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Liquid crystalline homopolyesters having main chain calamitic mesogens and one or two side chain azobenzene moieties in the repeat units

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Combined semi-rigid homopolyesters, containing both main chain calamitic mesogens and one or two side chain azobenzene units separated by aliphatic (hexamethylene, octamethylene and decamethylene) chains in the polymer repeat units, were prepared and their liquid crystalline properties characterized. Polyesters having two side chain azobenzene units and a main chain biphenyl moiety showed a higher ordered smectic B or smectic F phase, whereas the other polymers containing a main chain 2,5-diphenyl-1,3,4-thiadiazole unit and one or two side chain methoxyazobenzene units formed a smectic C phase despite the presence of different mesogens in the main and side chains. This is probably due to the compact molecular chain-packing and intra- and intermolecular interactions between the polymer backbones and the two azobenzene units.

1. Introduction

Side chain or combined-type polymers containing azobenzene moieties have received much attention not only as thermotropic liquid crystalline (LC) polymers, but also as materials for optical applications [1–13]. A large body of research concerning the chemical and physical properties of side chain and combined-type azobenzene-containing LC polymers has also been reported [14, 15]. It has been shown that combined-type polymalonates composed of a main chain biphenyl and side chain methoxyazobenzene units form higher ordered smectic phases in addition to smectic A and C phases [16, 17]. Copolymers composed of monomer units with specific interactions, such as electron donor–acceptor interactions, have been found to show smectic phases [18, 19].

In previous work we investigated the relationships between polymer structures and the LC and optical properties in combined-type homo- and copolyisophthalates having electron-withdrawing nitro and/or electron-donating methoxyazobenzene moieties in the side chain, and calamitic mesogens such as biphenyl units in the main chain [20, 21]. The homo- and copolymers showed smectic (B, C or E) phases, although specific interactions such as electron donor–acceptor interactions played no role in the formation or stabilization of the smectic phases. Among these, the homopolymers composed of side chain nitroazobenzene units and main chain biphenyl units formed the highly ordered crystal E phase, whereas the others showed smectic C or B phases. The polyesters showed no fluorescent properties, either in solution or as films, due to intra- and inter-molecular quenching.

We have also prepared a series of semi-rigid polyesters containing various aromatic derivatives of 1,3,4-thiadiazole (biphenyl [22, 23], terphenyl [24, 25], quarterphenyl [26, 27], quinquephenyl [28] and distyrylbezene analogues [29]) in the main chain, and discovered that they show thermotropic LC properties arising from the good mesogenicity of aromatic 1,3,4-thiadiazole units, even though they have bent molecular structures (160°).

In the present work, we report the preparation and LC properties of two kinds of combined-type polyesters: firstly, **3a**–**f** (see scheme 1), containing a main chain calamitic mesogen, and specifically, a terphenyl analogue of 1,3,4-thiadiazole, 2,5-diphenyl-1,3,4-thiadiazole (DPTD), and one side chain azobenzene unit separated by an aliphatic (hexamethylene, octamethylene and decamethylene) chain in the polymer repeat units; and secondly polymers **7a**,**b** (see schemes 2 and 3) having DPTD or biphenyl in the main chain, and two side chain azobenzene units and an octamethylene chain in the polymer repeat units. Their LC properties were compared with those of our previously reported

