Available online at www.sciencedirect.com

European Polymer Journal 40 (2004) 865–871

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Thermotropic polyesters. 1: Synthesis, characterization and thermal transition of poly[4,4′-bis(ω-alkoxy)biphenyl isophthalate]

Massoumeh Bagheri [a,*], Khadije Didehban [a], Zolfaghar Rezvani [a], Ali Akbar Entezami [b]

[a] *Department of Chemistry, Faculty of Science, Azarbaidjan University of Tarbiat Moallem, Tabriz 53751-71379, Iran*
[b] *Polymer Laboratory, Chemistry Faculty, Tabriz University, Tabriz 51666-14766, Iran*

Received 6 January 2003; received in revised form 24 November 2003; accepted 24 November 2003

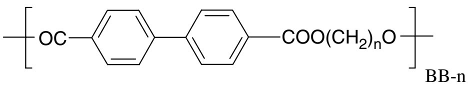
Abstract

A new homologous series of thermotropic polyesters has been synthesized by polycondensation reaction between isophthaloyl chloride and mesogenic diols 4,4′-bis(ω-hydroxyalkoxy)biphenyl in which the spacer length is varied from 3 to 6 methylene units. The thermal behavior of the polymers has been characterized using polarized light microscopy and differential scanning calorimetry (DSC). The odd members exhibit a smectic C (S_C) phase in a narrow temperature interval, while the even members form a smectic A (S_A) phase in a broader temperature range. All of the obtained compounds were characterized by conventional spectroscopic methods.

Keywords: Liquid crystals; Polyesters; Optical texture; DSC; Odd–even effect

1. Introduction

There has been lots of research on the synthesis of thermotropic polyesters with unique thermal and physical properties [1]. However, the necessity for rigid structure of the mesogen usually leads to high melting point and a very reduced solubility of these polyesters [2]. 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 [3–5]. The thermotropic liquid crystalline behavior of polymers with rigid mesogenic units interconnected through flexible spacers is well known from reports over the past two decades. The most typical examples of these polyesters are poly (alkylene 4,4′-bibenzoate)s, designated as BB-*n* (*n*: carbon number of the methylene spacer).

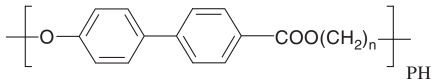


These BB-*n* polyesters invariably form smectic mesophases when *n* varies from 3 to 9 [6–8]. In BB-*n* with an even *n*, a S_A phase is formed. In contrast, the smectic structure of BB-*n* with an odd *n* was identified as a new type of smectic phase, S_{CA}, in which the tilt of the direction of the mesogenic group is the same in every second layer but opposite between neighboring layers [1]. The odd–even alternation of the smectic structures appears with an opposite trend for the following PHBC-*n* polymers [9]:

---

[*] Corresponding author. Tel./fax: +98-412-452-4991.
E-mail address: masbagheri@yahoo.com (M. Bagheri).

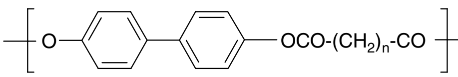
0014-3057/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2003.11.026



PHBC-n

The S_A phase is observed for odd *n*, whereas it is formed from even-*n* polymers in the BB-*n* series. Also, the S_{CA} phase is observed in PHBC-*n* with even *n*.

Asrar et al. [10] prepared a homologous series of polyesters (PB-*n*) upon 4,4′-biphenyldiol and aliphatic dibasic acids with 5 to 12 methylene units. The chemical structure of these polyesters is represented as follows:



PB-n

It is known that this family exhibits clearly an odd–even effect. The odd members exhibit a nematic phase in a narrow temperature interval, while the even members form a highly ordered smectic (S_H) phase in a broader temperature range.

Among them, thermotropic polyester made from the condensation of mesogenic diol 4,4′-bis(6-hydroxyhexyloxy)biphenyl (BHHB, Fig. 1) with isophthaloyl chloride forms a biphasic nematic-smectic A phase but terephthalic acid (TA) polyester crystallized directly on cooling the melt, without forming a mesophase [11,12]. The isophthalic acid (IA) polyester has a monotropic liquid crystal phase as the mesophase is only observed on cooling.

