Effect of methoxy substituent on mesophase-forming capacity of main-chain aromatic polyesters having polymethylene spacers

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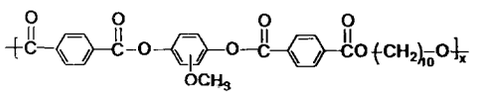
A new series of aromatic polyesters was prepared from bis(4-carboxy-2-methoxyphenoxy)alkanes and various aromatic diols such as hydroquinone, 4,4′-biphenol and bis(4-hydroxyphenyl)terephthalate; they were characterized especially for liquid crystalline properties. When the diol employed is hydroquinone and the alkylene spacer is hexa- or decamethylene, the polymer is not liquid crystalline. In contrast, the longer diols resulted in thermotropic compositions. Introduction of methoxy groups into the mesogenic units appeared to reduce the axial ratio of mesogenic groups, which caused depression in glass transition temperature, melting point and isotropization temperature of the polymers. Methoxy groups were also found to reduce the crystallizing tendency of polymers, probably due to their hindrance of chain and molecular packing in the solid.

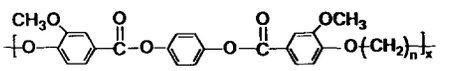
(Keywords: liquid crystalline polyesters; main chain; polymethylene spacer; methoxy substituent; nematic; axial ratio)

INTRODUCTION

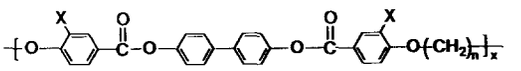
Since Roviello and Sirigu[1] reported the thermotropic behaviour of main-chain polymers with alternating mesogenic units and flexible spacers, there have been many studies[2-12] on the structure–property relation for this type of liquid crystalline polymer. Structural factors that have been examined to correlate with the properties of the polymers includes structure of mesogenic unit and flexible spacer, nature of substituent, presence of non-linear kinks along the chain, molecular weight, thermal history etc. Our earlier publication[3] describes how the van der Waals' radius of a substituent on the mesogenic unit influences the isotropization temperature, T_i, of a series of main-chain liquid crystalline polyesters containing polymethylene spacers. It was clearly demonstrated that the larger the substituent, the lower the isotropization temperature. In these polymers the substituents were located in the middle phenylene ring of the triad ester type mesogenic unit. Later, we found[13,14] that the presence of a methoxy group in the mesogenic unit reduces the polymer's ability to form a mesophase in melt and made it monotropic. Here again, the substituent is located at the middle ring of the mesogenic structure:



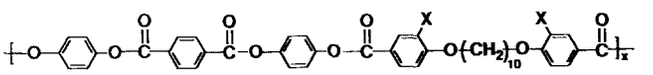
In order to investigate the substituent effect on the mesophase-forming ability of polymers with an alternating sequence of substituted mesogenic units and polymethylene spacers, we have synthesized the following series of polymers and studied their properties:



n = 6(P-1) and 10(P-2)



X = OCH_3 ; n = 6(P-3), 8(P-4), 10(P-5), and 12(P-6)
X = H ; n = 10(P-7)



X = OCH_3 ; (P-8) or H(P-9)

These polymers were characterized for their thermal behaviour, crystallinity and liquid crystallinity by differential scanning calorimetry (d.s.c.), polarizing microscopy and wide-angle X-ray diffractometry. The polymers P-1 to P-7 were prepared by high temperature transesterification in melt, whereas P-8 and P-9 were prepared in solution at 80°C using a condensing agent.

EXPERIMENTAL

Syntheses

α,ω-Bis(4-formyl-2-methoxyphenoxy)alkanes, **1**. Since the synthesis of compounds **1** required the same preparation method, only the synthetic procedure of 1,10-bis(4-formyl-2-methoxyphenoxy)decane is given as

