Liquid crystallinity in polythioethers of 1,4-bis(mercaptomethyl)benzene (MB) and 4,4'-bis(mercaptomethyl)biphenyl (MBP) with α,ω-dibromo-*n*-alkanes and polythioesters of MB and MBP with *n*-alkanedioyl dichlorides

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Liquid crystallinity in polythioethers of 1,4-bis(mercaptomethyl)benzene (MB) and 4,4′-bis(mercaptomethyl)biphenyl (MBP) with α,ω-dibromo-*n*-alkanes and polythioesters of MB and MBP with *n*-alkanedioyl dichlorides

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Polythioethers consisting of 1,4-bis(mercaptomethyl)benzene (MB) with α,ω-dibromo-*n*-alkanes (A*n*, the number of methylene groups, *n*=5–8) (MB-A*n*) and 4,4′-bis(mercaptomethyl)biphenyl (MBP) with A*n* (MBP-A*n*), and polythioesters containing MB and MBP with *n*-alkanedioyl dichlorides (AM*m*C, the number of methylene groups, *m*=5–8) (MB-AM*m*C and MBP-AM*m*C) were synthesised and their phase transition behaviour investigated using differential scanning calorimetry, polarising optical microscopy and X-ray diffraction. The MPB-A*n* thioether polymers exhibited a nematic phase with good thermal stability but the MB-A*n* thioether and MB-AM*m*C and MBP-AM*m*C thioester polymers exhibited no mesophase. The dependence of liquid crystalline behaviour on the chemical structure of the polymers is discussed.

Keywords: liquid crystal polymers; polythioesters; polythioethers

1. Introduction

As is well known, polyesters and polyethers are archetypal engineering plastics and so, many main-chain liquid crystalline (LC) polyesters and polyethers have been developed in an attempt to develop new functional properties in such materials (*1*). Liquid crystallinity has also been investigated for various polythioesters and polythioethers and some examples of LC thioester and thioether polymers have been reported (*2–13*). Recently, we found that some biphenyl derivatives having –CH$_2$SR (R=alkyl) as one of their terminal groups exhibit a nematic phase (*14, 15*), as well as those having a –CH$_2$OR terminal group (*16*), and furthermore that the viscosity in the nematic LC state is lower in the presence of a soft terminal –CH$_2$SR chain compared to that of a –SR terminal chain. These findings drew our attention towards clarifying how the existence of soft –CH$_2$S–(CH$_2$)$_n$–SCH$_2$– or –CH$_2$S–CO–(CH$_2$)$_n$–CO–SCH$_2$– segments affect the liquid crystallinity in main-chain LC polymers, because main-chain LC polymers are important engineering plastics, but such studies have not yet been reported to our knowledge. In the first stage of these studies, we chose polythioethers and polythioesters having soft –CH$_2$S–(CH$_2$)$_n$–SCH$_2$– and –CH$_2$S–CO–(CH$_2$)$_n$–CO–SCH$_2$– segments, respectively.

In this paper, we report the synthesis of two new types of polythioethers, 1,4-bis(mercaptomethyl)benzene (MB) with α,ω-dibromo-*n*-alkanes (A*n*, number of methylene groups, *n*=5–8) (MB-A*n*) and 4,4′-bis(mercaptomethyl)biphenyl (MBP) with A*n* (MBP-A*n*), and two types of polythioesters, MB with *n*-alkanedioyl dichlorides (AM*m*C, number of methylene groups, *m*=5–8) (MB-AM*m*C) and MBP with AM*m*C (MBP-AM*m*C), and an investigation their phase behaviour. The chemical structures of the polymers synthesised are shown in Figure 1.

2. Experimental

Materials

Polythioethers (MB-A*n* and MBP-A*n*) and polythioesters (MB-AM*m*C and MBP-AM*m*C) were synthesised according to the scheme shown in Figure 2, which shows MBP-A6 and MBP-AM7C as typical examples

Synthesis of MBP-A6.