In relation to these results, it could be interesting to incorporate other flexible spacers with different lengths in this aromatic polyester since the presence of nonlinear moieties substituted with different length spacer should lead to a better knowledge of the structure–property relationship in this class of materials. For this purpose, we report the synthesis and characterization of novel IA polyesters containing flexible alkylene spacers. The effect of the number of methylene units in the spacer on the transition temperatures and solubility behavior of these polymers were studied.

2. Experimental

2.1. Materials

The purifying or drying of compounds and solvents has been performed according to the common procedure. 1,5-Pentanediol, 1,6-hexanediol, 4, 4′-biphenol, isophthaloyl chloride and 3,4-dihydro-2-pyran were purchased from Merck. 1,3-Propanediol was purchased from Fluka. 1-Chloro-3-propanol [13], 1-chloro-4-butanol [14], 1-chloro-5-pentanol [15] and 1-chloro-6-hexanol [16] were prepared according to a literature procedure. The monomers and polymers were synthesized according to the route outlined in Schemes 1 and 2, and further details are given below.

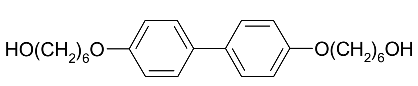


Fig. 1. Structure of mesogenic monomer BHHB.

2.1.1. 4,4′-Bis(ω-hydroxyalkyloxy)biphenyls (*n* = 3, 5, 6)

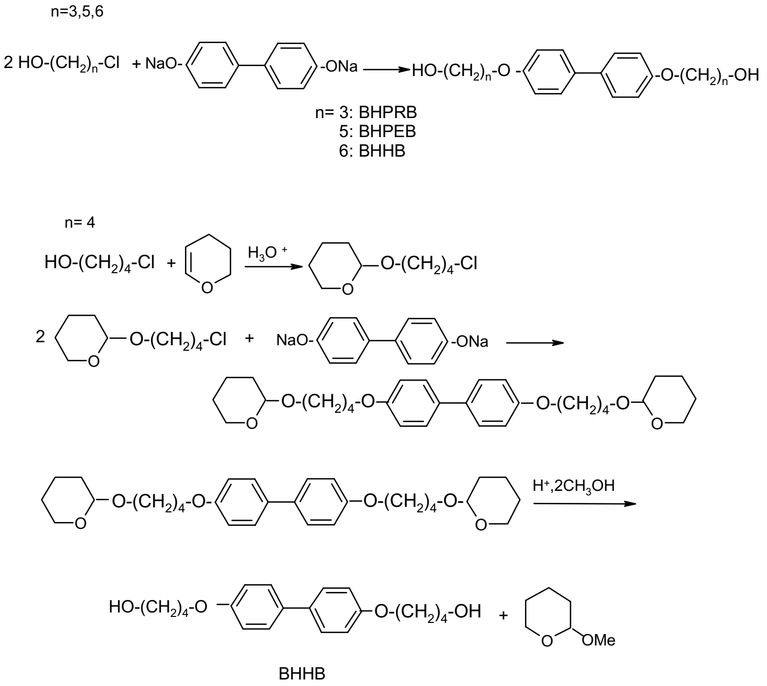
4,4′-Bis(ω-hydroxyalkyloxy)biphenyls having three, five and six methylene groups (BHPRB, BHPEB, and BHHB) were synthesized using a modification of the procedure described by Ando and Uryu [17] (Scheme 1). The synthesis of 4,4′-bis(6-hydroxyhexyloxy)biphenyl is described as a representative case. A mixture of sodium hydroxide (4 g, 0.1 mol), ethanol (250 ml), and 4,4′-biphenol (8.37 g, 0.045 mol) was stirred, whilst being refluxed under nitrogen. 6-Chlorohexanol (13.65 g, 0.1 mol) was added drop wise, over a period of 30 min. The mixture was left to stir for approximately 24 h (36 h for BHPEB), after which time a clear yellow solution was obtained. After standing at room temperature (about BHPEB the solution was poured into a beaker of water), the precipitate was filtered and washed with water. The product was recrystallized from isopropanol. Yield: 65%; FTIR (KBr): 3300 (OH), 2940 and 2860 (CH_2), 1607 and 1500 (aromatics), 1247 and 1040 (C–O–C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.52 (d, 2H aromatic, *ortho* to O), 6.96 (d, 2H aromatic, *meta* to O), 4.38 (t, OH), 3.97 (t, CH_2, α to –OAr), 3.39 (m, CH_2, α to –OH), 1.71 (m, CH_2, β to –OH), 1.42–1.38 (m, the rest CH_2 protons).