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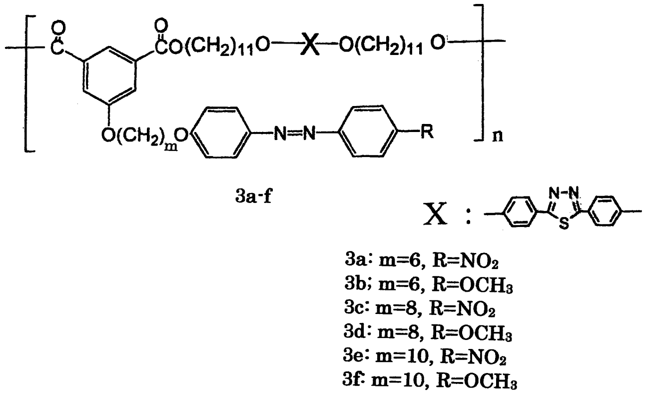
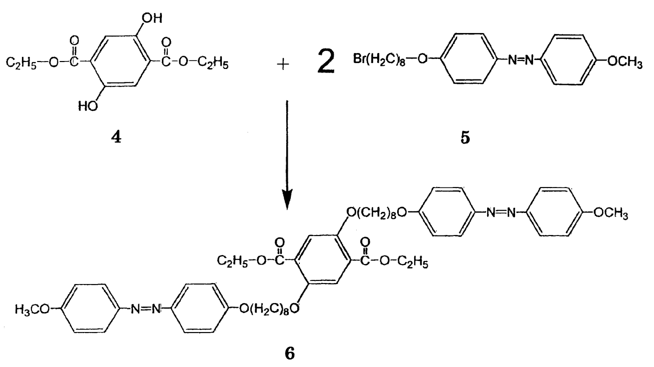
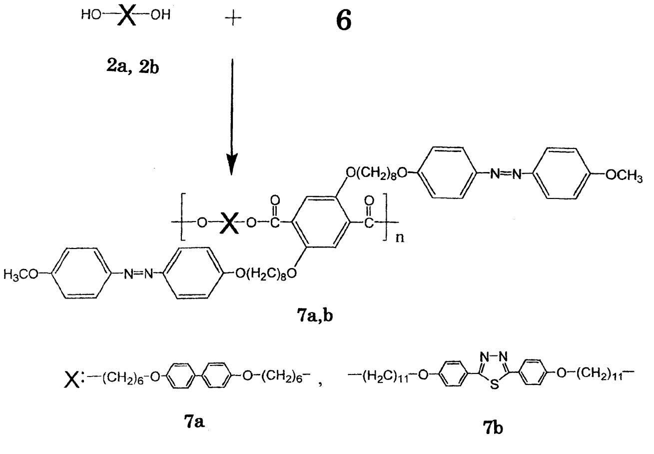


Scheme 1. Structures of polymers **3a**–**f**.



Scheme 2. Synthesis of monomer **6**.



Scheme 3. Synthesis of polymers **7a**,**b**.

combined-type polyesters [20, 21]. It is of interest to establish how the presence of one or two azobenzene units attached by the aliphatic chains in the side chain will affect the LC properties of combined-type polyesters containing the main chain calamitic mesogens.

2. Experimental

2.1. *Characterization*

FTIR and ^{1}H NMR spectra were recorded as described previously [20–29]. DSC measurements, optical texture observations, X-ray diffraction (XRD) and molecular weight measurements by size exclusion chromatography (SEC) were carried out according to previously published procedures [20–29].

2.2. *Materials*

6,6′-(4,4′-Biphenylenedioxy)dihexanol **2a** [30], 2,5-bis[4-(11-hydroxyundecyloxy)phenyl]-1,3,4-thiadiazole **2b** [24], diethyl 5-{6-[4-(4-nitrophenylazo)phenoxy]hexyloxy}isophthalate **1a** [20], diethyl 5-{8-[4-(4-nitrophenylazo)phenoxy]octyloxy}isophthalate **1b** [21], diethyl 5-{10-[4-(4-nitrophenylazo)phenoxy]decyloxy}isophthalate **1c** [20], diethyl 5-{6-[4-(4-methoxyphenylazo)phenoxy]hexyloxy}isophthalate **1d** [20], diethyl 5-{8-[4-(4-methoxyphenylazo)phenoxy]octyloxy}isophthalate **1e** [21], diethyl 5-{10-[4-(4-methoxyphenylazo)phenoxy]decyloxy}isophthalate **1f** [20] and 1-methoxy-4-[4-(8-bromooctyloxy)phenylazo]benzene **5** [21] were prepared by methods described in the literature. Diethyl 2,5-dihydroxyterephthalate **4** was used as received. Acetone and 1-chloronaphthalene were purified by standard methods.

2.3. *Synthesis of diethyl 2,5-bis{8-[4-(4-methoxyphenylazo)phenoxy]octyloxy}terephthalate* **6** *(Scheme 2)*