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a representative example. Vanillin (136.9 g, 7.5×10^{-1} mol) and 1.0 g of $Na_2S_2O_4$ were dissolved in 600 ml of 95% ethanol. To this solution was added a KOH (36 g, 9.0×10^{-1} mol) solution in 400 ml of 95% ethanol. The whole solution was refluxed under N_2 atmosphere for 8 h. The reaction mixture was poured into a large excess of distilled water and the precipitate was washed with 0.1M NaOH, 0.1M HCl and finally with distilled water. The crude product was recrystallized from ethanol. The product yield was 108.7 g (82%), m.p. 100–101°C. ^{1}H n.m.r. (DMSO-d_6): δ9.6 (s, 2H, CHO), 6.7–7.5 (m, 6H, ar.), 4.0 (t, 4H, OCH_2), 3.9 (s, 6H, OCH_3), 1.2–1.8 (m, 16H, $-CH_2-$). I.r. (KBr): 3050 (ar., C–H str.), 2920 (aliph. C–H str.), 2850, 2780 (CHO C–H str.), 1725 (>C=O str.), 1230 cm^{-1} (ether CH_2–O str.).

α,ω-Bis(4-carboxy-2-methoxyphenoxy)alkanes, **2.** Only the synthetic procedure of 1,10-bis(4-carboxy-2-methoxyphenoxy)decane is given as a representative example. Compound **1** (10.0 g, 2.26×10^{-2} mol) and dibenzo-18-crown-6 (3.0 g) were dissolved in 100 ml of 1,2-dichloroethane (DCE). To this solution was added a solution of $KMnO_4$ (12.6 g, 8.0×10^{-2} mol) in 700 ml of distilled water. The mixture was refluxed for 10 h and filtered through a fritted glass filter. DCE was removed from the filtrate using a rotary evaporatory. The aqueous solution was acidified with 2M HCl. The precipitate was collected on a filter and then redissolved in 0.1M NaOH. The precipitate reobtained by acidification of the alkaline solution was thoroughly washed with distilled water. The crude product was recrystallized from 95% ethanol. The product yield was 6.43 g (60%), m.p. 215–216°C. For the synthesis of the hexane derivative, chloroform was employed in place of DCE. ^{1}H n.m.r. (DMSO-d_6): δ6.8–7.7 (m, 6H, ar.), 4.2 (t, 4H, OCH_2), 4.0 (s, 6H, OCH_3), 1.2–1.8 (m, 16H, $-CH_2-$). I.r. (KBr): 3500–2400 (acid O–H str.), 3050 (ar. C–H str.), 2930 (aliph. C–H str.), 1720 (>C=O str.), 1250 cm^{-1} (CH_2–O str.).

Polymers P-1 to P-7. All the polymers, with the exception of P-8 and P-9, were prepared by melt condensation. The preparation of P-3 is given as a representative example. 1,6-Bis(4-carboxy-2-methoxyphenoxy) hexane (1.50 g, 3.6 mmol), **2**, and 0.97 g (3.6 mmol) of 4,4′-diacetoxybiphenyl, **4**, were placed in a polymerization reactor. The reactor was immersed in a salt bath at 240°C. The melt was stirred at 240°C under N_2 atmosphere for 20 min, at 260°C for 40 min, and then at 280°C for 40 min. The pressure inside the reactor was reduced to 21.33 kPa and the melt was stirred for a further 40 min at 280°C. The temperature was finally raised to and maintained at 300°C for 20 min under a pressure of 106.6 Pa. The polymer thus obtained was dissolved in a mixture of $CHCl_3$/CF_3COOH (1/1 v/v) and precipitated in ethanol. The precipitate was washed with distilled water and was subjected to ethanol extraction for 3 days using a Soxhlet extractor. The polymer yield was 1.84 g (90%), m.p. 235°C. ^{1}H n.m.r. [CF_3COOD/$CDCl_3$ (1/1 v/v)]: δ6.8–8.1 (m, 14H, ar.), 4.2 (t, 4H, OCH_2), 4.0 (s, 6H, OCH_3), 1.3–2.2 (m, 8H, $-CH_2-$). I.r. (KBr): 3060 (ar. C–H str.), 2920 (aliph. C–H str.), 1720 (>C=O str.), 1250–1100 cm^{-1} (CH_2–O str.).

Polymers P-8 and P-9. These two polymers were prepared in solution from compound **2** or **5** and bis(4-hydroxyphenyl)terephthalate, **6**. Equimolar amounts of the two monomers were dissolved in pyridine containing thionyl chloride and reacted for 12 h at 80°C. The detailed polymerization procedure can be found elsewhere[15,16].

