Synthesis and characterization of poly(oxy-1,4-phenyleneoxycarbonyl-1,4-phenyleneoxypolymethylene)s

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(Received 10 August 1992; revised 29 October 1992)

A multistep synthetic route for the preparation of a series of poly(oxy-1,4-phenyleneoxycarbonyl-1,4-phenyleneoxypolymethylene)s having a varying length of the polymethylene spacer from the di- to the hexamethylene group is reported. The polymers prepared were characterized particularly for their liquid crystalline properties by differential scanning calorimetry, wide-angle X-ray diffractometry and observation of their textures on a polarizing optical microscope. All the polymers, with the exception of the trimethylene polymer, formed the nematic phase in melt. They exhibited the well known odd–even effect at melting temperature as well as at isotropization temperature.

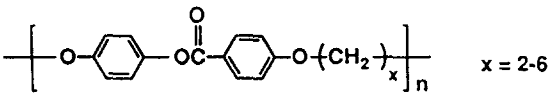
(Keywords: liquid crystalline polymers; main chain polyesters; poly(oxy-1,4-phenyleneoxycarbonyl-1,4-phenyleneoxypolymethylene))

INTRODUCTION

Numerous main-chain, thermotropic liquid crystalline polymers (LCPs)[1–16] containing flexible spacers have been reported in the past 20 years since Kuhfuss and Jackson[1] first described the mesophase formation by the copolymers prepared from the reaction between poly(ethylene terephthalate) and p-acetoxybenzoic acid. One of our earlier articles[9] and a recent report by Noel and Navard[17] critically review the structure–property relationship of these LCPs. Among reported LCPs a major group of structures studied in most detail are polyesters and copolyesters with polymethylene spacers. Many research groups have synthesized a wide variety of series of main-chain LCPs and have studied how their chemical structures affect LC properties, including thermal transitions, nature of mesophase and chain orientation etc.

A thorough examination of these compositions, however, led us to realize that most LC polyesters were prepared from a dicarboxylic acid and a diol and, therefore, they contain a structural irregularity in ester groups. For example, if we examine the atomic sequence of the ester groups along a single polymer chain we note that the ester bonds alternate between two different structures, i.e. $-\overset{O}{\overset{\|}{C}}-O-$ and $-O-\overset{O}{\overset{\|}{C}}-$ as shown in *Scheme 1*.

Such an alternation in the atomic sequence of ester linkages is a direct consequence of the particular monomers utilized in polymerization. This analysis prompted us to design a new synthetic route for the preparation of LC polyesters in which the ester linkage is always in a fixed order either of $-\overset{O}{\overset{\|}{C}}-O-$ or of $-O-\overset{O}{\overset{\|}{C}}-$ and to make the following series of polyesters;



We tried to compare general properties including LC properties of these polymers with those having similar structures but having the ester groups of alternating atomic sequence as explained above. The polymers prepared in this study were characterized by elemental analysis, i.r. and n.m.r. spectroscopy, differential scanning calorimetry (d.s.c.), wide-angle X-ray diffraction (WAXD) and by observation of their behaviour on a polarizing microscope. It was reported recently by us that microchemical structure of LCPs such as comonomer sequence[18–20] and regioregularity[21,22] of substituents influences the thermal and crystalline properties of LCPs very strongly.

EXPERIMENTAL

Synthesis of monomers

All monomers were synthesized via the same route and therefore only the synthetic method of 4-{6-(*p*-acetoxyphenoxy)hexyloxy}benzoic acid ($x = 6$) is described as a representative example.