Diethyl 2,5-dihydroxyterephthalate **4** (6.0 mmol, 1.53 g) and 1-methoxy-4-[4-(8-bromooctyloxy)phenylazo]benzene **5** (1.2 mmol, 5.01 g) were heated under reflux in acetone (40 ml) in the presence of potassium carbonate (1.2 mmmol, 1.66 g) under nitrogen for 24 h. The reaction mixture was cooled to room temperature and the separated solid removed by filtration. The filtrate was evaporated to dryness under reduced pressure to give solid **6**, which was recrystallized from acetone three times and dried at 60°C *in vacuo* for one day; yield 61%, 82.7°C Cr 102.3°C N 120.0°C. Elemental analysis for $C_{54}H_{66}N_4O_{10}$ (931.2): calcd C 69.64, H 7.16, N 6.02; found C 69.13, H 6.92, N 6.12%. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.84$–7.89 (m, 8H, ar CH), 7.35 (s, 2H, ar CH), 6.96–7.02 (m, 8H, ar CH), 4.37 (q, 4H, $-C(O)OCH_2-$), 4.01–4.06 (t, 8H, $-OCH_2-$), 3.89 (s, 6H, $-OCH_3$), 1.36–1.92 (m, 24H, $-CH_2-$), 1.25 ppm(t, 6H, $-CH_3$). FTIR (KBr disk): $\nu = 2938$, 2854 (CH stretching), 1730, 1699 (C=O), 1600, 1580 (C=C, N=N), 1500, 1245 (C–O–C) cm^{-1}.

2.4. *Polymer synthesis*

2.4.1. *Synthesis of polyisophthalates **3a–f***

The preparative method for polyester **3c** is described. A mixture of isophthalate monomer **1c** (0.5 mmol, 0.296 g) and diol **2b** (0.5 mmol, 0.306 g) was stirred at 180–190°C for 2 h in the presence of zinc acetate (5 mg) as a catalyst, under a nitrogen atmosphere. The reaction temperature was raised to 200–210°C over 30 min and then the reaction mixture was held at 200–210°C for 30 min at 21 Torr. The reaction mixture was finally held at the same temperature for 1.5 h below 1 Torr. After the polymerization, the solid obtained was dissolved in chloroform and the solution poured into ethanol to reprecipitate the polyester. The precipitated polymer **3c** was collected by filtration, washed thoroughly with water and boiling methanol three times, then dried at 60°C for one day *in vacuo*; yield 68%. ^{1}H NMR spectra (270 MHz, $CDCl_3$): $\delta = 8.33$–8.37 (d, 2H, ar CH), 8.26 (s, 1H, ar CH), 7.87–7.96 (m, 8H, ar CH), 7.74 (d, 2H, ar CH), 6.94–6.99 (m, 6H, ar CH), 4.30–4.35 (m, 4H, $-C(O)OCH_2-$), 3.99–4.04 (m, 8H, $-OCH_2-$), 1.31–1.80 ppm (m, 48H, $-CH_2-$). FTIR (KBr disk): $\nu = 2925, 2853$ (CH stretching), 1721 (ester C=O), 1604, 1580, (C=C and N=N), 1521, 1340 (NO_2), 1253 (C–O–C) cm^{-1}.

2.4.2. *Synthesis of polyterephthalates **7a,b***

The synthetic method for polyester **7b** is described. Diethyl terephthalate derivative **6** (0.4 mmol, 0.37 g) and diol **2b** (0.4 mmol, 2.44 g) were stirred at 150–160°C for 12 h in 1-chloronaphthalene (1.5 ml) in the presence of di-*n*-butyltin oxide (5 mg) in nitrogen. The byproduct, ethanol, was removed every 1 h. After polycondensation, the reaction mixture was dissolved in chloroform; this solution was poured into methanol to reprecipitate the product, which was collected by filtration and washed thoroughly with water and boiling methanol three times. The resulting polymer **7b** was dried at 60°C for 24 h under reduced pressure; yield 43%. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.85$–7.59, 7.35, 6.97–7.00 (m, 26H, ar CH), 4.30–4.38 (m, 4H, $-C(O)OCH_2-$), 4.01–4.05 (m, 12H.$-OCH_2-$), 3.89 (s, 6H, $-OCH_3$), 1.31–1.90 ppm (m, 60H, $-CH_2-$). FTIR (KBr disk): $\nu = 2920$, 2850 (CH stretching), 1730, 1699 (C=O), 1601, 1581 (C=C and N=N), 1250 (C–O–C) cm^{-1}.