Characterization

The structures of polymers were confirmed by elemental analysis (Analytical Department of Korea Research Institute of Chemical Technology, Daejon, Korea), and by i.r. and ^{1}H n.m.r. spectroscopy. Solution viscosities of the polymers were measured at 30°C or 40°C using a Cannon-Ubbelohde type viscometer on 0.3 g dl^{-1} or 0.1 g dl^{-1} solution in a solvent. Thermal behaviour of the polymers was studied by d.s.c. on a duPont DSC 910 instrument with a heating rate of 10°C min^{-1} and also on a polarizing microscope (Leitz, Ortholux) equipped with a Mettler FP-5 hot stage. The glass transition temperature, T_g, was taken at the temperature where the initial slope change occurred on the d.s.c. thermogram. The temperatures where minima of endothermic peaks appeared were taken as the melting transition, T_m, and isotropization temperature, 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 degrees of crystallinity of the polymers were estimated from the crystalline and the amorphous reflection areas in the diffractograms.

RESULTS AND DISCUSSION

Syntheses of monomer and polymers

Figure 1 shows synthetic schemes for monomers and polymers.

Preparation of compounds **1** with $n=6$, 8 and 10 was described by Li and Chang[17]. We decided to use slightly different reaction conditions, but nonetheless, melting points of the compounds prepared by us are the same as those reported by Li and Chang. The product yields ranged from 80 to 87% after purification by recrystallization. Compound **1** with $n=12$ has not yet been reported and has a melting point of 97°C. It was purified by recrystallization from an ethanol/water

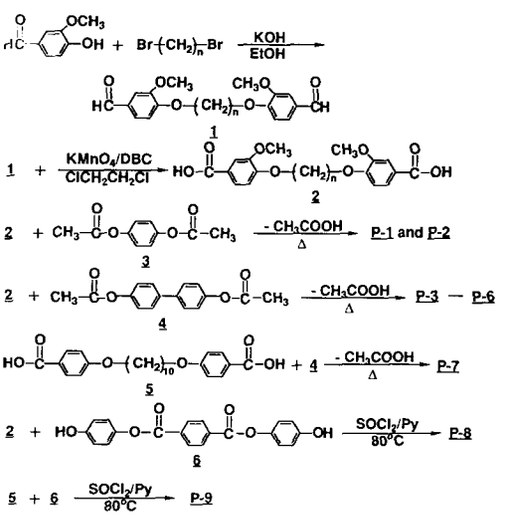


Figure 1 Synthetic schemes for the monomers and polymers

(8/2 v/v) mixture. *Table 1* summarizes the synthetic results of compounds **2**. We notice that melting point gradually decreases with increasing length, *n*, of the central polymethylene spacer. Results of elemental analyses of compounds **1** and **2** agree very well with those expected for the chemical formulae. Their structures were confirmed by their i.r. and ^{1}H n.m.r. spectra. Their high purity could be proved by thin layer chromatography.

Recovered polymer yields, solution viscosities and the results of elemental analysis are summarized in *Table 2*. Since monomer **6** (ref. 18) contains ester linkages, we had to use low temperature solution polymerization in the synthesis of polymers P-8 and P-9. The combination of thionyl chloride and pyridine was found to be satisfactory in our earlier works[15,16] for direct polycondensation between a dicarboxylic acid and a diol. For the other polymers, a common melt polymerization method was employed. As a representative example, i.r. and ^{1}H n.m.r. spectra of P-4 are given respectively in *Figures 2* and *3*. Spectral and elemental analyses agree very well with those expected from the chemical structures. The solution viscosity values (0.48–0.92) are reasonably high, and we did not try to increase the molecular weights of the polymers any further.