4,4′-biphenyldicarboxylic acid (5.0 g, 0.021 mol)/THF (25 ml) was added dropwise to LiAlH$_4$ (3.15 g, 0.083 mol)/THF (100 ml) and the mixture was refluxed for 24 h. After adding 3N HCl (50 ml), the crude compound II was extracted into diethyl ether, and then purified by recrystallisation from ethanol, giving 4,4′-biphenyldimethanol (compound II). 4,4′-Bis(chloromethyl)biphenyl (compound III) was

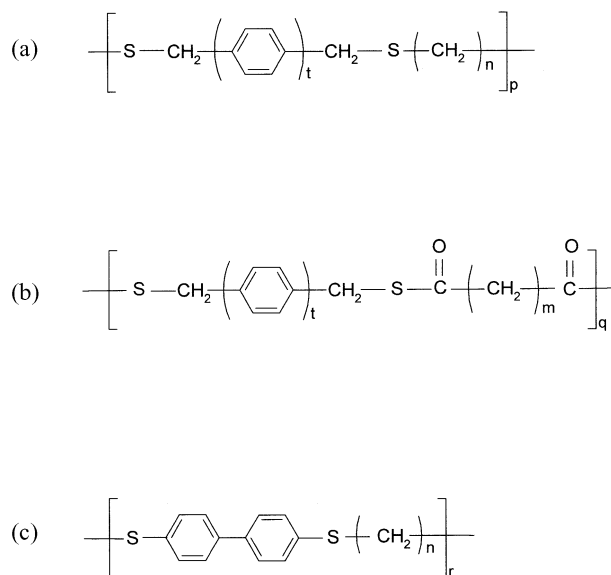*Corresponding author. Email: tadano@u-gifu-ms.ac.jp

(a)

(b)

(c)

Figure 1. Chemical structures of polymers used: (a) polythioethers of 1,4-bis(mercaptomethyl)benzene (MB: $t=1$) and 4,4′-bis(mercaptomethyl)biphenyl (MBP: $t=2$) with α,ω-dibromo-*n*-alkanes (A*n*: $n=5$–8); (b) polythioe-sters of MB and MBP with *n*-alkanedioyl dichlorides (AM*m*C: $m=5$–8); (c) polythioethers of 4,4′-dithiolbiphenyl and α,ω-dibromoalkanes (TB-A*n*) (5).

obtained by adding thionyl chloride (10.0 g, 0.084 mol) to compound II (4.50 g, 0.021 mol)/chloro-form (50 ml). The crude product obtained was purified by recrystallising from hexane. Compound III (3.50 g, 0.014 mol)/chloroform (100 ml) was added to potassium *O*-ethyl dithiocarbonate (4.4 g, 0.028 mol)/acetone (50 ml) and the mixture was refluxed under N_2. The crude product obtained was recrystallised from hexane, giving 4,4′-biphenyl di(methyl-*O*-ethyl dithiocarbonate) (compound IV). 4,4′-Bis(mercaptomethyl)biphenyl (compound V) was obtained by refluxing compound IV (2.80 g, 0.0016 mol)/chloroform (50 ml) with ethylenediamine (3.54 g, 0.059 mol) under N_2 for 1 h. The product was fully purified by use of a column chromatography (silicagel, chloroform). Finally, MBP-A6 was pre-pared by a condensation reaction of compound V with 1,6-dibromohexane. Compound V (1.0 g, 0.0041 mol)/6N NaOH (20 ml) was mixed with 1,6-dibromohexane (0.99 g, 0.041 mol)/*o*-dichlorobenzene (30 ml) and the mixture was stirred at 353 K for 10 h with tetrabutylammonium hydrogensulfate [$(C_4H_9)_4NHSO_4$] under N_2. The oil obtained was washed with 3N HCl and then poured into methanol, giving the crude MBP-A6 polymer. The crude polymer was purified by reprecipitating several times, using THF/acetone as a precipitant (pale yellow, yield: 65%). ^{1}H NMR (CDCl₃, 400 MHz): δ 1.34 [m, 4H, $(CH_2)_2CH_2CH_2(CH_2)_2$], 1.56 [m, 4H,
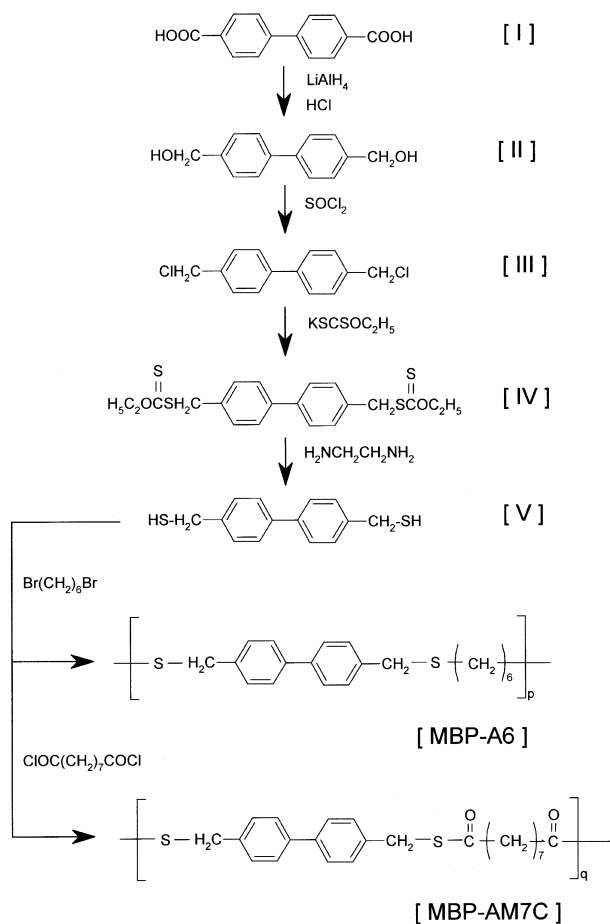