For other 4,4′-bis(ω–hydroxyalkyloxy)biphenyls, *n* = 3: Yield: 60%; FTIR (KBr): 3290 (OH), 2930 and 2870 (CH_2), 1605 and 1500 (aromatics), 1275 and 1056 (C–O–C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.51 (d, 2H aromatic, *ortho* to O), 6.97(d, 2H aromatic, *meta* to O), 4.59 (t, –OH), 4.05 (t, –CH_2, α to –OAr), 3.58 (m, CH_2, α to –OH), 1.87 (m, the rest CH_2).

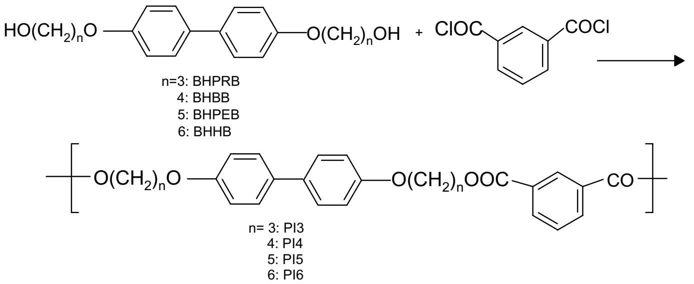
n = 5: Yield: 48%; FTIR (KBr): 3290 (OH), 2935 and 2865 (CH_2), 1605 and 1500 (aromatics), 1274 and 1035 (C–O–C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.48 (d, 2H aromatic, *ortho* to O), 6.97 (d, 2H aromatic, *meta* to O), 4.4 (t, –OH), 3.97 (t, CH_2, α to –OAr), 3.41 (m, CH_2, α to –OH), 1.72 (m, CH_2, β to –OH), 1.42–1.49 (m, the rest CH_2 protons).

2.1.2. 4-[(Tetrahydro-2-pyranyl) oxy]-1-chlorobutane

4-[(Tetrahydro-2-pyranyl) oxy]-1-chlorobutane was prepared according to the method described by Ando and Uryu [17]. Thus, 3,4-dihydro-2-pyran was added to a mixture of 4-chlorobutane (54.5 g, 0.5 mol) and concentrated HCl (0.5 ml) at 0 °C. After the resulting mixture was stirred at room temperature for 20 h, the solution was neutralized with KOH (0.9 g) and then



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.

filtered. The product was distilled under reduced pressure. Yield: 64%. Bp: 104–106 °C (6 mmHg) [lit. [17] bp: 99–101 °C (4 mmHg)].