Thermal transitions, crystallization behaviour and liquid crystallinity

Thermal behaviour and liquid crystallinity of the polymers are summarized in *Table 3*. The glass transition temperature, T_g, varies widely and ranges from 36 to 91°C depending on the structure of the rigid unit and the length

Table 1 Synthetic results of α,ω-bis(4-carboxy-2-methoxyphenoxy)-alkanes, **2**

n	Yield (%)	M.p. (°C)	Elemental analysis (wt%)[a] C	H
6	67	232–233	63.13(63.16)	6.21(6.22)
8	68	228–230	64.57(64.57)	6.70(6.73)
10	60	215–216	65.69(65.82)	7.15(7.18)
12	63	194–196	66.82(66.93)	7.61(7.57)

[a] The values in parentheses are those calculated for chemical formulae

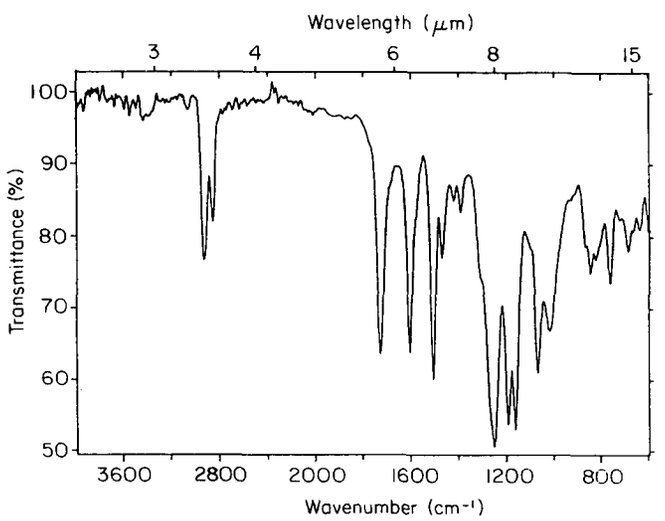


Figure 2 I.r. spectrum of P-4 (KBr)

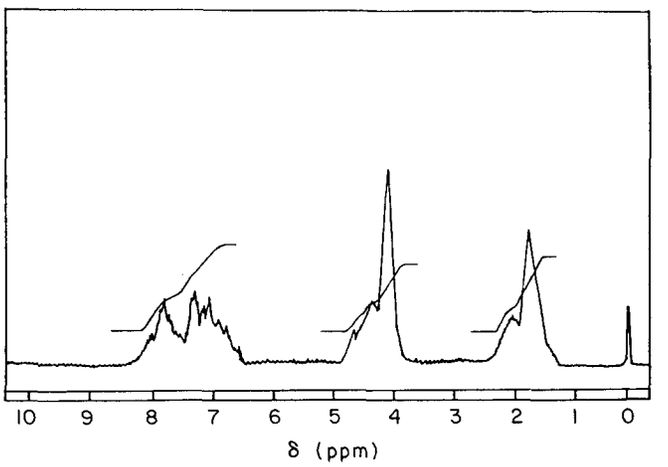


Figure 3 ^{1}H n.m.r. spectrum of P-4 ($CF_3COOD/CDCl_3$ (1/1 v/v))

Table 2 Polymer yields, solution viscosities and elemental analysis

Polymer	Yield (%)	η_{inh}	Elemental analysis (wt%)[a] C	H
P-1	92	0.56[b]	68.04(68.29)	5.63(5.69)
P-2	87	0.53[b]	70.01(70.07)	6.56(6.57)
P-3	90	0.78[b]	71.13(71.83)	5.69(5.63)
P-4	89	0.53[b]	71.52(72.48)	6.15(6.04)
P-5	90	0.85[b]	73.02(73.08)	6.44(6.41)
P-6	88	0.69[b]	73.77(73.62)	6.82(6.75)
P-7	92	0.92[b]	75.85(76.60)	6.72(6.38)
P-8	81	0.48[c]	70.12(70.05)	5.61(5.58)
P-9	89	0.62[c]	72.50(72.53)	5.43(5.49)

[a] The values in parentheses are those calculated for the chemical formulae of repeating units
[b] Measured at 30°C in the solution of 0.3 g dl^{-1} in a mixed solvent of phenol/1,1,2,2-tetrachloroethane = 60/40 (v/v)
[c] Measured at 40°C in the solution of 0.1 g dl^{-1} in a mixed solvent of *p*-chlorophenol/phenol/1,1,2,2-tetrachloroethane = 40/25/35 (w/w/w)