Figure 2. Synthetic scheme for the preparation of MBP-A6 and MBP-AM7C.

$CH_2(CH_2)_2CH_2$], 2.42 [t, $J=7.2$ Hz, 4H, $CH_2(CH_2)_4CH_2$], 3.71 [s, 4H, CH_2(biphenyl)CH_2], 7.34 [d, $J=8.4$ Hz, 4H, 3,3′,5,5′-CH(biphenyl)], 7.60 [d, $J=8.0$ Hz, 4H, 2,2′,6,6′-CH(biphenyl)]. ^{13}C NMR (CDCl₃, 100 MHz): δ 28.4 [$(CH_2)_2CH_2CH_2(CH_2)_2$], 29.0 [$CH_2(CH_2)_2CH_2$], 31.3 [$CH_2(CH_2)_4CH_2$], 34.0 [CH_2(biphenyl)CH_2], 127.0, 128.1, 137.6, 139.3 [C(biphenyl)]. IR (KBr/cm⁻¹): 3027 (aromatic C–H str), 2935, 2850 (aliphatic C–H str), 1602, 1560, 1495, 1463, 1436 (aromatic C–C str), 1143, 1115 (C–S str).

Synthesis of MBP-AM7C.

MBP with AM7C was prepared by a condensation polymerisation of dithiol (compound V) with AM7C [ClOC$(CH_2)_7$COCl] as follows. 4,4′-Bis(mercapt-omethy)biphenyl (compound V) (1.00 g, 0.0041 mol)/ 6N NaOH (20 ml) was mixed with azelaoyl dichloride (AM7C) (0.91 g, 0.0041 mol)/*o*-dichlorobenzene (30 ml), and the mixture was reacted at 353 K for 10 h with $(C_4H_9)_4NHSO_4$ under N_2. The oil obtained was washed with 3N HCl, and then was poured into methanol, the polymer being precipitated. The crude