Ethyl 4-(6-bromohexyloxy)benzoate, **1**. A mixture of ethyl *p*-hydroxybenzoate (15.0 g; 9.03×10^{-2} mol), 1,6-dibromohexane (96.5 ml; *ca* 0.72 mol) and Na_2CO_3 (10.52 g; 9.93×10^{-2} mol) dissolved in 200 ml of *N,N*-dimethylformamide (DMF) was stirred under N_2 atmosphere for 10 h at 130°C. The mixture was then poured into 2 l of cold distilled water. The organic layer was separated and washed thoroughly with 0.1 M NaOH and distilled water followed by drying with anhydrous $MgSO_4$. Excess 1,6-dibromohexane was removed by

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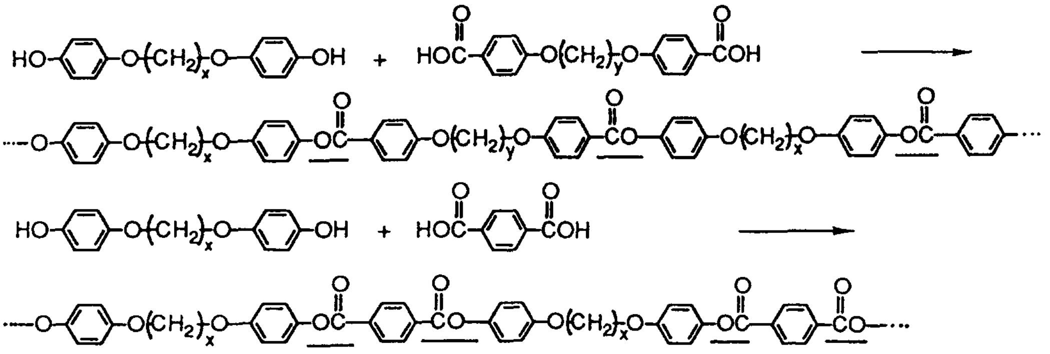


Scheme 1

distillation under a reduced pressure (*ca* 10 mmHg). The impure oily product mixture was recrystallized from H_2O/ethanol (v/v = 25/75). The product yield was 6.68 g (22.5%), m.p. 95°C. ^{1}H n.m.r. ($CDCl_3$); δ7.8 (d, 2H, Ar.), 6.8 (d, 2H, Ar.), 4.2 (m, 4H, OCH_2), 3.5 (t, 2H, CH_2Br), 1.6 (m, 11H, CH_2 and CH_3). I.r. (KBr); 3050 (Ar. C–H str.), 1717 (>C=O str.), 1150 cm^{-1} (ether CH_2–O– str.).

Ethyl 4-{6-(*p*-hydroxyphenoxy)hexyloxy}benzoate, **2**. Compound **1** (10.0 g; 3.04×10^{-2} mol) was dissolved in 250 ml of DMF containing 26.75 g (0.243 mol) of hydroquinone, 30.9 g (0.292 mol) of Na_2CO_3 and 3 g of $Na_2S_2O_4$. The mixture was stirred at 130°C under N_2 atmosphere for 20 h and then poured into 2 l of cold distilled water. The precipitate was washed with 0.1 M NaOH and then with distilled water. The crude product was recrystallized from CCl_4. The product yield was 5.99 g (55.0%), m.p. 89°C. ^{1}H n.m.r. ($CDCl_3$); δ7.8 (d, 2H, Ar.), δ6.9 (d, 2H, Ar.), δ6.7 (s, 4H, Ar.), 4.2 (t, 2H, CH_2O), 4.1 (t, 2H, CH_2O), 3.8 (quart, 2H, O–CH_2–CH_3), 1.5 (m, 11H, CH_2 and CH_3). I.r. (KBr); 3375 (O–H str.), 3050 (Ar. C–H, str.), 2910 (aliph. C–H, str.), 1700 (>C=O str.), 1600 (Ar. C=C str.), 1095 cm^{-1} (CH_2–O str.).

The compounds of $x = 3$ and 5 required a different purification method. The crude products were oily even after washing with 0.1 M NaOH and water. When we tried to recrystallize these oily products they did not precipitate out in solid form but exhibited phase separation from the solution. The oily layer was separated and again dissolved in CCl_4 and washed. When this procedure was repeated three to five times the products finally recrystallized out in solid form.