Table 3 Thermal behaviour, liquid crystallinity and degree of crystallinity (DC) of polymers

Polymer	T_g (°C)	T_m (°C)	T_i (°C)	DC[a] (%)	Liquid crystallinity
P-1	70	178	[b]	3(6)	no
P-2	36	139	[b]	2(12)	no
P-3	77	235	350	3(22)	nematic
P-4	63	232	334	20	nematic
P-5	59	229	265	19	nematic
P-6	47	217	243	18	nematic
P-7	70	268	388	51	nematic
P-8	84	263	dec.[c]	10(25)	nematic
P-9	91	304	380	43	nematic

[a] The values in parentheses are those for annealed samples. P-1 and P-2 were annealed for 30 min at 100°C; P-3 was annealed for 30 min at 120°C. The values for P-4 to P-7 and P-9 are given only for 'as-obtained' samples, because they changed very little even after annealing
[b] Not detected
[c] Decomposed before reaching T_i

of spacer. Comparison of T_g of P-1 (70°C) and P-2 (36°C) clearly demonstrates that the longer the spacer, the lower the T_g value becomes. The same trend is observed for the series P-3 to P-6. Among these, P-3 has the shortest spacer (hexamethylene group) and exhibits the highest T_g value of 77°C, whereas P-6 has the longest spacer (dodecamethylene group) and shows the lowest T_g of

47°C. When the central hydroquinone moiety of the rigid unit of P-1 is replaced with the longer 4,4'-biphenol moiety to make P-3, the T_g value increases from 70 to 77°C. Exactly the same tendency holds true in T_g values of P-2 and P-5; 36°C for the former compared to 59°C for the latter. Lengthening the rigid unit certainly increases the T_g value.

It is also observed that the presence of methoxy groups in the rigid units decreases T_g, which is most probably due to the increased free volume caused by the substituents. The T_g value of P-7, which does not contain substituents, is 70°C, which is substantially higher than that of P-5 (59°C) which has methoxy groups. Comparison of T_g values of P-8 and P-9 leads to the same conclusion. Polymers P-8 and P-9 exhibit relatively high T_gs compared with those of other polymers containing the same decamethylene spacers. Very long, aromatic ester type rigid units must be responsible for this observation.

Since all the present polymers are semicrystalline, they exhibit melting transitions. Their melting points, T_m, are included in *Table 3*. Their d.s.c. thermograms obtained under N_2 atmosphere at a heating rate of 10°C min^{-1} are shown in *Figure 4*. Dependence of T_m on polymer structure is very similar to that of T_g, but to a much greater extent; the presence of methoxy substituents in the rigid unit and longer polymethylene spacer reduce the T_m value, and the longer rigid unit, as in P-8 and P-9, causes an increase in T_m.

Figure 5 shows wide-angle X-ray diffractograms of the polymers. The P-7 and P-9 polymers, neither of which contain methoxy substituents, exhibit the sharpest and strongest diffraction patterns, implying a relatively high degree of crystallinity (*Table 3*). However, the diffractograms of the methoxy substituted polymers, P-5 and P-8, indicate that their degrees of crystallinity are much lower. It is our conjecture that the methoxy substituents hinder chain and molecular packing in the solid, resulting in the decreased crystallizing tendency of the substituted polymers.

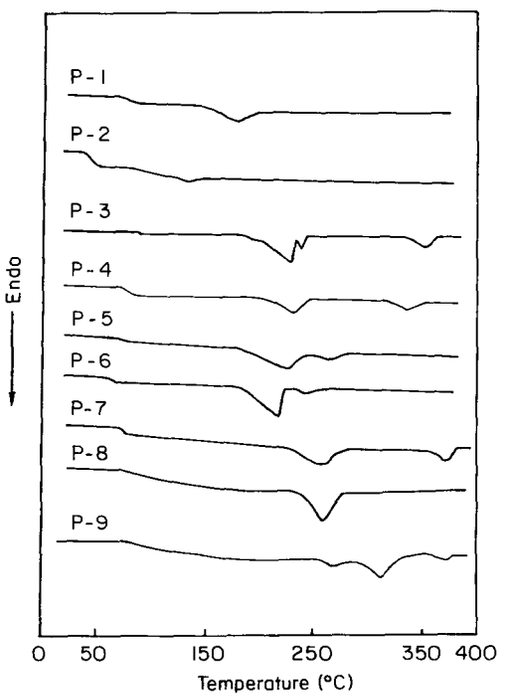


Figure 4 D.s.c. thermograms of polymers obtained under N_2 atmosphere at a heating rate of 10°C min^{-1}