3. Results and discussion

3.1. *Polymer syntheses*

Polyesters **3a–f** and **7a**,**b** having one or two side chain azobenzene moieties in the polymer repeat unit, except for the previously reported polyester **3a** [20], were preprared from the diethyl isophthalates **1b–f** with one azobenzene unit or terephthalate derivative **6** bearing two methoxyazobenzene units by melt or high temperature solution polycondensation with a dioxydiundecanol of DPTD **2a** or a dioxydihexanol of biphenyl **2b**. The terephthalate monomer **6** was prepared from diethyl 2,4-dihydroxyterephthalate **4** and monobromo compound **5** of methoxyazobenzene by the Williamson reaction in 61% yield; this showed an enantiotropic nematic phase in the range 102.3–120.0°C (schlieren texture) as given in §2.4, and an X-ray pattern of a sample quenched from the LC state showed a broad reflection at around $2\theta = 22°$. The assigned structures of polyesters **3a–f** and **7a**,**b** were characterized by ^{1}H NMR and FTIR spectroscopies, and elemental analysis. Preparative data of the polymers **3a–f** and **7a**,**b** are listed in table 1. The polyisophthalates **3a–f** were obtained in yields of 50–90%, and the polyterephthalates **7a**,**b** in yields of 40–43%, because of their low molecular masses. The number-average molecular weights (M_n) and molecular mass distributions (M_w/M_n) of the polyesters are 2 500–22 500 and 1.24–4.18, respectively. Some of the polyesters containing the side chain methoxyazobenzene units were obtained in low yields and had low molecular masses, probably because of steric hindrance and depoly*trans*-esterification during the polycondensation.

The ^{1}H NMR spectra of polymers **3a–f** and **7a**,**b** in $CDCl_3$ showed proton signals of the aromatic rings at 8.37–6.91 ppm, $-C(O)OCH_2-$ at 4.45–4.30 ppm, $-OCH_3$ (in polymers **3b**, **3d**, **3f** and **7a**,**b**) at around 3.88 ppm, $-OCH_2-$ near 4.00 ppm and aliphatic chains at 1.92–1.36 ppm. No $-OCH_3$ group proton signals were detected in the polyesters **3a**, **3c** and **3e** which have the nitro group. Measurements of molecular mass for the polyesters **3a–f** and **7a**,**b** by ^{1}H NMR spectra could not be carried out, because the proton signals for terminal ethyl ester and aliphatic hydroxy groups overlap with those for the methylene chains of the polymer main chains. The ^{1}H NMR spectrum for polymer **3b** in $CDCl_3$ is presented in figure 1.

The FTIR spectra of polyesters **3a–f** and **7a**,**b** displayed absorption bands due to CH_2 stretching at 2940–2850 cm^{-1}, ester C=O at 1730–1699 cm^{-1}, C=C and N=N at 1605–1580 cm^{-1}, the nitro group (in polymers **3a**, **3c**, **3e** and **7b**) at around 1520 and 1340 cm^{-1}, and C–O–C near 1250 cm^{-1}. The elemental analysis data for carbon of some of the polymers in table 1 did not agree well with calculated values, probably due to their low molecular masses, but the values for hydrogen and nitrogen are in agreement with the calculated values within experimental error. These data confirm the proposed structures of polyesters **3a–f** and **7a**,**b**.

Table 1. Synthetic data for polyesters **3a**–**f** and **7a**,**b**.

Polymer	Yield/%	M_n[a]	M_w/M_n[a]	Formula (Mol. mass)	Elemental analysis C/%	H/%	N/%
3a[b]	85	22200	2.85	$(C_{62}H_{75}N_5O_{10}S)_n$	Calc. 68.80	6.98	6.47
				$(1082.4)_n$	Found 68.59	6.78	6.44
3b	52	4100	1.99	$(C_{63}H_{78}N_4O_9S)_n$	Calc. 70.89	7.37	5.25
				$(1067.4)_n$	Found 69.66	6.98	5.31
3c	68	5100	3.40	$(C_{64}H_{79}N_5O_{10}S)_n$	Calc. 69.23	7.17	6.31
				$(1110.4)_n$	Found 67.98	6.82	6.21
3d	50	3200	2.09	$(C_{65}H_{82}N_4O_9S)_n$	Calc. 71.27	7.55	5.11
				$(1095.5)_n$	Found 69.47	7.19	5.06
3e	90	15600	4.18	$(C_{66}H_{83}N_5O_{10}S)_n$	Calc. 69.63	7.35	6.15
				$(1138.5)_n$	Found 68.92	7.25	5.27
3f	56	2500	2.00	$(C_{67}H_{86}N_4O_9S)_n$	Calc. 71.63	7.72	4.99
				$(1123.5)_n$	Found 70.62	7.57	4.93
7a	40	6700	2.05	$(C_{74}H_{88}N_4O_{12})_n$	Calc. 72.51	7.25	4.57
				$(1225.7)_n$	Found 71.50	7.14	3.62
7b	43	3800	1.24	$(C_{86}H_{108}N_6O_{12}S)_n$	Calc. 71.23	7.52	5.80
				$(1450.1)_n$	Found 67.57	7.43	5.32

[a] M_n = number average molecular mass; M_w/M_n = molecular mass distribution. Measured in chloroform using polystyrene as a standard at room temperature.