4-{6-(*p*-Hydroxyphenoxy)hexyloxy}benzoic acid, **3**. Compound **2** (4.00 g; 1.12×10^{-2} mol) was dissolved in 150 ml of 95% ethanol containing 0.893 g (2.23×10^{-2} mol) of NaOH and 0.5 g of $Na_2S_2O_4$. The mixture was refluxed for 8 h and then ethanol was removed using a rotatory evaporator. The residue was dissolved in 1 l of distilled water and the insoluble was filtered off. The filtrate was acidified with 0.2 M HCl. The precipitate formed was washed thoroughly with distilled water and recrystallized from ethanol/water (v/v = 15/85). The product yield was 2.50 g (67.7%), m.p. 190°C. ^{1}H n.m.r. (DMSO-d_6); δ7.8 (d, 2H, Ar.), 6.8 (m, 2H, Ar.), 6.6 (s, 4H, Ar.), 3.9 (t, 2H, OCH_2), 3.8 (t, 2H, OCH_2), 1.5 (m, 8H, CH_2). I.r. (KBr); 3400 (O–H, str.), 3050 (Ar. C–H str.), 2900 (aliph. C–H, str.), 1760 and 1710 (>C=O str.), 1160 and 1100 cm^{-1} (ether CH_2–O str.).

4-{6-(*p*-Acetoxyphenoxy)hexyloxy}benzoic acid, **4**. Compound **3** (2.10 g; 6.36 mmol) was dissolved in 50 ml of acetic anhydride and the solution was refluxed for 8 h. The mixture was mixed with 1 l of distilled water. The precipitated crude product was purified by recrystallization from ethanol/water (v/v = 1/1). The product yield was 1.52 g (64%), m.p. 140°C. ^{1}H n.m.r. (DMSO-d_6); 7.8 (d, 2H, Ar.), 7.0 (d, 2H, Ar.), 6.9 (s, 4H, Ar.), 4.0 (t, 2H, OCH_2), 3.8 (t, 2H, OCH_2), 2.2 (s, 3H, CH_3), 1.0 (m, 8H, CH_2). I.r. (KBr); 3450 (O–H str.), 3050 (Ar. C–H str.), 2920 (aliph. C–H str.), 1740 (>C=O str.), 1680 (>C=O str.), 1620 (Ar. C=C str.), 1160 (ether CH_2–O str.).

Synthesis of polymers

All the polymers were prepared by melt polymerization. Since the monomers have an acetoxy group at one end and an carboxylic acid group at the other, simple heating of the monomers at elevated temperatures generated acetic acid with the formation of polymers. As a representative example, polymerization of 4-{4-(*p*-acetoxyphenoxy)butoxy}benzoic acid ($x = 4$) is described.

The monomer (11.20 g) was placed in a glass-tube reactor and heated to 200°C and the melt was stirred for 1 h at that temperature under N_2 atmosphere. Then it was slowly heated to 260°C for 2 h. The pressure inside the reactor was reduced to 200 torr and the reaction was allowed to proceed further for 30 min. Finally, the reaction mixture was stirred at the temperature for 70 min under a pressure of 0.8 torr. The product obtained was ground and subjected to ethanol extraction for 3 days by a Soxhlet extractor. The polymer yield was 9.98 g (94%).

Characterization of polymers

I.r. and ^{1}H n.m.r. spectra of polymers were recorded on Perkin–Elmer 710B and Varian EM360A spectrometers, respectively. Solution viscosities were measured at 30°C for 0.2 g dl^{-1} solutions in a mixture of phenol/*p*-chlorophenol/1,1,2,2-tetrachloroethane (TCE) (w/w/w = 25/40/35). D.s.c. thermograms were obtained under N_2 atmosphere on a DuPont DSC 910 instrument with a heating rate of 10°C min^{-1}. The glass transition temperature, T_g, was taken as the temperature where initial slope change occurred on the d.s.c. thermogram. The temperatures where minima of endothermic peaks appeared were taken for melting transition, T_m, and isotropization temperatures, T_i. Temperature was calibrated against an indium reference.

Wide-angle X-ray diffractograms of powder samples were recorded on a Rigaku Flex D-Max IIIa instrument using nickel-filtered Cu Kα radiation (1.542 Å). Scanning speed was 4° min^{-1}. The approximate degree of crystallinity was estimated from the crystalline and the amorphous reflection areas in the diffractogram. Optical textures of polymer melts were observed on a polarizing microscope (Leitz, Ortholux) equipped with a Mettler FP-5 hot stage.

