

Synthesis and Properties of TLCPs with 2,6-Naphthalene-Based Mesogen, Polymethylene Spacer, and Nonlinear 4,4'-Thiodiphenyl Links

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ABSTRACT: A series of new thermotropic main-chain liquid crystalline copolyesters were prepared by polycondensation of 2,6-naphthalenedicarbonyl chloride, 4,4'-thiodiphenol, and α,ω -alkanediols ($n = 4-10$) in diphenyl ether at 200°C. Thermal transition behaviors of these copolyesters were investigated by differential scanning calorimetry. Moreover, their thermal stabilities and mesomorphic textures were studied by thermogravimetric analysis and polarizing optical microscopy, respectively. Corresponding model compounds with terminal mesogenic units and central polymethylene spacers were also synthesized for comparison. Both copolymers and model compounds exhibit odd-even dependency of melting temperatures, transition enthalpy (ΔH_m), and entropy (ΔS_m) on the number of methylene units in the spacer. However, the odd-even effects in model compounds are much more distinctive. Nematic mesophases are the only texture observed in melts, except the model compounds with longer methylene units ($n = 8, 10$), in which smectic mesophases can be observed. The T_m values of the copolyesters (TDP/HD = 1/1) are between 233 and 259°C, depending on spacer length. The initial decomposition temperatures of the copolyesters are above 419°C under N₂ atmosphere. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1536–1546, 2002

Key words: 2,6-naphthalene; 4,4'-thiodiphenyl; copolyesters; odd-even effect

INTRODUCTION

It is well known that wholly aromatic thermotropic liquid crystalline polymers (TLCPs) possess high-performance properties such as thermal stability and excellent mechanical strength. TLCPs have been gradually applied in many fields such as heat-resistant container, connector, electronic switch, molded interconnection device, audio, and medical parts.^{1,2} However, completely

rigid rodlike polymers such as poly(4-oxybenzoate) or poly(*p*-phenylene terephthalate) tend to be highly crystalline and intractable, with melting points above their decomposition temperatures (>450°C). This problem can be circumvented by decreasing the regularity of para-linked aromatic chromophores to the point at which mesomorphic behavior is manifested below the decomposition temperature. In this way, the materials can be processed in fluid yet ordered states. The requirements that the polymers must retain some rodlike nature but simultaneously be melt-processable below decomposition temperature have limited TLCPs mainly to those based on the linear ester or ester/amide bonds. The regularity disruption in these polymers is normally achieved by copolymerization techniques,³ that is, frustrated

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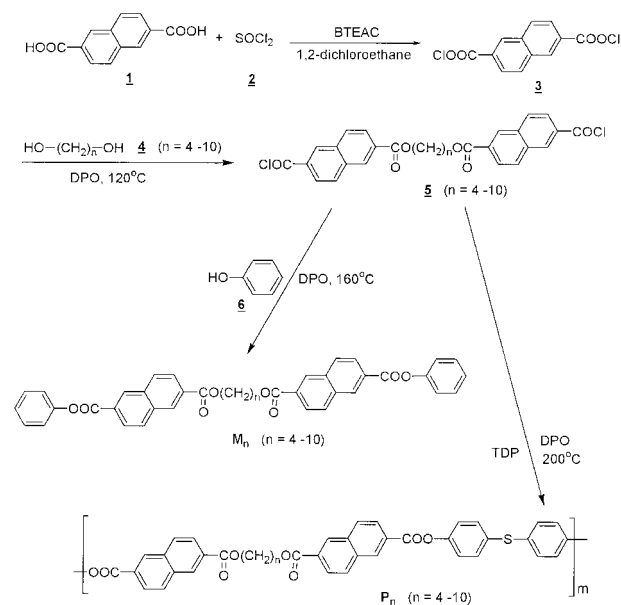
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chain packing,⁴⁻⁷ flexible spacers,⁷ and nonlinear links.^{8,9}

Among the many interesting observations made for the TLCPS, the odd–even dependency of transition temperatures on spacer length is a matter of importance, which generalizes the thermal behavior of a homologous series of polymers with different spacer length.¹⁰ However, direct comparison of thermal-transition temperatures obtained experimentally may become erroneous because of the strong dependency of transition temperatures not only on molecular weights of the polymers but also on their polydispersity. While trying to establish the structure–property relationship of the TLCPS having flexible spacers, we became interested in the liquid crystalline behaviors of model compounds to see whether there is any correlation between their properties and those of the corresponding polymers, especially in thermal behavior and in the nature of the mesophase derived from them.

A series of new TLCPS were synthesized by polycondensation of 2,6-naphthalenedicarbonyl chloride with α,ω -alkanediols ($n = 4-10$) and 4,4'-thiodiphenol. The copolyesters were incorporated at the same time with parallel-offset or crankshaft naphthalene unit, flexible polymethylene spacers, and kinked 4,4'-thiodiphenyl groups. The thermal properties and odd–even effect in the copolyesters and corresponding model compounds are presented.



Scheme 1

Table I Yields and Properties of Copolyesters from Different Diphenols^a

Diphenol	Yield (%)	η_{red}^b (dL/g)	LC Phase
Bisphenol A	86	0.46	—
4,4'-Thiodiphenol	88	0.45	Nematic
4,4'-Dihydroxydiphenol Ether	53	0.22	Nematic
Hydroquinone	45	0.20	Nematic

^a 3: HD : diphenol = 2 : 1 : 1.