[b] Previously reported data [20].

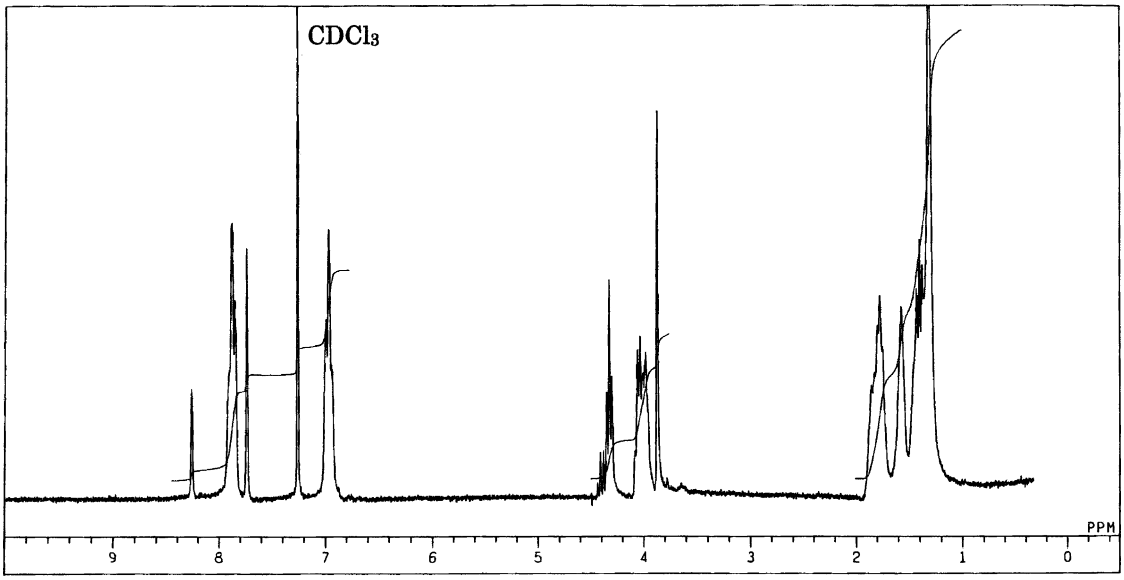


Figure 1. ^1H NMR spectrum of polymer **3b** in $CDCl_3$.

3.2. *Liquid crystal behaviour*

In our previous papers [20, 21], combined-type homo- and copolyisophthalates composed of calamitic mesogens in the main chain and azobenzene units in the side chain were found to form smectic (B, C or E) phases. Among these, the homopolymers having both the main chain biphenyl and the side chain nitroazobenzene units showed the highly ordered crystal E phase. Most of the other homo- and copolymers formed the ordered smectic B phase despite the coexistence of different mesogens in the main and side chains. Only homopolyesters containing main chain biphenyl and side chain methoxyazobenzene moieties attached by hexa- or octamethylene chains formed smectic C phases. In this work the LC properties of the combined-type homopolyesters **3a**–**f** composed of DPTD and nitro- or methoxyazobenzene units attached by three different aliphatic (hexamethylene, octamethylene and decamethylene) chains, and polyesters **7a**,**b** having two methoxyazobenzene units in the polymer repeat units are discussed.

The DSC curves of the polyesters **3a**,**b** for the first and second heating scans, show two endotherms associated with the melting transition (T_m) at 96°C and 97°C and isotropization (T_i) at 206°C and 156°C, together with glass transitions (T_g) at 40°C and 47°C, respectively. Polymers **3e**,**f** containing the nitro- and methoxyazobenzene units and a decamethylene chain, and **3c** containing nitroazobenzene and an octamethylene chain, showed one clearing endothermic peak T_i at 196, 140 and 178°C, and a T_g at 42, 47 and 43°C, respectively, in the DSC curves during heating. Only the DSC curve of polymer **3d** containing the methoxyazobenzene unit and the octamethylene chain showed multiple transitions specifically three endotherms, T_i at 144°C, T_m at 109°C and a solid-to-solid transition (T_{Cr}) at 92°C, and two exotherms due to crystallization (T_c) at 77 and 98°C in addition to T_g at 43°C on heating. The temperature ranges of the smectic phases (ΔT) were 35–145°C and had a tendency to be broader in the polyesters **3a**, **3c** and **3e**.