2.1.3. 4, 4′-Bis(tetrahydro-2-pyranyloxy-butyloxy) biphenyl

4,4′-Bis(tetrahydro-2-pyranyloxy-butyloxy)biphenyl was synthesized by reaction of 4-[(tetrahydro-2-pyranyl) oxy]-1-chlorobutane (57.7g, 0.3 mol) and 4, 4′-biphenol (27.9 g, 0.15 mol) in the same way as BHHB. After product was dissolved in hot ethanol (200 ml), concentrated H_2SO_4 (10 ml) was added drop wise. The mixture was refluxed under stirring for 0.5 h. After cooling, the precipitate was filtered and successively washed with ethanol and water. The product, 4,4′-bis(4-hydroxybutyloxy)biphenyl(BHBB),was recrystallized from isopropanol. Yield 80%; FTIR (KBr): 3290 (OH), 2945 and 2875 (CH_2), 1606 and 1499 (aromatics), 1272 and 1048 (C–O–C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.48 (d, 2H aromatic, *ortho* to O), 6.94 (d, 2H aromatic, *meta* to O), 4.45 (b, –OH), 3.97 (t, CH_2, α to –OAr), 3.43 (m, CH_2, α to –OH), 1.72 (m, CH_2, β to –OH), 1.55 (CH_2, β to –OAr).

2.1.4. Synthesis of polyesters- general experimental procedure

The polyesters were prepared using a procedure described by Khan et al. [12] shown in Scheme 2. The synthesis of polyester of BHHB and isophathaloyl chloride is described as a representative case. BHHB

(4 g, 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 4 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 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 polymer was purified further by dissolving in dichloromethane (or chloroform about PI3 and PI5), filtering, and reprecipitating with acetone. Yield: 96%. FTIR (KBr): 3410 (OH), 2940 and 2860 (CH_2), 1723 (C=O), 1607 and 1500 (aromatics), 1239 and 1074 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 10 (s, –OH, carboxylic acid), 8.68 (s, 1H aromatic, between the –C=O), 8.21 (m, 2H aromatic, *ortho* to each of –C=O), 7.51 (t, 1H aromatic, *meta* to each of –C=O), 7.43 (d, 2H aromatic, *ortho* to O), 6.93 (d, 2H aromatic, *meta* to O), 4.36 (t, CH_2, α to –O–C=O), 3.98 (t, CH_2, α to –OAr), 3.66 (t, –OH), 3.55 (t, CH_2, α to –OH), 1.80–1.86 (m, CH_2, β to –O–C=O and –OH and γ to –O–C=O), 1.54–1.55 (b, the rest CH_2 protons).

For other polymers, PI3: Yield: 94%; FTIR (KBr): 3420 (OH), 2958 and 2860 (CH_2), 1723 (C=O), 1607 and 1500 (aromatics), 1234 and 1094 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 10 (s, –OH, carboxylic acid) 8.68 (s, 1H aromatic, between the –C=O), 8.22 (m, 2H aromatic, *ortho* to each of –C=O), 7.52 (t, 1H aromatic, *meta* to each of –C=O), 7.43 (d, 2H aromatic, *ortho* to O), 6.92 (d, 2H aromatic, *meta* to O), 4.55 (t, CH_2, α to–O–C=O), 4.13 (t, CH_2, α to –OAr), 4.06 (m, CH_2, α to terminal –OAr), 3.88 (t, –OH), 3.75 (m, CH_2, α to –OH), 2.27 (m, CH_2, β to –O–C=O), 2.05 (m, CH_2, β to –OH).

PI4: Yield: 90%; FTIR (KBr): 3421 (OH), 2952 and 2870 (CH_2), 1720 (C=O), 1607 and 1500 (aromatics), 1237 and 1094 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$: δ 10 (s, –OH, carboxylic acid), 8.70 (s, 1H aromatic, between the –C=O), 8.21 (m, 2H aromatic, *ortho* to each of –C=O), 7.50 (t, 1H aromatic, *meta* to each of –C=O), 7.41 (d, 2H aromatic, *ortho* to O), 6.92 (d, 2H aromatic, *meta* to O), 4.43 (t, CH_2, α to –O–C=O), 4.03 (t, CH_2, α to –OAr), 3.62 (t, –OH), 3.62 (t, CH_2, α to –OH), 1.99 (b, CH_2, β to –O–C=O and –OAr), 1.77 (m, CH_2, β and γ to –OH).