^b Measured with 0.3 g/dL in trifluoroacetic acid/chloroform (1/4) at 30°C.

EXPERIMENTAL

Materials

2,6-Naphthalenedicarboxylic acid was a generous gift from Amoco Chemical Co. and thionyl chloride was purchased from Merck (West Point, PA). α,ω -Alkanediols [HO-(CH₂)_n-OH, $n = 4-10$] and benzyltriethylammonium chloride (BTEAC) were from Tokyo Kasei (Japan) and Fluka Chemie (Buchs, Switzerland), respectively, and used without further purification. Bisphenol A (Showa Co.), 4,4'-thiodiphenol (Lancaster Chemicals, UK), 4,4'-dihydroxydiphenyl ether (Tokyo Kasei), hydroquinone (Merck), and phenol (Riedel-de-Haën, Seelze, Germany) were used as received. Diphenyl ether and 1,2-dichloroethane were purified by distillation over KOH and NaH, respectively, before using.

Measurements

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AC-400 spectrometer (Bruker Instruments, Billerica, MA). Chemical shifts were reported in ppm using tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured as KBr pellets on a Fourier transform infrared spectrometer, model Valor III from Jasco Co. (Japan). Elemental analyses were carried out on a Hereaus CHN-Rapid elemental analyzer. Thermal properties of the polymers and model compounds were measured using a differential scanning calorimeter (DSC; model DSC-50; Shimadzu, Japan), under nitrogen atmosphere at a heating rate of 10°C/min. The thermogravimetric analysis (TGA) was measured under nitrogen atmosphere at a heating rate of 20°C/min using a Perkin–Elmer TGA-7 thermal analyzer (Perkin

Table II Yields and Properties of Copolyesters P₆ Prepared by Polycondensation of **3 with 1,6-Hexanediol and 4,4'-Thiodiphenol**

Feed (Mole) TDP/HD	Yield (%)	$\eta_{\text{red}}^{\text{a}}$ (dL/g)	T_g^{b} (°C)	T_m^{b} (°C)	T_i^{c} (°C)	T_d^{d} (°C)	LC Phase ^c
30/70	90	0.32	74	172	180	396	Nematic
40/60	93	0.43	78	189	220	388	Nematic
50/50	88	0.45	79	236	>300	400	Nematic
60/40	70	0.21	76	238	>300	395	Nematic
70/30	80	0.17	85	263	>300	395	Nematic

^a Measured with 0.3 dL/g in trifluoroacetic acid/chloroform (1/4) at 30°C.

^b Determined using DSC heating scan at 10°C/min.

^c Estimated by polarized microscope equipped with a heating stage.

^d Temperature at 5% weight loss measured by TGA under N₂ atmosphere.

Elmer Cetus Instruments, Norwalk, CT). Liquid crystalline (LC) textures were identified using a Nikon LABOPHOT-POL polarizing microscope equipped with a Mettler FP84 heating stage and a Mettler FP80 control unit. X-ray diffractograms were obtained on a Rigaku Geiger Flex Max IIIv instrument using the nickel-filtered CuK_α radiation.

Synthesis of 2,6-Naphthalenedicarbonyl Chloride (**3**) (Scheme 1)

To a two-necked 250-mL round-bottom flask was added 2,6-naphthalenedicarboxylic acid (**1**) (25 g, 0.116 mol), 1,2-dichloroethane (200 mL), and benzyltriethylammonium chloride (0.034 g, 0.15 mmol). The slurry was stirred gently and brought to reflux, and then thionyl chloride (**2**) (18 mL) was added and allowed to react for 24 h. The

mixture was filtered to remove a small amount of intractable solids, and the filtrate was allowed to recrystallize. The solids were isolated by filtration, washed with *n*-hexane, and then dried to give yellow crystals of **3**. The yield was 91% (m.p.: 188.5–189.5°C). IR (KBr, cm⁻¹): 1745 cm⁻¹. ¹H-NMR (CDCl₃, ppm): δ 8.0 (d, 2H, aromatic), 8.3 (d, 2H, aromatic), 8.7 (s, 1H). ¹³C-NMR (CDCl₃, ppm): δ 168.0, 135.2, 133.7, 133.6, 130.8, 126.7.

Synthesis of Model Compounds (M₄–M₁₀)

For example, to a two-necked 50-mL round-bottom flask was added 2,6-naphthalenedicarbonyl chloride (**3**) (3.036 g, 12 mmol) and diphenyl ether (30 mL). The mixture was fully stirred and 1,6-hexanediol (**4**) (0.709 g, 6 mmol) was added all at once, followed with reacting at 120°C for 1 h. After the flask was cooled down to

Table III Yields and Properties of Copolyesters Prepared by Polycondensation of **3 with 4,4'-Thiodiphenol and Different Aliphatic Diols**

Polymer	Reaction Time (h)	Yield (%)	$\eta_{\text{red}}^{\text{a}}$ (g/dL)	T_g^{b} (°C)	T_m^{b} (°C)	T_d^{c} (°C)	ΔH_m^{d} (kJ/mol)	ΔS_m^{d} (J K ⁻¹ mol ⁻¹)	D.C. ^e (%)	LC Phase ^f
P₄	1.5	64	0.17	97	250	420	8.75	16.73	—	Nematic
P₅	1.75	50	0.16	90	225	422	5.16	9.75	—	Nematic
P₆	24	96	0.66	95	240	424	5.83	11.08	23.3	Nematic
P₇	24	85	0.45	88	237	419	4.41	8.89	20.3	Nematic
P₈	24	97	0.73	83	238	426	5.45	10.46	24.6	Nematic
P₉	24	91	0.66	62	235	430	4.81	9.08	21.3	Nematic
P₁₀	24	93	0.88	60	236	433	8.06	15.13	23.9	Nematic

^a Measured with 0.3 dL/g in trifluoroacetic acid/chloroform (1/4) at 30°C.