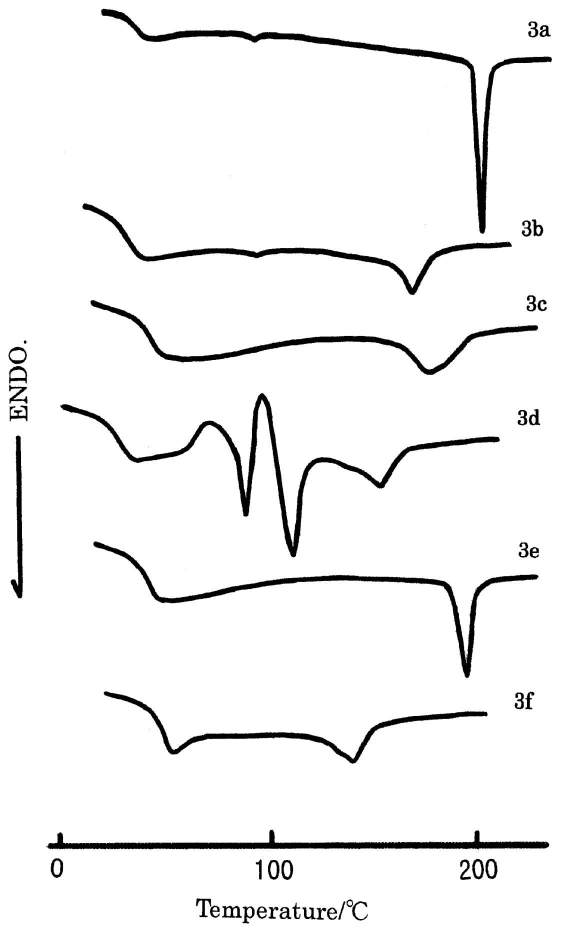


Figure 2. DSC curves for polymers **3a**–**f** on second heating.

The DSC curves of polymers **3a**–**f** on second heating are shown in figure 2 and their phase transitions (T_m and T_i) and thermodynamic data (ΔH_m and ΔH_i) together with those of polyesters **7a**,**b** are given in table 2. Polarizing microscopy indicated that they form enantiotropic thermotropic LC phase between T_m and T_i or in the range between T_g and T_i. Typical LC textures (broken fan and shlieren) for the polymers **3b** at 145°C on cooling and **3d** at 154°C on cooling are shown in figure 3, suggesting that these polymers form smectic C or nematic phases.

The LC phases were characterized using XRD. Typical patterns for polymers **3b**, **3c** and **3e** together with those for polymers **7a**,**b** are shown in figure 4 and the data are listed in table 3. In the XRD patterns for polyesters **3a**–**f** quenched from the LC states, one or more sharp reflections at middle angles ($2\theta =$ 2.10–2.49°, 4.33–4.75° and 7.07°) and broad reflections at $2\theta = 20$–30° are observed, which suggests that the

Table 2. Phase transition data for polyesters **3a**–**f** and **7a**,**b** for DSC curves on second heating. T_g = glass transition temperature, T_{Cr} = solid-to-solid transition temperature, T_m = solid-to-smectic phase transition temperature, T_i = smectic phase-to-isotropization transition temperature, $\Delta T = T_i - T_m$ = temperature range of smectic phase, ΔH_m = transition enthalpy for T_m, ΔH_i = transition enthalpy for T_i.

Polym.	T_g/°C	T_{Cr}/°C	T_m/°C	ΔH_m/J g^{-1}	T_i/°C	ΔH_i/J g^{-1}	ΔT/°C	LC phase
3a[a]	40	—	96	0.36	206	14.5	110	Smectic C
3b	47	—	97	0.36>	156	5.39	59	Smectic C
3c	43	—	—	—	178	11.5	135	Smectic C
3d	43	92 (77, 98)[b]	109	—	144	5.58	35	Smectic C
3e	42	—	—	—	196	16.2	145	Smectic C
3f	47	—	—	—	140	9.23	87	Smectic C
7a	—	—	90	3.23	139	16.0	49	Smectic B or F
7b	—	—	70	11.8	141	6.91	71	Smectic C

[a] Previously reported data [20].
[b] Crystallization temperature (T_c).