MBP-AM7C polymer was purified by precipitation using methanol as a precipitant. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.30 [m, 6H, (CH$_2$)$_2$CH_2CH$_2$CH_2 (CH$_2$)$_2$], 1.66 [m, 4H, CH_2(CH$_2$)$_3$CH_2], 2.55 [t, $J=7.6$ Hz, 4H, CH_2(CH$_2$)$_5$CH_2], 4.14 [s, 4H, CH_2(biphenyl)CH_2], 7.32 [d, $J=8.4$ Hz, 4H, 3,3′,5,5′-CH(biphenyl)], 7.47 [d, $J=8.0$ Hz, 4H, 2,2′,6,6′-CH(biphenyl)]. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 25.4 [CH$_2$(CH$_2$)$_3$CH_2], 28.6 [(CH$_2$)$_2$CH_2CH$_2$CH_2(CH$_2$)$_2$], 28.8 [(CH$_2$)$_3$CH_2(CH$_2$)$_3$], 32.8 [CH_2(CH$_2$)$_5$CH_2], 43.7 [CH$_2$(biphenyl)CH_2], 127.2, 129.2, 136.8, 139.6 [C(biphenyl)], l98.8 [C=O]. IR (KBr/cm^{-1}): 3027 (aromatic C–H str), 2927, 2852 (aliphatic C–H str), 1684 (C=O str), 1615, 1558, 1496, 1464 (aromatic C–C str), 1102 (C–S str).

Number-average and weight-average molecular weights (M_n and M_w) of the polymers were determined by gel permeation chromatography and the results are listed in Table 1.

Measurements

Phase transition temperatures and the associated enthalpy changes were measured using differential scanning calorimetry (DSC, Seiko, DSC210) at a heating/cooling rate of 10 K min^{-1}, and calibrated using indium and tin as standards. Thermal gravimetric measurements were performed using a Seiko TG300 differential thermal gravimetric analyser at a heating rate of 10 K min^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL α-400 NMR spectrometer, with CDCl$_3$ and TMS used as the solvent and the internal standard, respectively. IR spectra were measured using KBr discs and a FT-IR spectrometer (Perkin Elmer 1640). Gel permeation chromatographs (GPCs) were measured with a high-speed chromatometer (TOSO, HCL-802UR), with

THF used as solvent and the compounds were detected with a differential refractometer or an ultra-violet spectrometer. The molecular weight was estimated using polystyrene standards. The type of mesophase was determined by texture observations under crossed polarisers using a polarising optical microscope (Nikon OPTIPHOT-POL XTP-11) equipped with a hot stage (Mettler FP82) at a heating/cooling rate of 5 K min^{-1}. Wide-angle X-ray scattering measurements were also used for the determination of type of mesophase, which were made using a Rigaku, Rinto 2000 diffractometer equipped with a home-made cell, using Cu K$_\alpha$ radiation (30 kV, 40 mA), where the scattering intensities were detected with a scintillation counter incorporating a pulse-height analyser.

3. Results and discussion

Figure 3 shows DSC curves at the heating/cooling rate of 10 K min^{-1} for four polymers as typical examples. In MB-A7, one endothermic peak is observed near 333 K during the first heating, corresponding to a melting from as-grown crystallites in the polymer, but during the first cooling, there is only one band near 234 K, which corresponds to a glass transition (T_g). During the second heating/cooling processes, only one band, corresponding to T_g, appeared. Specifically, melting or crystallising processes were not observed after the first heating runs, indicating that the polymer forms a glassy state on cooling from the molten state. This phase transition behaviour was seen for the other MB-An polymers ($n=5$–8).

The DSC curve in Figure 3 for MBP-A6 reveals the behaviour of a polymer with biphenyl as the rigid core. During the first heating, one endothermic peak

Table 1. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) for the MB and MBP polymers.