RESULTS AND DISCUSSION

Synthesis

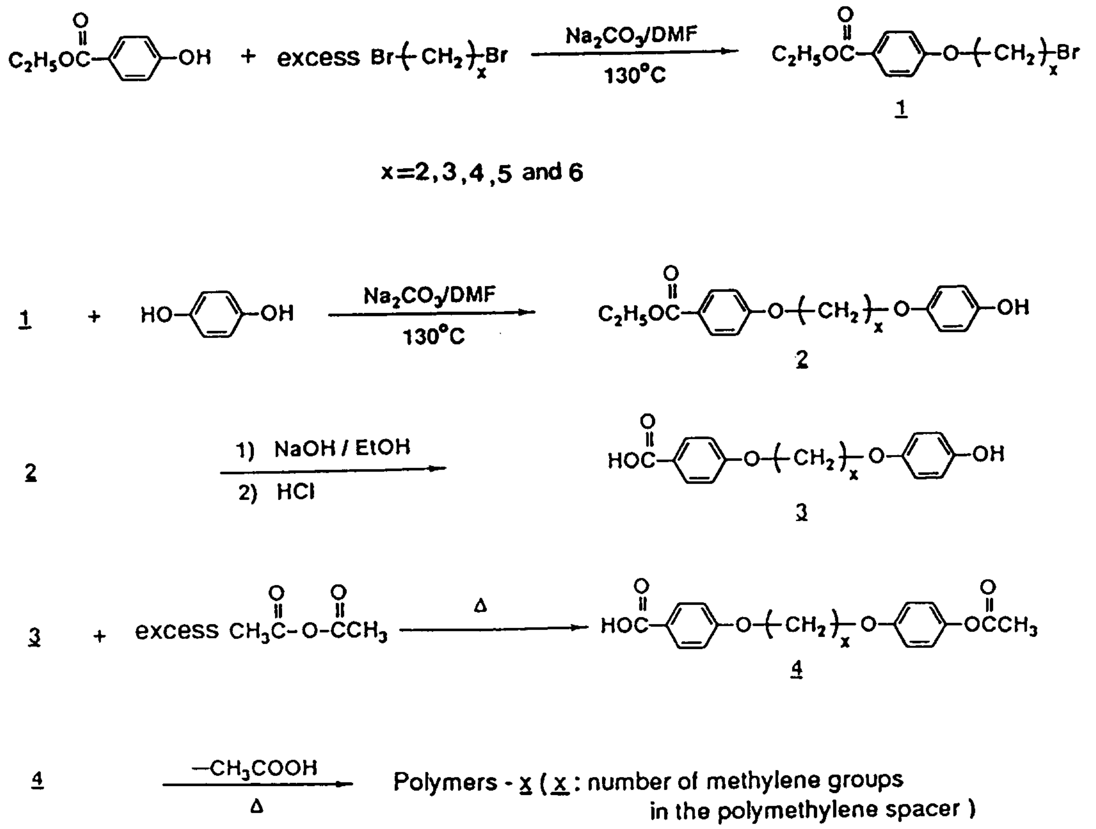
All the monomers and polymers were synthesized following the route shown in *Scheme 2.*

Tables 1 and *2* show the results of elemental analysis for the intermediate compounds and polymers, which agree very well with theoretical values. Their i.r. (*Figure 1*) and n.m.r. spectra (*Figure 2*) also show the spectral features anticipated for their structures. Polymer-2 which contains dimethylene spacer exhibits poor solubility in common solvents, while the rest are soluble in mixed solvents such as phenol/*p*-chlorophenol/TCE. Polymer-5 was found to be soluble also in a mixture of $CHCl_3/CF_3COOH$ (v/v = 1/1).

Properties of polymers

Solution viscosities, thermal transition temperatures and the approximate degrees of crystallinity of the polymers are summarized in *Table 3.* The approximate degrees of crystallinity of 'as-obtained' samples were estimated from the relative areas of crystalline and amorphous diffractions in the diffractograms.

