.7	—	132.4	2.63	—	4.4
$n = 3, m = 4$ (50:50)	104.9	—	132.5	3.4	—	4.85
$n = 3, m = 4$ (75:25)	119.3 [*]	165 ^c	178	6.64	20.5 ^c	^c
$n = 4, m = 6$ (25:75)	97.3	—	110.7	n.s.	—	5.76
$n = 4, m = 6$ (50:50)	107.6	—	121.5	4.35	—	11.9
$n = 4, m = 6$ (75:25)	108.4	—	119.9	4.05	—	10.8

* Transitions containing S_C phase.

^a Overlapping of the two peaks due to the crystal to smectic C and smectic C to isotropic transition.

^b Monotropic.

^c Overlapping of the two peaks due to the smectic A to smectic C and smectic C to isotropic transition.

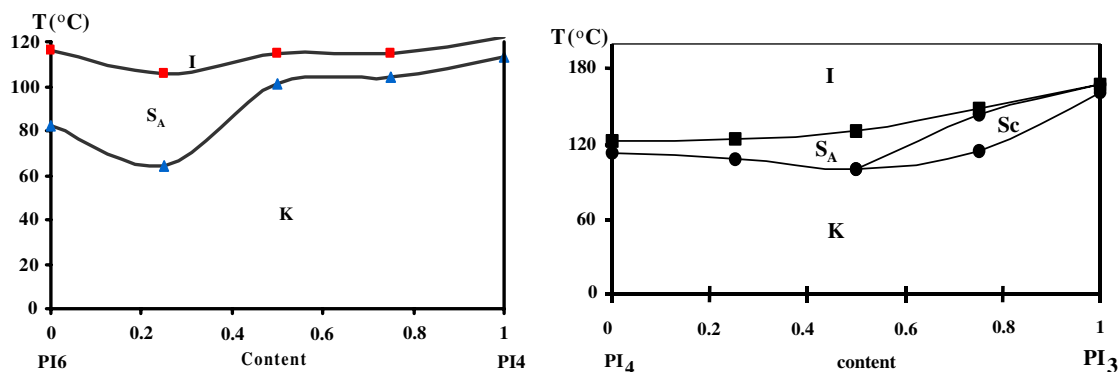


Fig. 3. Composition dependence of phase behavior in (a) PI4-co-PI6 and (b) PI3-co-PI4.

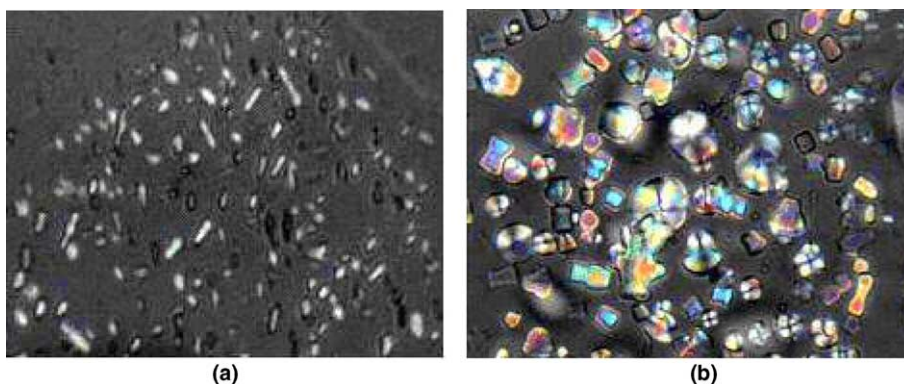


Fig. 4. Optical polarized microphotograph at scanning rate of $0.7^{\circ}\text{C}/\text{min}$ on the second cooling of (a) PI3-co-PI4 (P:X = 50:50) at 121°C and (b) PI4-co-PI6 (P:X = 25:75) at 112°C .

was almost 60°C and 13°C lower than each PI3 and PI4 homopolymers, respectively.

To obtain a clear texture from which such as assignments were possible, the samples were cooled slowly from the isotropic phase into the mesophase. The smectic phase was characterized by a batonnets texture with the polarized microscope observation for PI3-co-PI4 (P:X = 50:50) copolymer, as shown in Fig. 4a. The focal conic domains are present along with the batonnets for PI4-co-PI6 (P:X = 50:50) copolymer in Fig. 4b. On cooling from the isotropic melt, batonnets were initially formed, which immediately grow and coalesced into the focal conic texture typical of the smectic mesophase [23].

4. 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 mod-

ifications have been resulted reducing melting point and extending (LC) range accompanied by LC properties. These results show the importance of the copolymerization method to modulate the thermal properties of such polyesters.

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