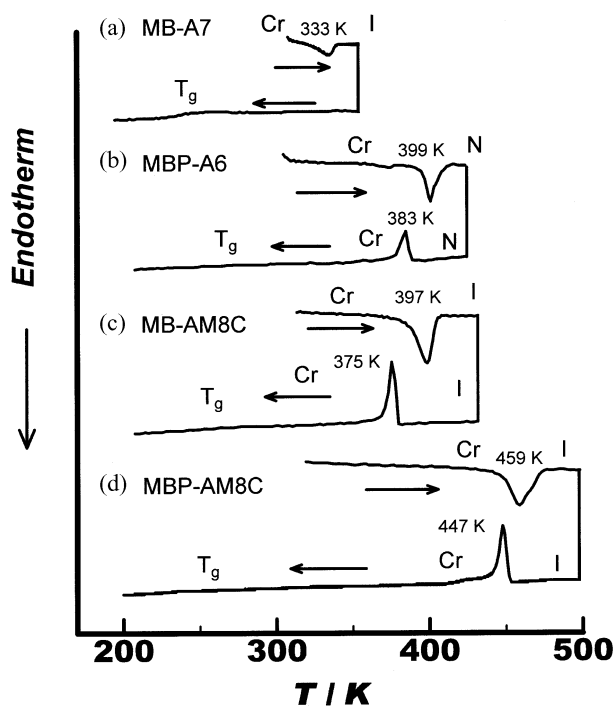| Polymer	n, m	M_n	M_w	M_w/M_n	Yield/%
MB-An	5	3900	12 400	3.17	53
	6	6100	20 900	3.43	59
	7	11 800	30 800	2.61	43
	8	7900	25 600	3.24	61
MBP-An	5	4200	13 500	3.21	62
	6	4800	13 100	2.72	64
	7	5100	18 600	3.64	51
	8	4100	12 900	3.14	68
MB-AMmC	5	4500	12 300	2.73	59
	6	2900	8200	2.82	54
	7	5100	12 300	2.41	67
	8	3300	8800	2.66	51
MBP-AMmC	5	3700	8300	2.25	60
	6	3100	8400	2.72	61
	7	4100	10 400	2.53	63
	8	2800	7800	2.78	44

Figure 3. DSC curves for MB-A7 (a), MBP-A6 (b), MB-AM8C (c) and MBP-AM8C (d). The curves show the melting on first heating and crystallisation temperatures (K) during the first cooling.

is observed near 399 K and one exothermic peak appears near 383 K during the first cooling, corresponding to the melting and freezing of crystallites, respectively. For MB-AM8C and MBP-AM8C [curves (c) and (d)], one endothermic peak is seen near 397 and 459 K, respectively, in the heating process, and near 375 and 447 K, respectively, in the cooling process. Both texture observations under crossed polarisers and X-ray diffraction measurements were used to explore the phase behaviour above the melting temperature (T_m).

In the texture observations, a typical Schlieren texture was observed for MBP-An at temperatures above T_m (399 K for MBP-A6, see Figure 3(b)). Therefore, the 399 K peak is assigned to a transition from the crystalline to a nematic state. On the other hand, in the MB-An, MB-AMmC and MBP-AMmC polymers, no texture was observed above T_m, and so the peak temperatures are identified as associated with melting from crystallites to isotropic liquid.

The variation of X-ray diffraction patterns with temperature is shown for MBP-A6 and MB-A5 in Figure 4. In MBP-A6 (Figure 4(a)), there exists a small broad peak near 7° (2θ) and sharp peaks near 20° at 303 and 388 K below T_m (melting temperature, 399 K), indicating the existence of crystallites, but at 419 and 454 K (above T_m) the sharp peaks near 20°
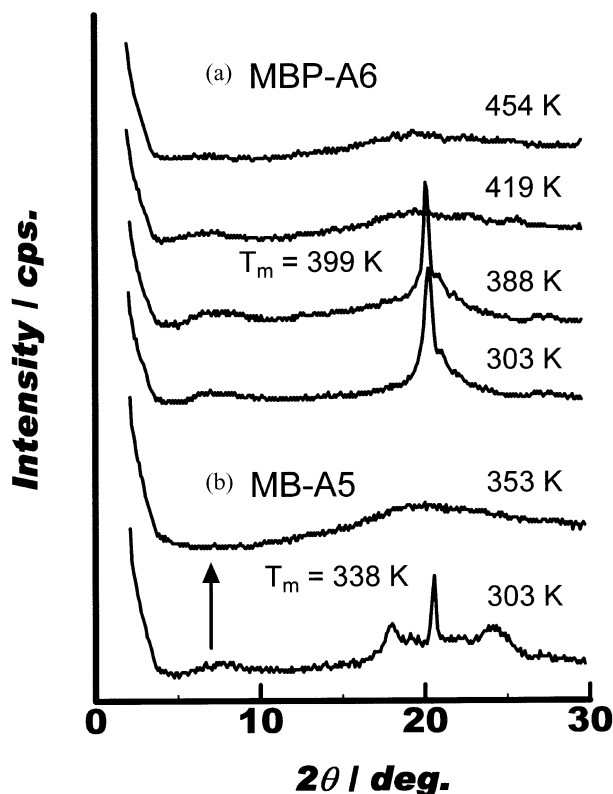