Solution viscosity (0.48–1.64) values indicate that the molecular weights of the polymers are reasonably high. Glass transition temperature ranges from 58°C to 84°C



Scheme 2

Table 1 Results of elemental analyses and melting points of intermediates[a]

x	Compound 2			Compound 3			Compound 4		
	C (%)	H (%)	m.p. (°C)	C (%)	H (%)	m.p. (°C)	C (%)	H (%)	m.p. (°C)
2	67.09	6.03	112	65.97	5.65	220	64.77	5.06	203
	(67.54)	(6.00)		(65.69)	(5.15)		(64.55)	(5.10)	
3	67.54	6.00	65	65.85	5.46	185	65.48	5.84	136
	(68.34)	(6.37)		(66.66)	(5.59)		(65.45)	(5.49)	
4	69.31	6.82	102	66.63	6.12	204	66.26	5.88	178
	(69.07)	(6.71)		(67.54)	(6.00)		(66.27)	(5.85)	
5	69.41	7.28	78	67.69	6.52	125	67.26	6.69	80
	(69.75)	(7.02)		(68.34)	(6.37)		(67.03)	(6.19)	
6	69.82	7.33	89	68.31	6.80	190	66.94	6.25	140
	(70.37)	(7.31)		(69.08)	(6.71)		(67.73)	(6.50)	

[a] The values in parentheses are those calculated for molecular formulas

Table 2 Results of elemental analyses of polymers

	Elemental analysis[b] (wt%)	
Polymer-X[a]	Carbon	Hydrogen
Polymer-2	70.50 (70.31)	4.72 (4.72)
Polymer-3	71.73 (71.10)	5.44 (5.22)
Polymer-4	70.75 (71.82)	5.66 (5.67)
Polymer-5	71.97 (72.47)	6.17 (6.08)
Polymer-6	72.63 (73.06)	6.42 (6.45)

[a] The chain length of the flexible spacer

[b] Values in parentheses represent calculated values assuming that contribution by terminal groups can be neglected

Table 3 General properties of polymers

X[a]	η_{inh}[b]	Yield (wt%)	T_g (°C)	T_m (°C)	T_i (°C)	D.C. (%)[c]	LC
2	ins	94	84	352	397	52	Nematic
3	1.64	63	64	213		23	No
4	0.48	88	72	224	277	36	Nematic
5	1.36	78	58	180	227	28	Nematic
6	1.24	84	75	218	269	31	Nematic

[a] The number of methylene groups in the flexible spacer

[b] Inherent viscosity (η_{inh}) was measured on a $0.2\,g\,dl^{-1}$ solution in a mixture of phenol: *p*-chlorophenol: TCE = 25:40:35 (w/w/w) at 30±0.1°C

[c] The degree of crystallinity (before annealing)