PI5: Yield: 66%; FTIR (KBr): 3420 (OH), 2942 and 2868 (CH_2), 1723 (C=O), 1607 and 1500 (aromatics), 1241 and 1094 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 10 (s, –OH, carboxylic acid), 8.69 (s, 1H aromatic, between the –C=O), 8.22 (m, 2H aromatic, *ortho* to each of –C=O), 7.54 (t, 1H aromatic, *meta* to each of –C=O), 7.44 (d, 2H aromatic, *ortho* to O), 6.92 (d, 2H aromatic, *meta* to O), 4.38 (t, CH_2, α to –O–C=O), 4.00 (t, CH_2, α to –OAr), 3.82 (b, –OH), 3.57 (b, CH_2, α to –OH), 1.87 (m, CH_2, β to –O–C=O and –OAr), 1.64 (m, 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 Brucker spectrometer. ^1H NMR spectra were taken on a 400 MHz Brucker versus, TMS in $CDCl_3$ and DMSO-d_6. The intrinsic viscosities of the samples were determined by an Ubbelhode 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 a long working distance objective 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 viscose and did not form a thin layer spontaneously. Hence, it was sheared between the glass plates in the isotropic state [11,12]. 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. Monomer synthesis

The monomers 4,4′-bis(3-hydroxypropyloxy)biphenyl (BHPRB), 4,4′-bis(5-hydroxypentyloxy)biphenyl (BHPEB) and 4,4′-bis(6-hydroxyhexyloxy)biphenyl (BHHB) were synthesized by the standard method. The synthesis involves the nucleophilic displacement of chlorine from *n*-chloro-1-alkanol by sodium 4,4′-biphenoxide. The monomer 4,4′-bis(4-hydroxybutoxy)biphenyl (BHBB) was synthesized by protecting the hydroxyl groups of 4-chlorobutanol. Synthetic routes to these structures are shown in Scheme 1.

Ando and Uryu [17] concluded that all of these monomers have a smectic liquid crystalline phase. Here we shall merely confirm that our monomers were pure and the phase transitions determined by polarizing microscopy are summarized in Table 1. Such thermal transition behavior is in good accord with the previously reported [17].

Table 1 shows that the variation of the transition temperatures with carbon number of alkylene spacer (n). The mesophase temperature region of odd or even pairs

Table 1
Phase transition of 4,4′-bis(ω-hydroxyalkyloxy) biphenyls

Material	Heating[a]	Cooling[a]	Heating[b]	Cooling[b]
BHPRB	K185S210I	K162S203I	K179S208I	K163S202I
BHBB	K101S192I	K99S199I	K99S194I	K91S187I
BHPEB	$K_1$106K163S174I	$K_1$102$K_2$153S168I	$K_1$106$K_2$165S178I	$K_1$101$K_2$153S171I
BHHB	K94S175I	K88S171I	K95S174I	K86S167I

[a] Phase transitions determined at first cooling and second heating by polarizing microscopy at a scanning rate of 10 °C/min in this work; K: Crystal; S: Smectic and I: Isotropic.

[b] Phase transitions determined from DSC measurements of first cooling and second heating at a scanning rate of 10 °C/min and polarizing microscopy in Ref. [17].

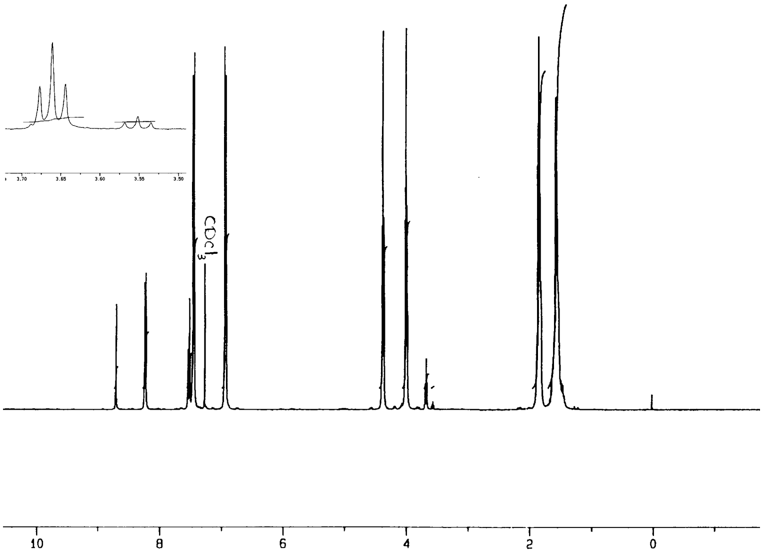


Fig. 2. ^{1}H NMR spectra of PI6 in chloroform solution.