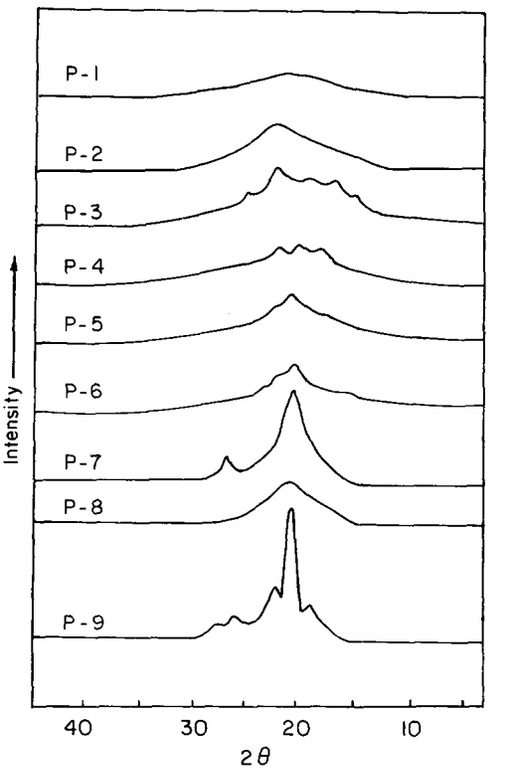
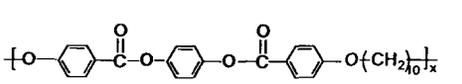


Figure 5 Wide-angle X-ray diffractograms of annealed polymers

Another observation made in the present series is that, in general, the crystallization tendency of the polymers increases with increasing length of the mesogenic unit. For example, the degree of crystallinity decreases in the order of P-8 > P-5 > P-2 (*Table 3*) for annealed samples. The degree of crystallinity of P-5 changed very little even after annealing at 50°C. Certainly a longer rigid unit in the repeating unit facilitates chain packing, leading to the higher degree of crystallization.

With the exception of P-1 and P-2, the present polymers form mesophases in the melt. According to a molecular model, the axial ratio (L/D) of the rigid unit of P-1 and P-2 polymers is about 2.1 when only the rigid structure extended to the two terminal phenylene rings in the mesogenic units is taken into consideration. We reported previously[19] that a similar polymer to P-2, which does not have methoxy substituents, is able to form a nematic melt.



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The approximate axial ratio of this polymer's mesogenic unit is 2.85, which is substantially greater than that of P-1 and P-2. Therefore, the reduction of the axial ratio by the presence of the two methoxy groups in the mesogenic units appears to be sufficient to deprive the P-1 and P-2 polymers of the ability to form a liquid crystalline phase in the molten state.

Interestingly, the monotropic polymer described in the Introduction consists of rigid units whose axial ratio (~2.6) lies in between those discussed above. Such an