^b Determined using DSC heating scan at 10°C/min.

^c Temperature at 5% weight loss measured by TGA under N₂ atmosphere.

^d Estimated from DSC traces obtained at heating rate of 10°C/min.

^e Degree of crystallinity determined from XRD diffractograms.

^f Observed using a polarized microscope equipped with a heating stage.

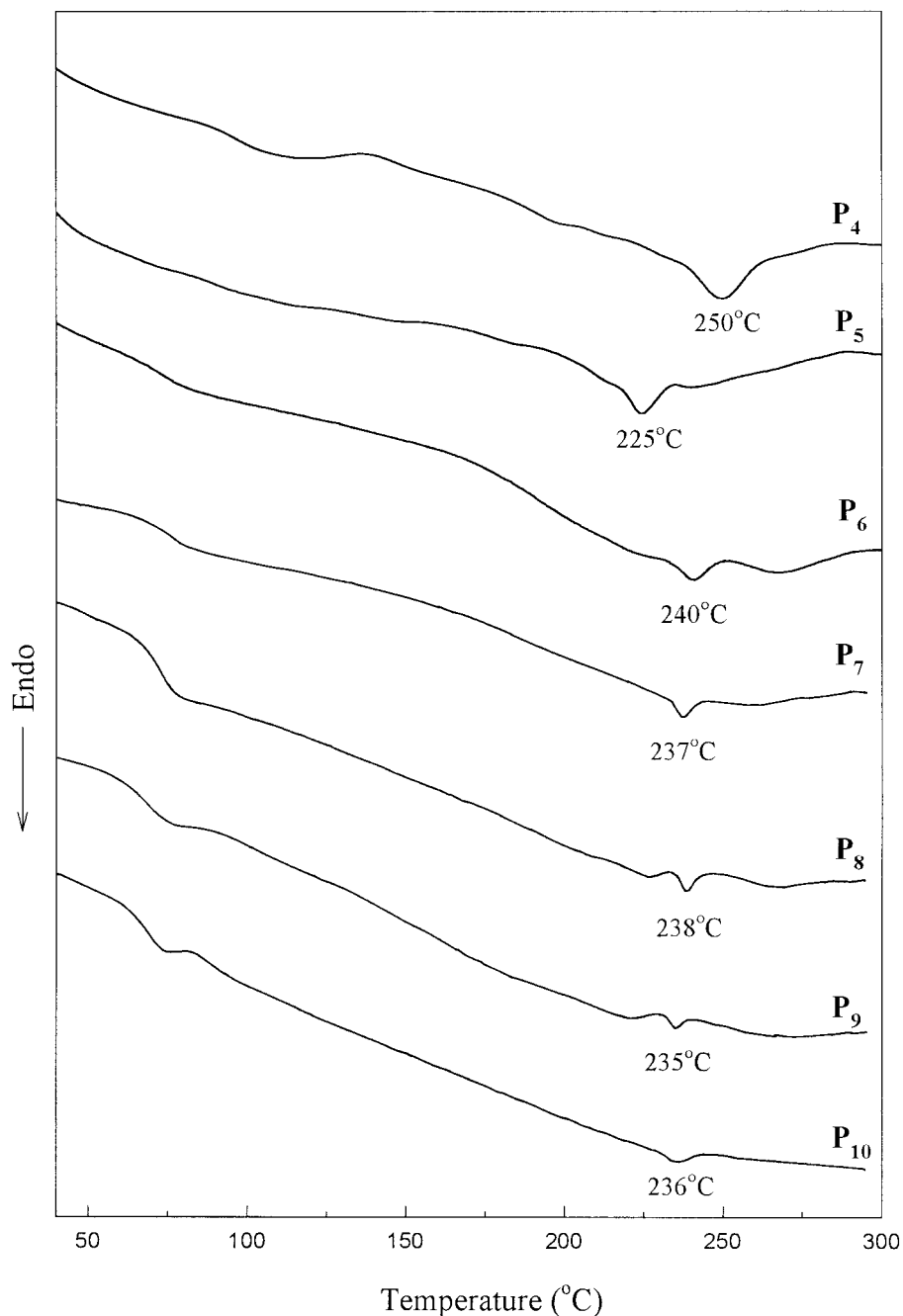


Figure 1 DSC traces of copolyesters P_4 – P_{10} .

ambient temperature, excess phenol (**6**) (1.242 g, 13 mmol) was added and heated to 160°C to react for 24 h. The reaction mixture was poured into methanol to precipitate the product M_6 . The solids were isolated by filtration and dried in a vacuum oven. The yield was 85% (m.p.: 138°C). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 1.2–2.2 [m, 8H $\text{CH}_2(\text{CH}_2)_4\text{CH}_2$], 4.4 (m, 4H, CH_2O), 7.13–8.80 (m, 20H, aromatic).