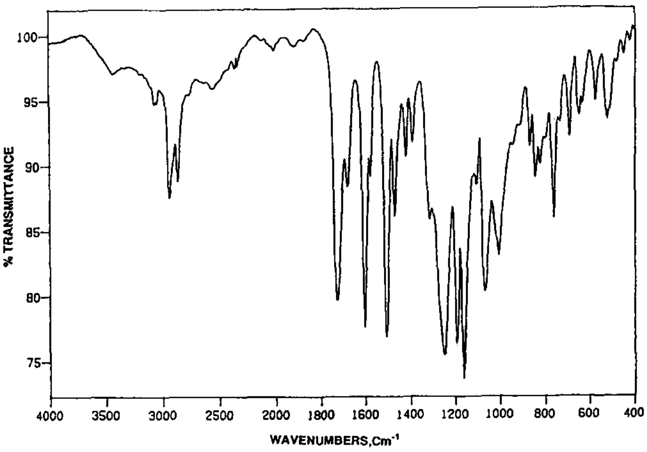


Figure 1 I.r. spectrum (KBr) of polymer-5

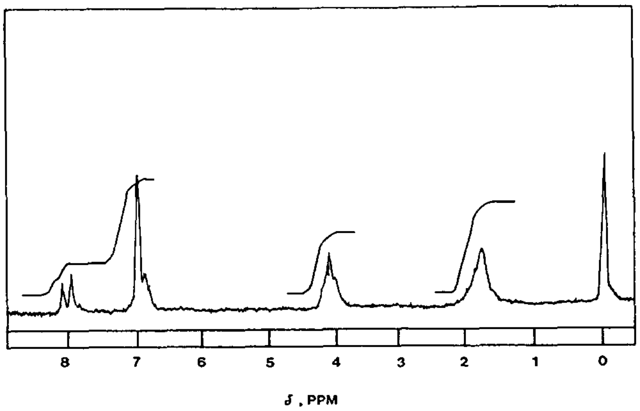


Figure 2 ^1H n.m.r. spectrum ($CDCl_3/CF_3COOH$) of polymer-5

depending on the length of spacer and whether the x value is odd or even. Difference in the molecular weights of the polymers also should influence the T_g values to a certain extent. All the polymers are semi-crystalline and exhibit melting transitions as demonstrated in their thermograms (*Figure 3*). In addition to T_g and T_m, with the exception of polymer-3, another endothermic transition appears in the higher-temperature region for each polymer. This transition was verified to be mesophase-to-isotropic transition, i.e. isotropization, by observing the optical textures of the melts through a polarizing microscope. Reverse transition could be observed on cooling the isotropic melts. In other words, these polymers are enantiotropically thermotropic with the only exception of polymer-3.

The T_m and T_i values of the present polymers are given in *Figure 4*. Even with the limited number of data points, it is clear that we observe the so-called odd–even effect[23–26] in T_m as well as in T_i. The values for the polymers having an even number of methylene units in the spacer are higher than those with an odd number of methylene groups. Similar observations were made for many other series of LCPs containing polymethylene spacers and many experimental as well as theoretical

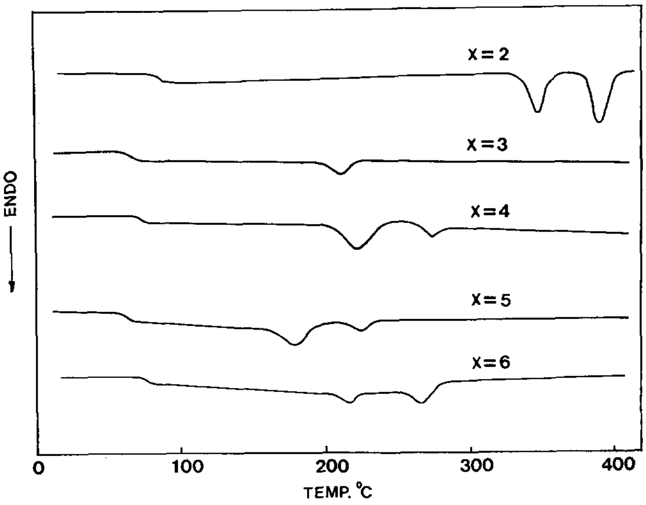


Figure 3 D.s.c. thermograms of polymers

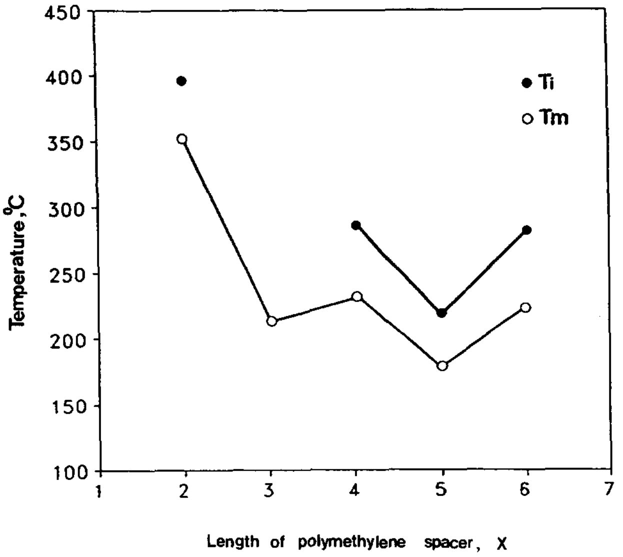
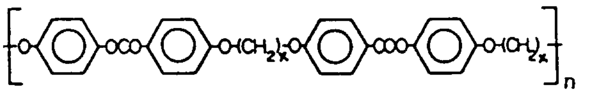


Figure 4 T_m and T_i values *versus* x

explanations[26–32] have been put forward for this phenomenon.