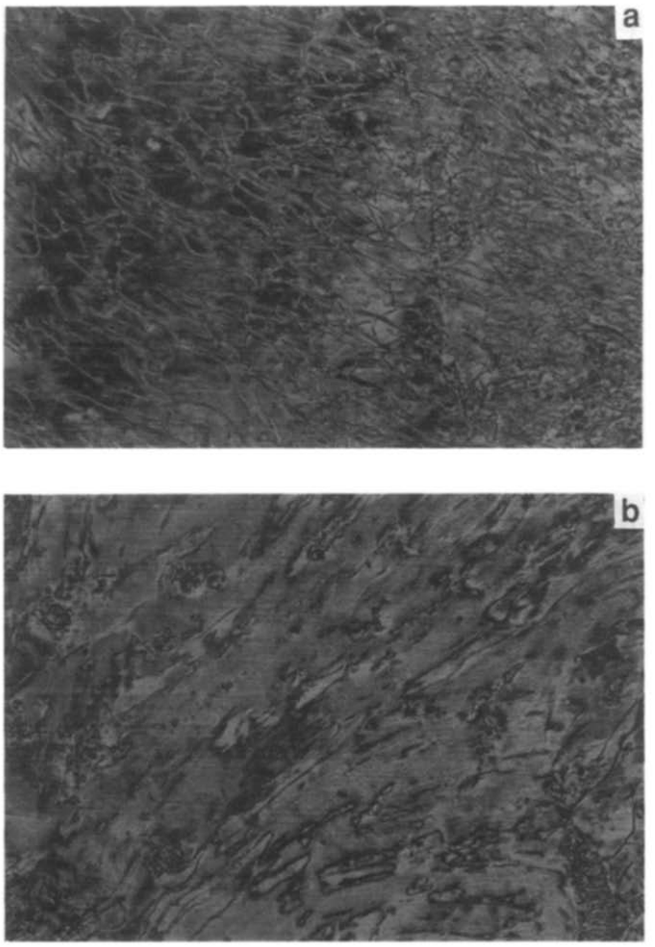
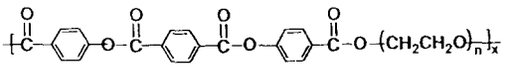


Figure 6 Photomicrographs of (a) P-3 and (b) P-6 taken at 280 and 229°C, respectively (magnification 133 ×)

analysis implies that the methoxy substituent controls the mesophase-forming ability of those polymers mainly by changing the breadth, and thus the L/D ratio of their rigid units. In other words, the steric effect is dominant over the polar effect. The mesogenic units of the other polymers, regardless of whether or not they contain methoxy substituents, are long enough ($L/D > 3.0$) and therefore they are able to form nematic melts. *Figure 6* shows photomicrographs of the optical textures of P-3 and P-6. They reveal typical nematic textures[20].

The isotropization temperature, T_i, of the present polymers also exhibits a strong dependence on structure; longer mesogenic unit and shorter spacer result in higher T_i, and smaller axial ratio of the mesogenic unit results in lower T_i. Another important phenomenon observed is that the mesophase temperature range, i.e. $\Delta T = T_i - T_m$, narrows as the length of the spacer increases. For example, ΔT for P-3, with hexamethylene spacer, is 115°C, whereas ΔT for P-6, with dodecamethylene spacer, is only 26°C. This is due to the fact that the decrease in T_i (350°C for P-3 vs. 243°C for P-6) with increasing spacer length far surpasses the decrease in T_m (235°C for P-3 vs. 217°C for P-6). Certainly longer spacers destabilize the mesophase due to their more flexible nature, arising from higher conformational freedom around the single bonds that they contain. In relation to this Galli *et al.*[21] observed that the polymers with n up to 8.7 were liquid crystalline whereas those with n greater than 13 were not.



We observed similar phenomena[22] for related model compounds.

CONCLUSIONS

A new series of polyesters with an alternating sequence of aromatic ester type mesogenic units, containing two methoxy substituted phenylene rings bracketing unsubstituted *p*-phenylene or related structures, and polymethylene spacers could be prepared via multistep synthetic routes. The length of mesogenic units was varied to examine how it influences the mesophase-forming ability of the polymers. Polymers P-1 and P-2 containing rigid units ($L/D \simeq 2.1$) of triad aromatic esters having methoxy substituents are not liquid crystalline, whereas those (P-3–P-6) containing 4,4′-biphenylene mesogenic units of $L/D \simeq 3.2$ are mesomorphic. The monotropic polymer that was mentioned in the Introduction has an axial ratio of about 2.6. Although the nature and length of spacers must also play an important role in controlling the mesophase-forming ability of a polymer, it is clear from the present study that the greater the axial ratio of mesogens, the higher the probability of a polymer forming the liquid crystalline phase. The introduction of methoxy groups at the terminal parts of the mesogenic units results in a substantial increase in breadth of the rigid unit and leads to a reduction in a polymer's ability to form a mesophase.

ACKNOWLEDGEMENT

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