Synthesis of Copolyesters

The copolyesters were prepared by two-step polycondensation, that is, first reaction of 2,6-naphthalenedicarbonyl chloride (**3**) with half equivalent of 1,6-hexanediol (**4**) and followed with another half equivalent of 4,4'-thiodiphenol (**8**). The polymerization was stopped when insoluble precipitates appeared; otherwise, the reaction time

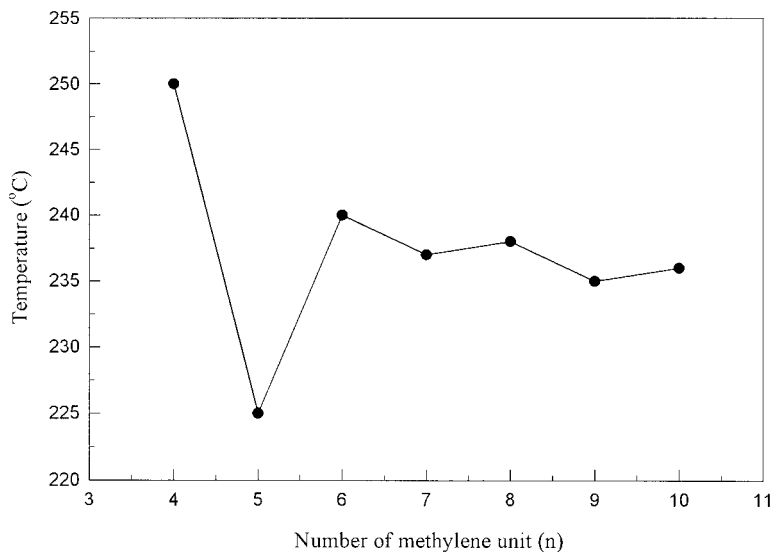


Figure 2 Odd-even effect in T_m of copolyesters P_4 – P_{10} .

was continued for 24 h. For example, 2,6-naphthalenedicarbonyl chloride (**3**) (1.012 g, 4 mmol) and diphenyl ether (10 mL) were added to a two-necked 50-mL glass reactor. 1,6-Hexanediol (**4**) (0.236 g, 2 mmol) was added dropwise to the mixture under vigorous stirring and then allowed to react at 120°C for 1 h. After cooling to ambient temperature, 4,4'-thiodiphenol (**8**) (0.437 g, 2 mmol) was added and allowed to react at 200°C. The mixture was precipitated in a large amount of methanol, after which the copolymer P_6 was isolated by filtration and then dried *in vacuo* at 80°C for 24 h after extracting with toluene using a Soxhlet apparatus. The yield was 88% and the reduced viscosity was 0.45 dL/g. $^1\text{H-NMR}$ ($\text{CF}_3\text{COOD}/\text{CDCl}_3 = 1/4$, ppm): δ 1.2–2.2 [m, 8H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_2$], 4.36 (m, 4H, CH_2O), 7.1–8.8 (m, 20H, aromatic). ANAL. calcd (%) for $\text{C}_{42}\text{H}_{32}\text{O}_8\text{S}$: C, 72.33; H, 4.56; S, 4.66. Found: C, 72.40; H, 4.63; S, 4.60.

RESULTS AND DISCUSSION

Synthesis and Characterization

The melt polycondensation routes offer many technological advantages, although there are some drawbacks. Because the reaction is carried out at very high temperature in the presence of catalysts, structural rearrangement can occur within the polymer as a result of transesterification reactions. Moreover, because complete re-

moval of the catalysts is very difficult, thermal degradation and structural reorganization can also occur during subsequent thermal treatments.¹¹ Therefore, polycondensation of diacid dichlorides with diphenols and diols may be considered to be an alternative method to obtain copolyesters with regular structure. The rate of this reaction is much higher than that of competing side reactions.

A series of model compounds (M_4 – M_{10}) with different lengths of central polymethylene spacer were also synthesized for comparison in thermal investigation. Two ends were attached successively with crankshaft 2,6-naphthalene and phenyl chromophores through ester linkage.

To evaluate suitable diphenol for TLCPs we first prepared copolyesters from **3**, 1,6-hexanediol, and different aromatic diphenols. As shown in Table I, the copolyester containing 4,4'-thiodiphenol residue has high viscosity (0.45 dL/g) and shows a typical nematic LC texture. Although the copolyester from bisphenol A exhibits the highest viscosity (0.46 dL/g), it does not show LC texture. The other copolyesters derived from 4,4'-dihydroxydiphenol or hydroquinone precipitate out from DPO during polycondensation. Therefore, their viscosities are limited to about 0.2 dL/g. Evidently, 4,4'-thiodiphenol (TDP) turns out to be a potential comonomer for LC copolyesters with 2,6-naphthalene chromophores. Then, copolyesters from **3**, TDP, and HD (TDP/HD = 30/70–70/30) were also prepared

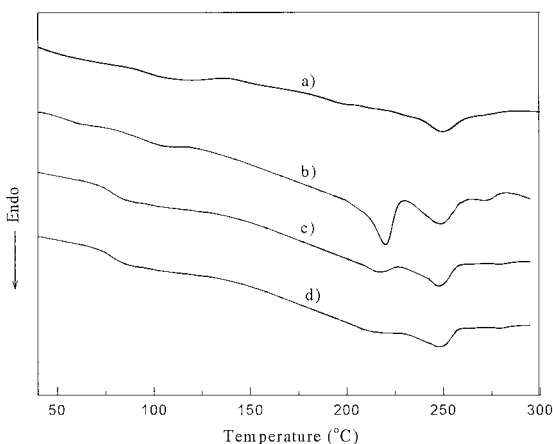


Figure 3 DSC thermograms of P_4 : first heating of (a) slowly cooled sample and (b) quenched sample; (c) second and (d) third heating of quenched sample.