Figure 4. X-ray scattering intensity versus scattering angle (2θ) for (a) MBP-A6 and (b) MB-A5 at different temperatures.

almost disappear but the broad peak near 7° still remains, which indicates the existence of a nematic phase near 450 K above T_m (399 K), consistent with the result of microscopic texture observations described previously. In MB-A5 (Figure 4 b), on the other hand, a few sharp peaks between 18 and 25° 2θ and a small peak near 7° are observed at 303 K below T_m (338 K), but at 353 K above T_m both the wide-angle sharp peaks and the broad peak near 7° disappear, indicating that MB-A5 is in an isotropic liquid phase at 353 K above T_m.

The X-ray data support the identification based on texture observations under crossed polarisers using polarising optical microscopy. The phase transition temperatures are listed for all samples in Table 2.

Figure 5 shows gravimetric thermographs for two polymers (MB-A7 and MBP-AM8C) as typical examples. Here, the thermal decomposition temperatures (T_d) were determined as the temperature at which the weight of compound decreased by 5%, and are listed for all the polymers in Table 2. In MB-A7, T_d is about 503 K and thermal decomposition scarcely took place below the melting point of the crystallites (T_m=333 K). This indicates that the

Table 2. Phase transition parameters for the MB and MBP polymers.

Polymer	n, m	T_g/K	T_m/K	ΔH_m/J g^{-1}	N	I	T_d/K
MB-An	5	246	338	64		●	507
	6	241	372	50		●	547
	7	234	333	17		●	503
	8	230	330	32		●	538
MBP-An	5	264	381	11	●		497
	6	267	399	39	●		520
	7	263	373	13	●		538
	8	267	383	27	●		569
MB-AMmC	5	262	412	39		●	588
	6	261	399	50		●	561
	7	258	399	75		●	559
	8	257	397	67		●	556
MBP-AMmC	5	295	463	48		●	586
	6	236	465	27		●	564
	7	273	435	39		●	570
	8	256	459	54		●	571

absence of melting and crystallising behaviour during the second and subsequent heating/cooling runs in MB-An is not caused by thermal decomposition. On the other hand, the MBP-An polymers exhibit a nematic phase above T_m, as described already, but the clearing point (T_c) was not able to be determined because it was higher than T_d; the nematic Schlieren texture under the crossed polarisers gradually disappeared on increasing temperature and formed droplets above T_d, perhaps due to thermal decomposition.

In conclusion, the MBP-An ($n=5$–8) polymers exhibit a nematic phase over a wide temperature

Figure 5. Variation of weight loss with temperature in MB-A7 and MPB-AM8C.

range from the melting point to over the decomposition temperature, but the MB-An, MB-AMmC and MPB-AMmC polymers exhibit no mesophase. These results can be explained in terms of their chemical structures. In MB-An and MB-AMmC, the mesogenic rigid core is composed of only one phenylene ring, which may be too short to generate a mesophase, whereas in MPB-AMmC, the carboxyl thioether (thioester) bond may broaden the lateral width of the backbone chains, resulting in the suppression of the mesophase. Above all, in the present polymers, only the MPB-An polymers exhibit a nematic phase with good thermal stability due to the rather lath-like rigid biphenyl core.

As described in the introduction, several polythioethers have been synthesised and their liquid crystalline behaviour investigated by several researchers. Shaffer *et al.* (5) have reported that polythioethers of 4,4′-dithiolbiphenyl and α,ω-dibromoalkanes (TB-An), in which the biphenyl ring is linked with the alkyl segment via $-\Phi-SR-$ bond, as depicted in Figure 1 c, exhibit a smectic phase. Figure 6 shows the variation of LC phase with the alkyl chain length (n) for TB-An and MBP-An.