We tried to compare the T_m and T_i values of polymer-4, polymer-5 and polymer-6 with the corresponding values of the following polymers reported earlier by Strzelecki *et al.*[7]:



x	T_m (°C)	T_i (°C)
4	210	300
5	165	230
6	200	245

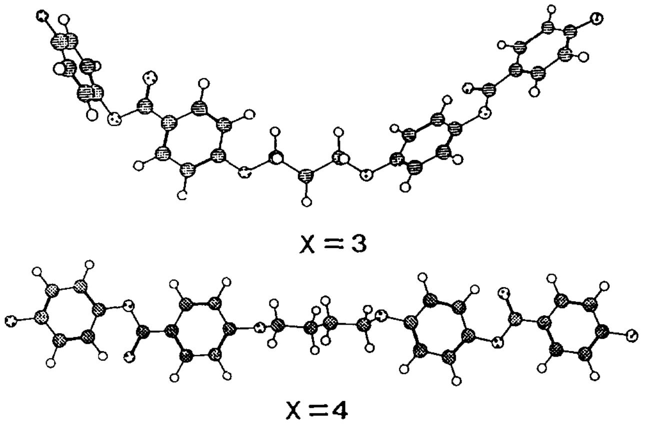


Figure 5 Molecular structures of polymer-3 and polymer-4

These polymers contain two ester linkages $(-\overset{O}{\overset{\|}{C}}O-$ and $-O-\overset{O}{\overset{\|}{C}})$ alternately along the chain, in contrast to the present polymers that contain only one mode of ester linkages. Surprisingly, the T_m values of the present polymers are consistently higher than those of the corresponding Strzelecki's polymers. Better structural regularity of the present polymers appears to be the reason for higher T_ms. Molecular weight differences of the polymers in the two series, however, may obscure our judgement. Strzelecki *et al.* did not give any information on the molecular weight of their polymers. For T_i values, however, we do not observe any general difference between these two series of polymers. Such a minor structural difference probably does not give rise to any significant difference in isotropization temperature.

According to optical textures, it was found that all the polymers, with the exception of polymer-3, form the nematic phase. *Figure 5* compares segmental molecular structures of polymer-3 and polymer-4. As can be seen, polymer-3, containing an odd number of methylene groups in the spacer, adopts a bent chain architecture whereas polymer-4 has a fairly linear molecular shape. This difference in chain shape is believed to be the major reason why polymer-4 is mesomorphic whereas polymer-3 is not. A question arises as to why polymer-5, which also contains an odd number of methylene groups in the spacer, is mesomorphic. This can be explained by the conjecture that the pentamethylene spacer is long enough or contains a sufficient number of methylene groups to make a conformational adjustment in mesomorphic melt