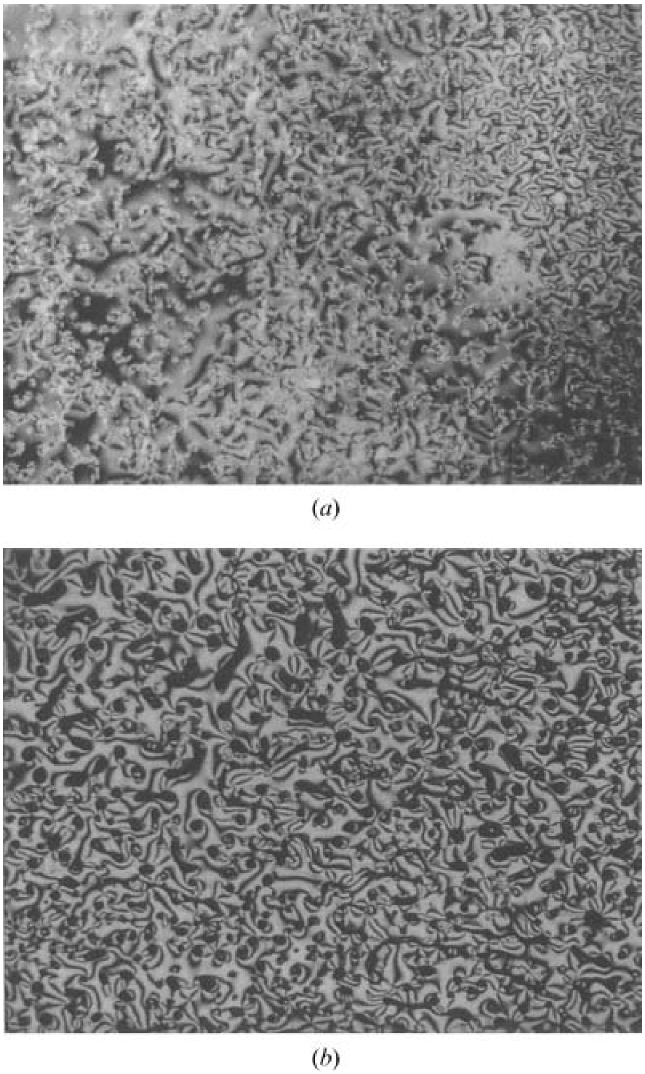


Figure 3. Polarizing photomicrographs of (*a*) polymer **3b** at 145°C on cooling and (*b*) polymer **3d** at 154°C on cooling (magnification × 200).

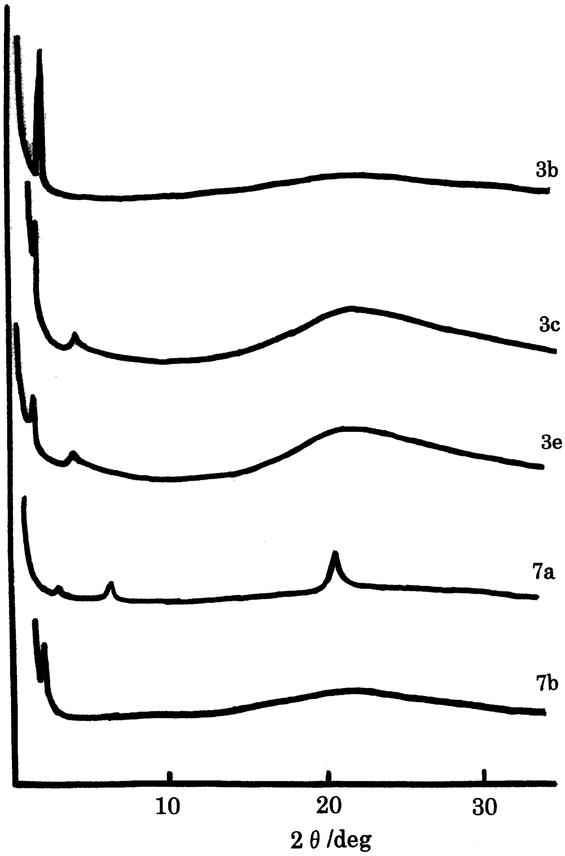


Figure 4. X-ray diffraction patterns of polymers **3b**, **3c**, **3e**, and **7a**,**b** quenched from the LC states.

d-spacing values of polymers **3a**–**f** are 35.5–42.1 Å and that they form either a smectic A or C phase. These *d*-spacing values are shorter than the calculated layer distances of polyesters **3a**–**f**. From these X-ray data and the texture observations (schlieren and broken fan textures), the LC phase is assigned as a smectic C and similar to our previously described combined-type homopolyesters containing a biphenyl unit in the main chain and the methoxyazobenzene in the side chain [20, 21].