to investigate the influence of mesogenic content. As shown in Table II, the yields are greater than 70% and the reduced viscosities are between 0.17 and 0.45 dL/g. Given that equal moles of TDP and HD give rise to both high yield and viscosity, this ratio is kept in the following preparation of copolyesters with different spacer length. As depicted in Table III, the yields are between 50 and 97%, and the viscosities show a trend of increasing with spacer length. This result can be ascribed to enhanced solubility of the copolyesters in DPO at 200°C with increasing spacer length. The copolyesters precipitate out within 2 h when

n is smaller than 6. Therefore, the viscosities of the copolyesters ($n < 6$) are limited to only 0.16–0.17 dL/g by their low solubility in DPO. However, at $n \geq 6$ the products remain soluble in DPO and the polymerization can be extended to 24 h to obtain a much higher viscosity (0.88 dL/g for P_{10}). In P_6 , the reduced viscosity increases from 0.45 to 0.66 dL/g as the polymerization time is extended from 2 to 24 h.

The copolyesters are difficult to be dissolved in common organic solvent at ambient temperature because of their rigid rodlike structures. Only highly active acids and phenols exhibit solubility to these copolyesters. However, in such cases care must be taken to prevent hydrolytic or exchange reactions that can degrade the polymers. Nevertheless, by trial and error, a solvent combination of trifluoroacetic acid/chloroform (1/4) was found to be a suitable solvent for solution viscosity measurement and NMR structure analysis.

Thermal Properties

Thermal properties of the copolyesters prepared by polycondensation with different molar ratios of 4,4'-thiodiphenol (TDP) and 1,6-hexanediol are summarized in Table II. The T_m and T_i values are in the range of 172–263°C and 180 to >300°C, respectively, and seem to increase with TDP content. The T_g 's are very close (74–85°C) and also show a trend to increase with TDP content. These should be attributable to the increased content of

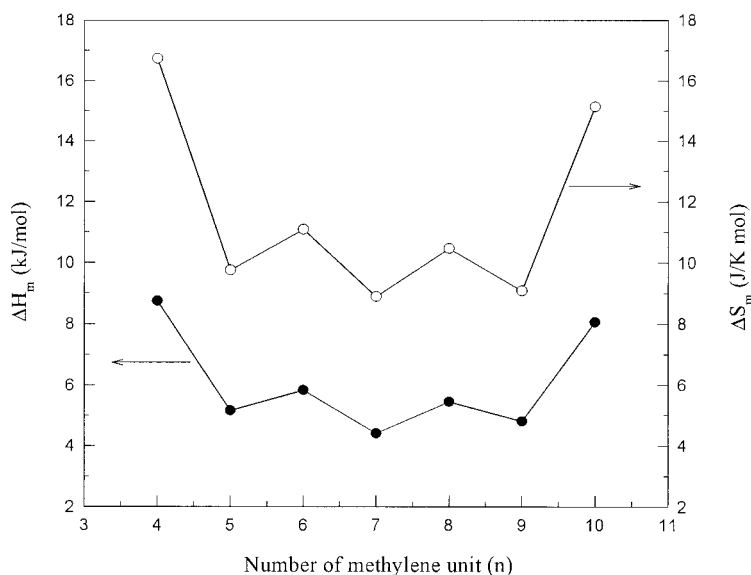


Figure 4 ΔH_m (●) and ΔS_m (○) of copolyesters P_4 – P_{10} .