Table 2
Molecular weight and intrinsic viscosity of polyesters

Polyesters	[η](dl/g)[a]	M_n (g/mol)	DP[b]
PI3	0.25	22 000	50
PI4	0.11	10 000	21
PI5	0.19	13 000	25
PI6	0.21	19 500	37
PI6[c]	–	5000	13

[a] Solvent: $CHCl_3$; 25 °C.

[b] Estimated from end group analysis by ^{1}H NMR.

[c] Ref. [11].

Table 3
Solvent test result of polyesters

Solvent	PI3	PI4	PI5	PI6
Cyclohexan	–	–	–	–
Toluene	–	–	–	–
Dichloromethane	–	+	–	+
Chloroform	+	+	+	+
THF	–	+	–	–
Acetone	–	–	–	–
DMSO	–	–	–	–
DMF	–	–	–	–
Methanol	–	–	–	–

decreases with increasing n and the monomers with an even number of methylene groups have a wider mesophase and also the lower values on crystal-smectic transitions. This clear odd–even effect is known to be based on such a difference in structure. Polarizing optical micrographs of monomers show a highly ordered smectic mesophase.

3.2. Synthesis and characterization of polyester

A series of polyesters (PI3, PI4, PI5 and PI6) were prepared by melt polycondensation of respective synthesized monomers with isophthaloyl chloride and characterized by FTIR and ^{1}H NMR.

A ^{1}H NMR spectra of PI6 is shown in Fig. 2. The observation of very small peak at 10 ppm in ^{1}H NMR

Table 4
Phase transition temperatures T_1, T_2, and enthalpies of the polyesters on the first cooling at scan rate 10 °C /min

Polyesters	T_1 (°C)	T_2 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
PI3	166.7	–	−25.8[a]	–
PI4	121.9	113.3	−12.3	−2.5
PI5	130.3	–	−23.4[a]	–
PI6	115.6	82.5	−11.6	n.s.[b]
PI6[c]	100	68	−18	−1.9

[a] Significant overlapping of the two peaks due to the isotropic to smectic and smectic to crystal transition.

[b] Negligibly small.

[c] Ref. [12].

Table 5
Phase transition temperatures T_1, T_2, and enthalpies of the polyesters on the second heating at scan rate 10 °C /min

Polyesters	T_1 (°C)	T_2 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
PI3	190.8	196.5	25.4[a]	
PI4	116.8	127.4	3.3	11.8
PI5	155.3	161	23.7[a]	
PI6	–	120	–	12.1
PI6[b]	–	114	–	10

[a] Overlapping of the two peaks due to the crystal to smectic and smectic to isotropic transition.

[b] Ref. [12].