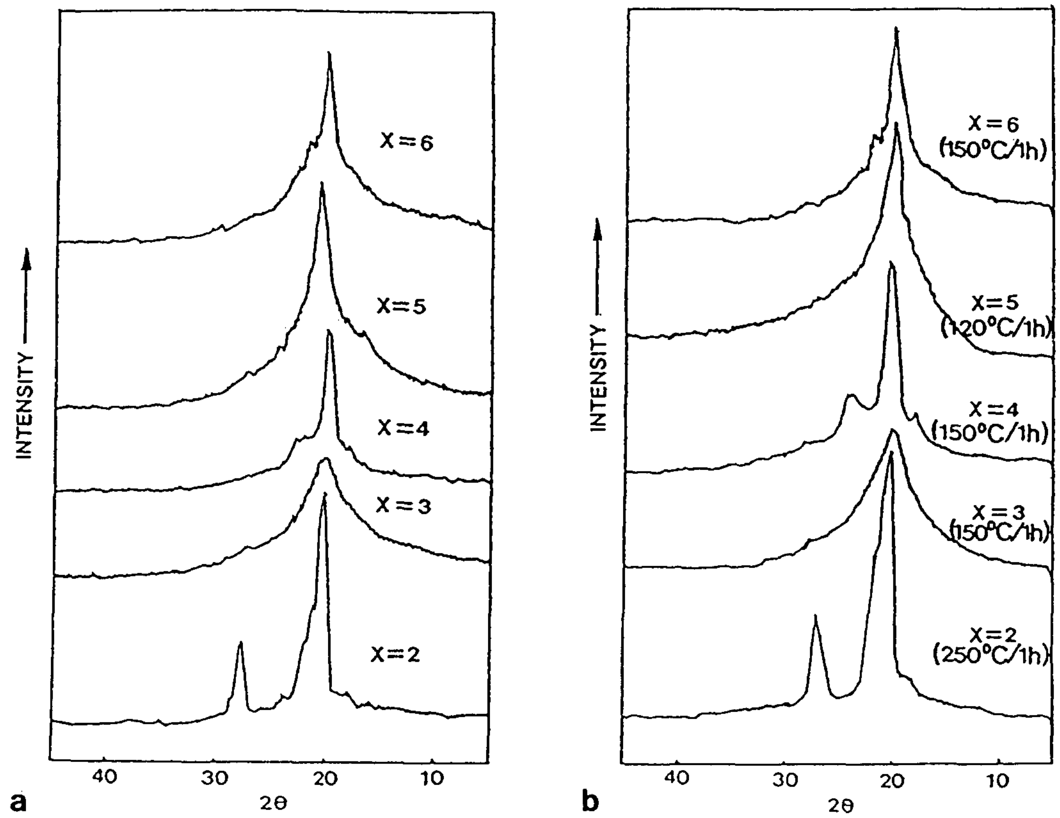


Figure 6 Wide-angle X-ray diffractograms of polymer (a) before and (b) after annealing

to attain a more or less linear molecular shape[33,34]. Some of the carbons in polymer-5 may have a *gauche* conformation, which is not possible in polymer-3 due to its insufficient number of carbon atoms in the spacer.

Wide-angle X-ray diffractograms for the 'as-obtained' samples are shown in *Figure 6*. With the exception of polymer-3, all the polymers exhibit rather sharp diffractions at about $2\theta = 20.6°$ (4.31 Å). Polymer-2 shows an additional sharp diffraction peak at $2\theta = 27.8°$ (3.21 Å). The approximate degree of crystallinity determined from the relative areas of crystalline and amorphous diffraction is the highest (52%) for polymer-2 and the lowest (23%) for polymer-3. In general, the degree of crystallinity is higher for the polymers having even-number x than those of odd-number x. An even number certainly favours easier molecular packing. Annealing increases the degree of crystallinity only slightly, as shown in the diffractograms of annealed samples in *Figure 6* compared with those of the 'as-obtained' ones.

CONCLUSIONS

A series of new LCPs having well defined chemical structures and consisting of dyad aromatic ester type mesogens and polymethylene spacers can be prepared via a multistep synthetic route. These polymers have only one mode of ester linkage and therefore can be taken as true homopolyesters based on their microchemical structure along the polymer chains. They are semicrystalline and reveal clear T_g, T_m and T_i transitions on d.s.c. analysis. The so-called odd–even effect was observed for T_m and T_i values. The T_g and T_m values for polymer-2 are 84°C and 352°C, respectively, which are significantly higher than those (69°C and 270°C, respectively) of poly(ethylene terephthalate). The presence of one more phenylene ring in the repeating unit causes such an increase in T_g and T_m due to the enhanced rigidity of the polymer chain. All the polymers, with the exception of that containing a trimethylene spacer, are enantiotropically thermotropic and form the nematic phase in melt.

ACKNOWLEDGEMENTS

This research was supported by the Korea Sanhak Foundation. Y.-I. Cho wishes to express his thanks to Lucky Ltd for the financial assistance given for his MS thesis.

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