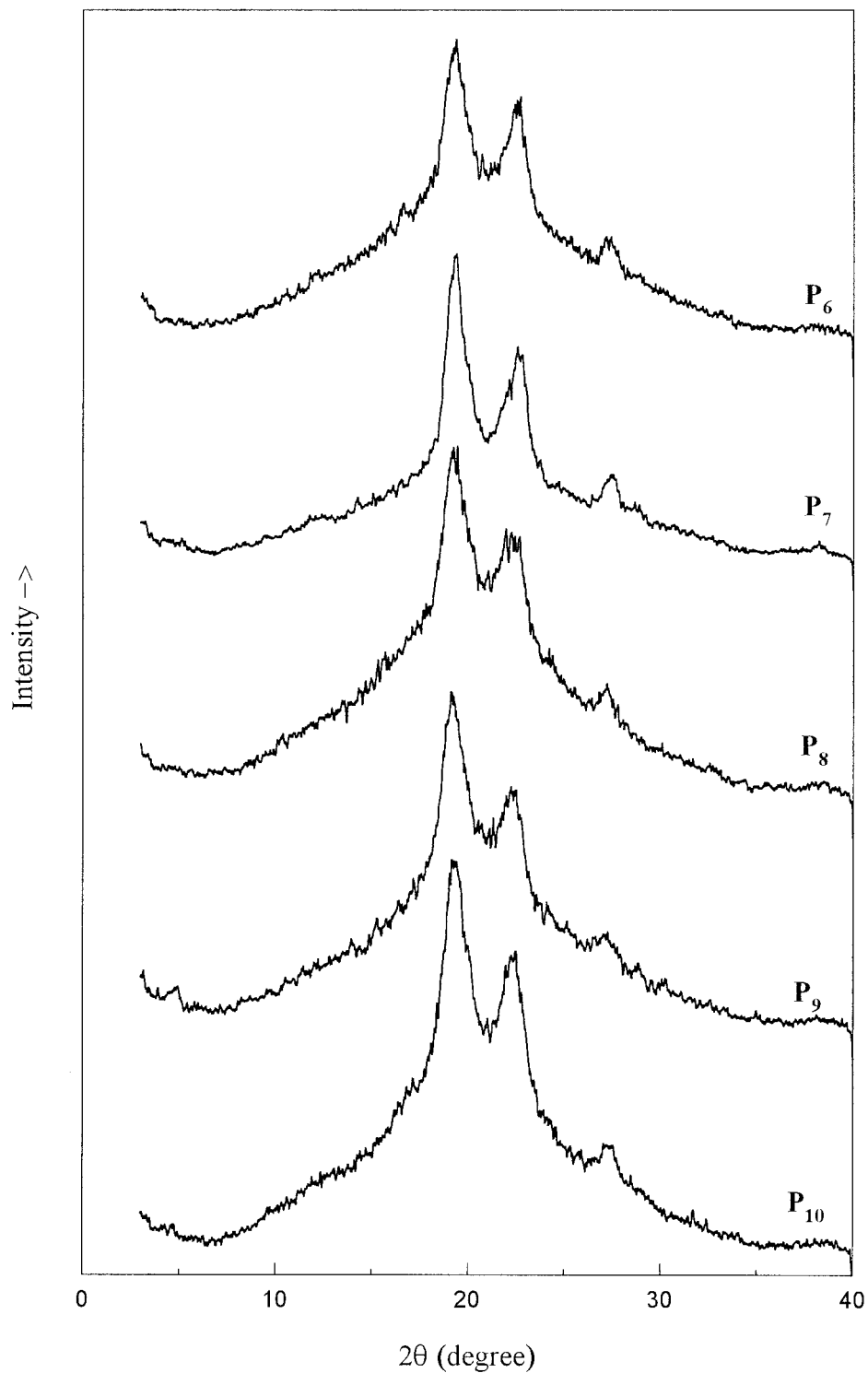


Figure 5 XRD diffractograms of copolyesters **P₆–P₁₀**.

rigid LC mesogen that results in decreased free chain rotations.

Moreover, spacer length primarily determines thermal-transition temperatures of the copoly-

esters. As shown in Table III, the T_m 's are in the range of 250–225°C, whereas the T_g 's are between 60 and 97°C. All the T_i 's are greater than 300°C. This seems to be attributable to the crank-

Table IV Thermal Properties of Model Compounds

Model Compound	Yield (%)	T_m^a (°C)	T_i^a (°C)	ΔH_m^a (kJ/mol)	ΔS_m^a (J K ⁻¹ mol ⁻¹)	LC Phase ^b
M₄	79	151	184	23.94	56.47	Nematic
M₅	75	131	177	15.61	38.63	Nematic
M₆	85	138	171	35.80	87.11	Nematic
M₇	77	100	167	31.82	85.30	Nematic
M₈	88	143	160 ^c	64.36	154.72	Smectic
M₉	82	98	158	30.30	81.67	Nematic
M₁₀	83	115	153	52.33	134.86	Smectic

^a Determined using DSC heating scan at 10°C/min.

^b Observed using a polarized microscope equipped with a heating stage.

shaft structure of the naphthalene unit that raises the T_i 's. Yonetake et al.¹² previously found that naphthalene groups not only increased the thermal decomposition temperature but also expanded the LC range ($T_i - T_m$).

The effect of polymethylene length on the properties of main-chain TLCPS has been very well documented in a number of publications.¹³ Essentially two effects can be observed in our system. First, the transition temperatures reduce with increased spacer length. This is clearly observed in Figure 1 and Table III for T_m values of copolyesters **P₄–P₁₀**. Particularly, high T_m variations from copolyesters **P₄** to **P₅** (Fig. 2) should originate from their low molecular weight compared to that of other copolyesters (**P₆–P₁₀**). Second, transition temperatures exhibit distinct odd–even dependency on the number of methylene units. The copolyesters with even numbers possess higher transition temperatures than those with odd numbers (Fig. 2). The existence of an odd–even effect also suggests that the packing of mesogenic units is influenced by the conformation around C–C bonds of the spacer. Under fully extended trans conformations, the even-numbered polymethylene spacers give rise to more or less collinear or parallel alignment of mesogenic units, whereas the odd-numbered ones would result in angled orientation of mesogenic units.¹⁴ This is in accordance with the observed higher T_m 's for the copolyesters with even-numbered spacer (Fig. 2).

Most of the copolyesters show more than one T_m peak during the first heating scan in DSC measurement. However, during the second and subsequent scans, the low-temperature peaks gradually decrease in intensity and combine to a single peak. For example, Figure 3(b) shows that for the quenched sample there are two distinct endothermic peaks at 220 and 249°C during the

first heating scan. The peak at 220°C shrinks significantly and almost disappears during the second scan. Only a single peak can be observed during the third heating scan [Fig. 3(d)]. All other copolyesters show similar thermal behaviors. It is also found that this behavior is not significantly influenced by the ratio of HD and TDP. Therefore, it is clear that the multiple T_m phenomena are not caused by the structure variations.