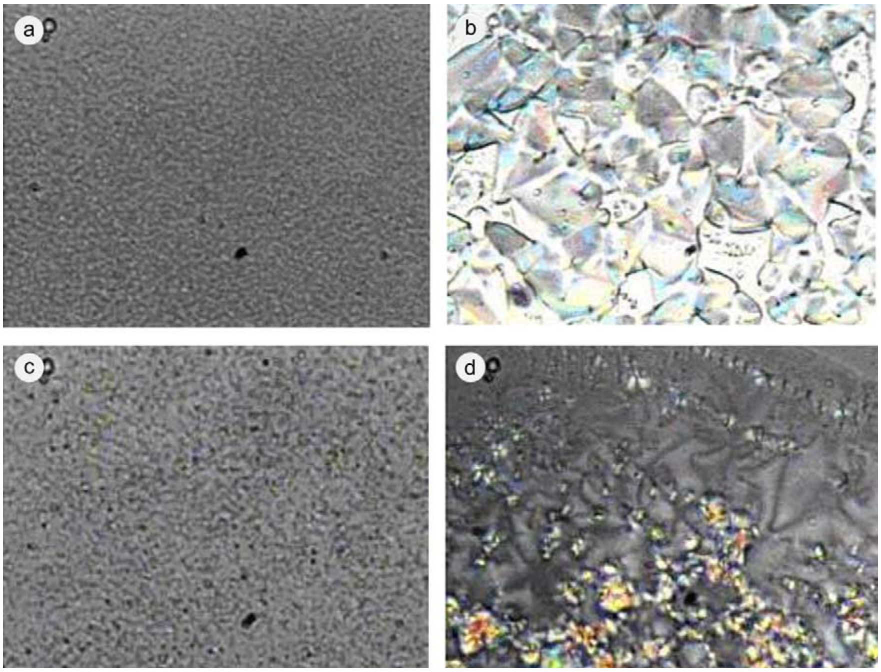


Fig. 3. Polarizing optical micrograph showing (a) the schlieren texture of the S_C phase of PI3 on cooling at 167 °C (b) the focal conic texture formation of the S_A phase of PI4 from isotropic phase on cooling at 117 °C and (c) the schlieren texture of the S_C phase of PI5 on cooling at 134 °C and (d) simultaneous presence of schlieren texture of the nematic and focal conic texture of the S_A texture of PI6 on cooling at 113 °C.

spectra of polyesters shows that the terminal –COCl group in polyesters hydrolyses to –COOH group during the purification process. The number-average molecular weight (M_n) was estimated from end group analysis by ^{1}H NMR. The intensity of the C-H proton peak of methylene unit$_{\text{in}}$ α-position to terminal –OH group (at 3.55 ppm for PI6) was used for this purpose.

The intrinsic viscosities [η] of polymers were determined by an Ubbelhode viscosimeter at 25 °C in chloroform. The molecular weights, average degree of polymerization (DP) and intrinsic viscosities of polyesters are listed in Table 2. These amounts show that the prepared polyesters are low molecular weight polymers and intrinsic viscosity increases with M_n. The reduced rigidity of polymers leads to increased solubility with increasing the spacer length. The results of solvent test are presented in Table 3.

3.3. Thermal transition of polyesters

To examine effect of the alkylene spacers on the transition temperature, we prepared homologous series of this polyester with odd and even carbons in spacer. DSC measurements and polarizing optical microscopic observations performed to confirm the existence of the liquid crystalline phase for the samples. Thermal properties of the polymers are summarized in Tables 4 and 5. Tables 4 and 5 show the variation of the transition temperatures with *n*. The polymers with an even number of methylene groups have a wider mesophase and also the lower values on crystal–liquid crystal transitions and isotropization of liquid crystal in comparison with odd members. This effect, so-called the odd–even effect.

Fischer et al. [18] originally reported that the polyesters formed by the condensation BHHB with isophthalic acid (IA) has a smectic A mesophase. However, Khan and Bashir [11,19] corroborated that the mesophase was monotropic and there was a nematic phase, besides smectic A (nematic-smectic biphase). The PI6 polyester has a monotropic liquid crystal phase as the mesophase is only observed on cooling at 0.7 °C/min. The phase sequence is K–I on heating, and I–N/S_A–K on cooling (K = crystal, N = nematic, S_A = smectic, I = isotropic melt phase) [11].