This result is interesting, because a nematic phase appears in MBP-An in contrast with a smectic phase in TB-An, although MBP-An have the same chemical structure as that of TB-An, except for the $-\Phi-CH_2S-CH_2-$ bond. The thioether bond $-\Phi-SCH_2-$ in TB-An may be more rigid than that of $-\Phi-CH_2S-CH_2-$ in MBP-An, which would cause the smectic phase in TB-An. Moreover, both melting and clearing points reveal an odd–even effect against n in TB-An, which is also seen for the melting point in MBP-An. The temperature range of the nematic mesophase in MBP-An is much wider than that of the smectic phase in TB-An.
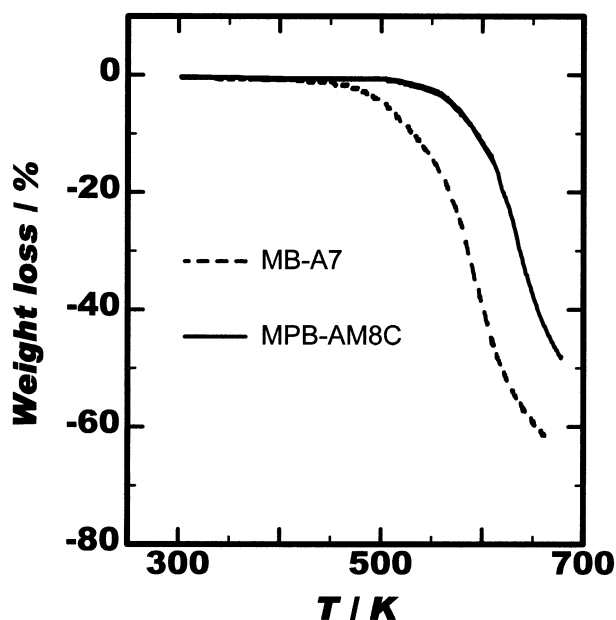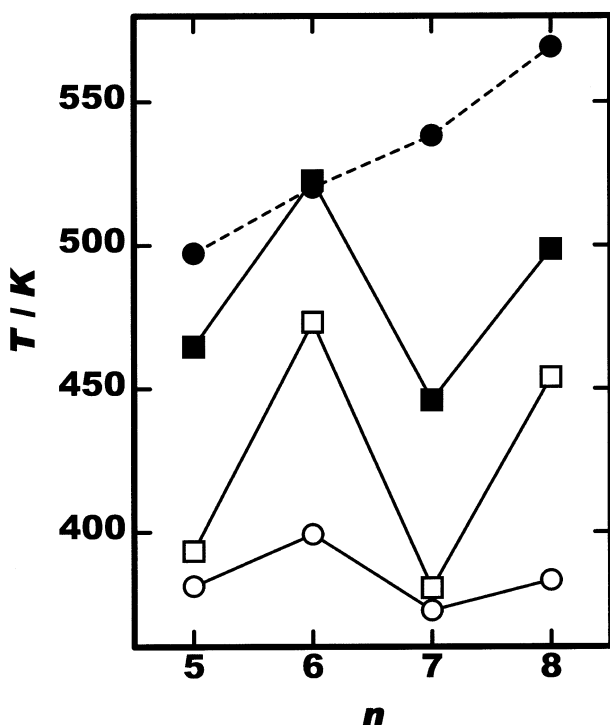
Figure 6. Plots of phase transition temperatures versus alkyl length (*n*). ○ and ●: crystal–nematic phase transition on first heating and thermal decomposition temperatures, respectively, for MPB-A*n*. □ and ■: crystal–smectic phase transition and smectic–isotropic liquid phase transition temperatures, respectively, on first heating for TB-A*n* obtained by Shaffer and Percec (5).

Main-chain liquid crystalline (LC) polythioethers have not been investigated as much as main-chain LC polyethers and polyesters, although they have application potential as engineering plastics. The present work suggests that the MBP-A*n* polymers, which are regarded as new main-chain LC polymers, exhibit nematic phase behaviour over a wide temperature range. This appearance of a nematic phase with good thermal stability may come from the presence of the Φ–CH_2S–R bond. The decomposition temperature (T_d) is not strongly dependent on *n* (Figure 6) between MB-A*n* and MBP-A*n* (Table 2). These results suggest that T_d is related to the –S– bond. We note that the appearance of the nematic phase is of industrial and fundamental interest.

Further studies of the liquid crystal behaviour of various polythioethers and polythioesters are certainly worthwhile and are progressing in our laboratories.

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