Multimelting behavior seems to be a feature in common to many thermotropic liquid crystalline polymers,^{15,16} and it is also observed for many conventional polymers such as poly(ethylene terephthalate).¹⁷ It is reasonably considered that a low-temperature peak corresponds to less-perfect crystals formed in the reprecipitation procedure of hot polymerization solution. During a DSC heating scan, the less-perfect crystals reorganize, and partially melt and recrystallize to form more perfect crystals, which melt at higher temperature, that is, if the completed polymerization solution was cooled down slowly to let the crystallites grow more perfectly.^{18,19} The isolated copolyester shows only one melting peak in its DSC trace, as shown in Figure 3(a).

Enthalpy and entropy changes (ΔH_m and ΔS_m , respectively) of melting also exhibit the odd–even effect, as shown in Figure 4. Even-numbered copolyesters show greater ΔH_m and ΔS_m values than those of the odd-numbered ones. This odd–even effect can be explained in terms of different degrees of order, depending on odd or even numbers of methylene units in the spacer. The order is greater for even-numbered samples in solid state. This assumption was verified by X-ray diffraction patterns, as shown in Figure 5. The degrees of crystallinity were determined on the basis of these diffraction patterns and the data are presented in Table III.

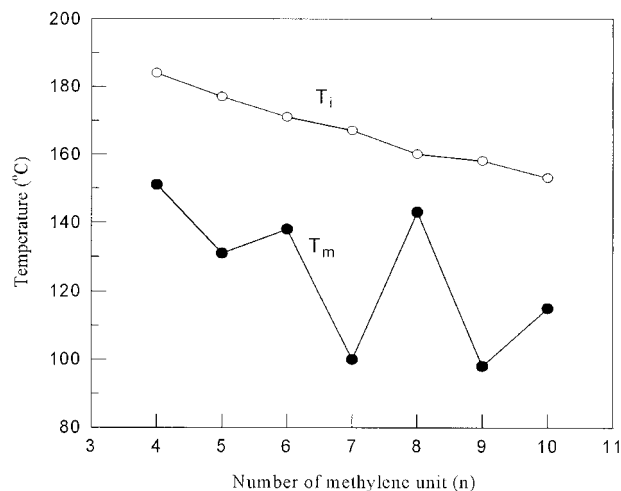


Figure 6 T_m (●) and T_i (○) of model compounds M_4 – M_{10} .

The thermal properties of the model compounds M_4 – M_{10} are tabulated in Table IV. The T_m values of the compounds are in the range of 98–151°C and the T_i values are in the range of 153–184°C, depending on the number of methylene units. Like copolyesters P_4 – P_{10} , they also exhibit odd–even dependency of melting temperatures (Fig. 6), enthalpy change (ΔH_m), and entropy change (ΔS_m) upon the number of methylene units in the spacer (Fig. 7). However, the transition temperatures are lower than those of corresponding copolyesters, which can be ascribed to their much lower molar mass.

Liquid Crystalline Behavior

The formation and stability of the mesophase depend on the amount of TDP units presented in the copolyesters. Decreasing the content of TDP will decrease the ratio of mesogenic units, resulting in an indistinct mesophase; for example, the copolyester from TDP/HD = 30/70 has endothermic peaks at 172 and 180°C (Table II). When the copolyester was observed by polarizing optical microscopy (POM), a birefringent texture was seen on melting at 172°C [Fig. 8(a)]. Meanwhile, certain regions become dark, but the birefringent domains remained until 180°C. The mesophase range ($T_i - T_m$) is very narrow and only 8°C. However, the mesophase ranges of copolyesters from TDP/HD = 40/60 and TDP/HD = 50/50 are expanded to 31°C and greater than 64°C, respectively. It is obvious that the mesophase range increases with mesogenic content. Under POM, they exhibit only nematic mesophase at melt [Fig. 8(b)] and their clearing temperatures are all above 300°C. Similarly, T_i was not observed in DSC thermograms, which may be attributed to low transition enthalpy.

Under cooling from isotropic melt, the model compounds M_8 and M_{10} first appear with batonet texture and star texture, respectively. These structures gradually combine to a fan-shaped texture, which is typical for the smectic LC phase.²⁰ However, for M_4 – M_7 and M_9 , luminous droplet texture is observed first and then grows into schlieren texture of nematic mesophase. For M_8 and M_{10} , paral-

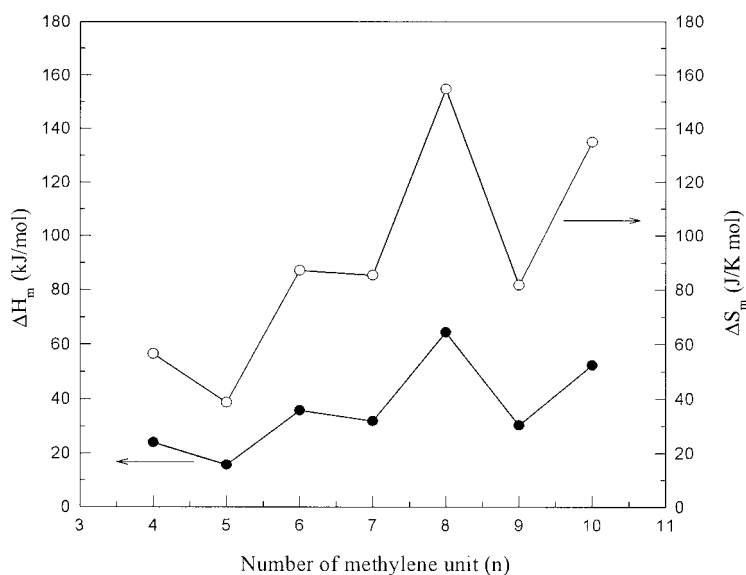


Figure 7 ΔH_m (●) and ΔS_m (○) of model compounds M_4 – M_{10} .