As shown in the Table 2, our prepared PI6 has higher molecular weight in comparison with prepared sample by Khan et al. Increasing the molecular weight leads to a shift of the crystallization and isotropization temperatures to the higher values (Tables 4 and 5). However, other polymers were enantiotropic. The odd-numbered polyesters (PI3 and PI5) had two peaks on heating process correspond to the isotropic mesophase transition and the second to the crystallization transition. But the mesophase windows were very narrow as two peaks slightly overlapped. On cooling, two overlapping exothermic transitions at 166.7 and 130.3 °C correspond to the isotropic mesophase transition, respectively. The mesophase window on heating of odd-numbered polyesters was narrow (only 5.3 and 5.7 °C wide). Furthermore, polarizing optical microscopic observations confirm that the S_C liquid crystalline phase for PI3 and PI5 in the temperature region between the two DSC peaks on both cooling and heating processes. On cooling of PI4, one strong exothermic peak at 121.9 °C and a smaller exothermic peak at 113.3 °C appeared. These peaks also observed on heating process. The polarizing microscopic observation of PI4 and PI6 showed a S_A and N/S_A phase respectively in a relatively broad temperature region between the two DSC peaks on both cooling and heating processes of PI4 and on cooling process of PI6. Fig. 3(a) and (c) show the schlieren texture of the smectic C phase of PI3 and PI5. The focal conic texture formation of the S_A phase of PI4 from isotropic phase observes in Fig. 3(b). Simultaneous presence of schlieren texture of the nematic and focal conic S_A texture appears for PI6 on the cooling process (Fig. 3(d)).

4. Conclusion

In this work we have synthesized and characterized polyesters formed by condensation of the smectic monomers with isophthaloyl chloride. The presence of non-linear moiety (IA unit) substituted with different length spacer led to a reduced rigidity of polymers and increased solubility in common organic solvents like chloroform and dichloromethane. The thermotropic polyesters exhibited a remarkable odd–even effect with the higher values in odd-numbered polyesters. The odd members exhibit a S_C phase in a narrow temperature interval, while the even members form a S_A phase in broader temperature range. These results show the importance of the flexible spacer understanding the mesophase structure and properties for these polyesters.

Acknowledgements

The authors would like to thank Research Vice Chancellor of Azarbaidjan University of Tarbiat Moallem for financial support of this research.

References

[1] Han H, Bhowmik PK. Prog Polym Sci 1997;22:1431.

[2] Grasser W, Schmidt H-W, Giesa R. Polymer 2001;42:8529.

[3] Watanabe J, Hayashi M, Morita A, Tokito M. Macromolecules 1995;28:8073.

[4] Huang HW, Horie K, Tokita M, Watanabe J. Polymer 1999;40:3013.

[5] Lin LL, Hong JL. Polymer 2000;41:4501.

[6] Tokita M, Osada K, Watanabe J. Polymer J 1998;30(7): 589.

[7] Tokita M, Takahashi T, Hayashi M, Inomata K, Watanabe J. Macromolecules 1996;29:1345.

[8] Osada K, Niwano H, Tokito M, Kawauchi S, Watanabe J. Macromolecules 2000;33:7420.

[9] Nakata Y, Watanabe J. J Mater Chem 1994;4:578.

[10] Asrar J, Toriumi H, Watanabe J, Krigbaum WR, Ciferri A. J Polym Sci: Polym Phys Ed 1983;21:1119.

[11] Khan N, Bashir Z. J Polym Sci: Polym Phys 1996;34:2077.

[12] Khan N, Patel VL, Bashir Z, Price M. J Polym Sci: Polym Phys 1995;33:1957.

[13] Horning EC, editor. Organic syntheses. New York: Wiley; 1955. p. 533.

[14] Horning EC, editor. Organic syntheses. New York: Wiley; 1955. p. 571.

[15] Pattison FL, McHowell WC, McNamara AJ, Schneider JC, Walker JF. J Org Chem 1956;21:739.

[16] Horning EC, editor. Organic syntheses. New York: Wiley; 1955. p. 446.

[17] Ando M, Uryu T. J Polym Sci: Polym Chem Ed 1990;28:2575.

[18] Fischer H, Karasz FE, MacKnight W. J Polym Int 1993;31:291.

[19] Bashir Z, Khan N. Thermochim Acta 1996;276:145.