The DSC curves of polyesters **7a**,**b** with two azobenzene units in the polymer repeat unit during first and second heating, show two endotherms due to T_m at 90 and 70°C and T_i at 139 and 141°C, respectively. On the first cooling the corresponding exothermic peaks associated with T_i and the LC phase-to-solid (T_c) transitions were observed. The ΔT values were 49°C (**7a**) and 71°C (**7b**). Polymers **7a**,**b** showed enantiotropic thermotropic LC phases in the range T_m or T_c and T_i, and a fine texture was observed under the polarizing microscope. Figure 5 shows the polarizing photomicrograph for polyester **7a** at 120°C on heating. The phase transition data for polymers **7a**,**b** are listed in Table 2.

Table 3. X-ray reflection data for polyesters **3a**–**f** and **7a**,**b** quenched from mesophases.

Polymer	Middle angle		Wide angle
	2θ/°	*d*-spacing/Å	2θ/°
3a[a]	2.45	36.0	—
3b	2.49	35.5	—
3c	2.28, 4.64	38.6, 19.0	—
3d	2.35, 4.75, 7.07	37.7, 18.6, 12.5	—
3e	2.10, 4.33	42.1, 20.4	—
3f	2.24	39.3	—
7a	3.16, 6.50	28.0, 13.6	20.8
7b	2.21	40.0	—

[a] Previously reported data [20].

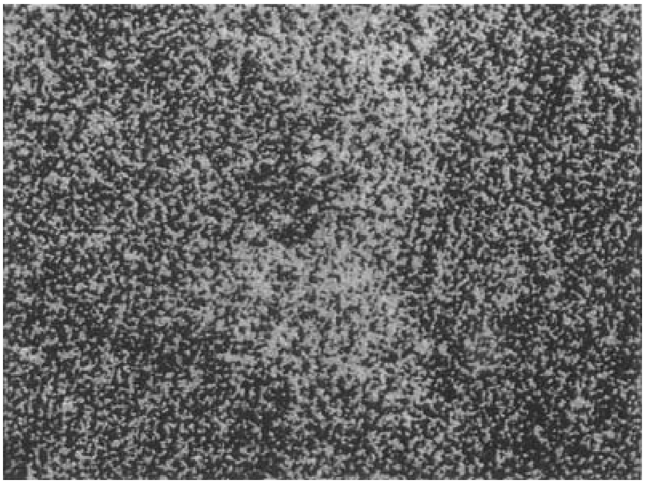


Figure 5. Polarizing photomicrograph of polymer **7a** at 120°C on heating (magnification ×200).

The XRD pattern for polymer **7a**, containing the biphenyl unit in the main chain, showed one sharp reflection at middle angles ($2\theta = 3.16°$ and $6.50°$) and a sharp reflection at $2\theta = 20.8°$, (figure 4) implying that the mesophase is a smectic B phase similar to combined-type copolyisophthalates [21] or a smectic F phase [31]. In the X-ray pattern of polymer **7b** (figure 4) having the DPTD unit in the main chain, a sharp reflection at middle angle ($2\theta = 2.21°$) and broad reflection at $2\theta = 20°–30°$ were detected, whose *d*-spacing value is 4.0 Å suggesting that this might be a smectic C phase as was that for the homopolyesters **3a**–**f** having one side chain azobenzene. Table 3 lists the X-ray reflection data for polymers **7a**,**b**.

We have seen that these combined-type polyesters having either one or two side chain azobenzene units together with a main chain DPTD unit in the polymer repeat unit, form smectic C phases while the polyester with two side chain azobenzenes and a main chain biphenyl unit exhibits a smectic B or F phase. This is probably because the polyesters bearing two side chain azobenzene units and the main chain biphenyl moiety have higher orientational order than the polyesters with the one or two side chain azobenzene units and the main chain DPTD, resulting from a more linear structure and its compact molecular chain packing given the terephthalate linkage; in addition to stronger intra- or intermolecular interactions between the two azobenzene units and the biphenyl moiety in the polymer backbones.

4. Conclusion

It is suggested that the polyesters bearing one or two side chain azobenzenes and a main chain DPTD moiety show a smectic C phase, and the polymer having two side chain methoxyazobenzenes and a main chain biphenyl exhibits a smectic B or F phase. This is despite the presence of different mesogens in the main and side chains, as well as the behaviour of the previously reported combined-type polyisophthalates.

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