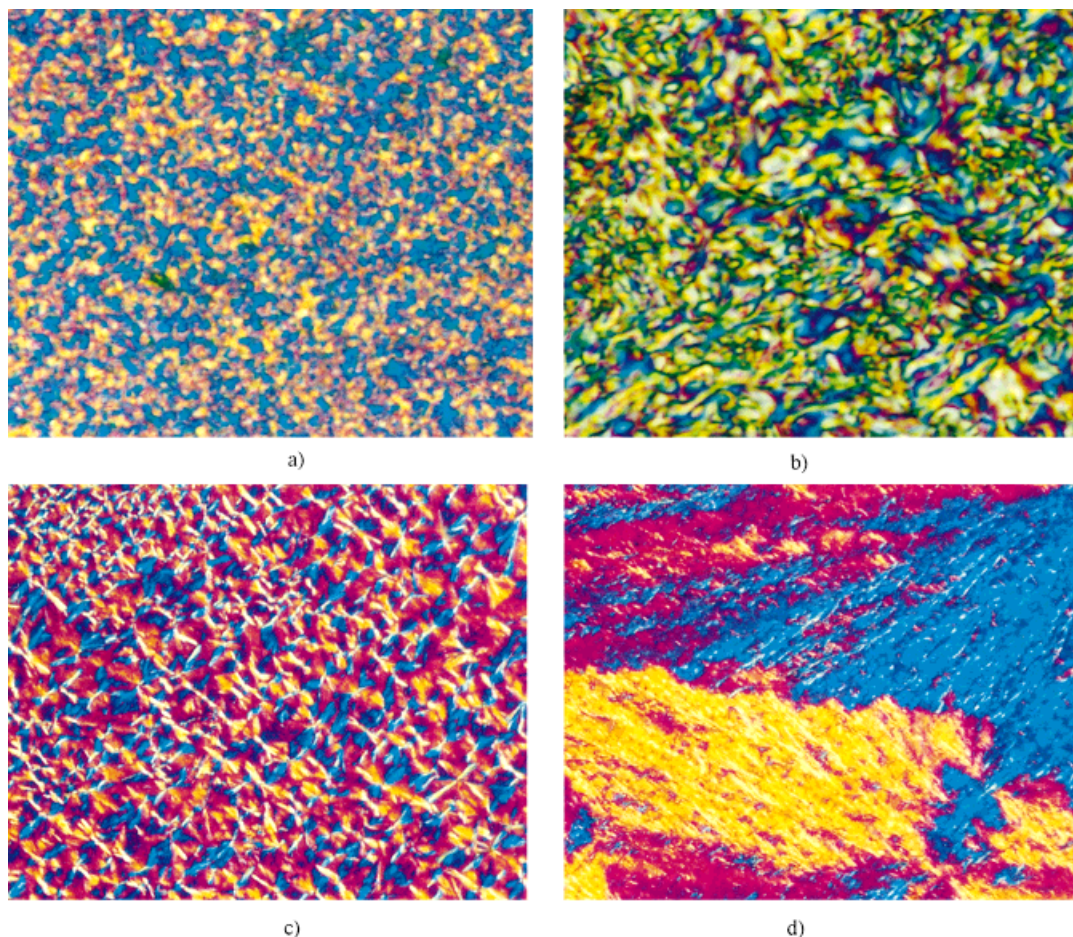


Figure 8 Photomicrographs of the copolyesters: (a) TDP/HD = 30/70 at 175°C ($\times 400$); (b) \mathbf{P}_{10} at 240°C ($\times 400$); (c) compound \mathbf{M}_{10} at 100°C ($\times 40$); (d) compound \mathbf{M}_9 at 120°C ($\times 40$).

lel molecular packing is possible because of their long flexible spacer and could form as ordered smectic phase. In the case of copolyesters, nonlinear thiodiphenyl groups prevent parallel molecular packing required for the smectic phase. However, although \mathbf{M}_9 possesses a longer spacer than that of \mathbf{M}_8 , the mesogenic units on both ends of the spacer form an angle of about 120°. Accordingly, the molecules are difficult to align in parallel form and only nematic texture could be observed. The example LC textures of \mathbf{M}_{10} and \mathbf{M}_9 are shown in Figure 8(c) and (d), respectively.

CONCLUSIONS

A series of new copolyesters, containing 2,6-naphthalene dicarboxylate, kinked 4,4'-thiodiphenyl unit, and polymethylene spacer, were prepared by solution polycondensation in diphenyl oxide at

200°C. Corresponding model compounds were also synthesized for comparison in thermal investigation. Both copolymers and model compounds exhibit odd-even dependency of melting temperatures, enthalpy (ΔH_m), and entropy (ΔS_m) on the number of methylene units in the spacer. Nematic mesophase is the only LC texture for the copolyesters, whereas for the model compounds with longer methylene units ($n = 8, 10$) the smectic mesophase can be observed.

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