Macromolecules **1987**, *20*, 2340–2344

(6) Hashimoto, K.; Hogen-Esch, T. E. *Macromolecules* **1983**, *16*, 1809.

(7) Hogen-Esch, T. E.; Jenkins, W. L. *Macromolecules* **1981**, *14*, 510.

(8) Hogen-Esch, T. E.; Jenkins, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 3666.

(9) Khan, I. M.; Hogen-Esch, T. E. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 569.

(10) Khan, I. M. Ph.D. Dissertation, University of Florida, 1984.

(11) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.

(12) Furue, M.; Sumi, K.; Nozakura, S. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 291.

(13) Bovey, F. A.; Hood, F. P.; Anderson, E. W.; Synder, L. C. *J. Chem. Phys.* **1965**, *42*, 3900.

(14) Meverden, C. C. Ph.D. Dissertation, University of Florida, 1983.

(15) Mathis, C.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1982**, *104*, 634.

(16) Laupretre, F.; Jasse, B.; Monnerie, L. *C. R. Acad. Sci. Paris* **1975**, *280*, 1255.

(17) Soum, A. H.; Hogen-Esch, T. E. *Macromolecules* **1985**, *18*, 690.

(18) Bovey, F. A. *High Resolution NMR of Macromolecules*, Academic: New York, 1972; pp 157–166.

(19) Sato, H.; Tanaka, Y.; Hatada, K. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 181.

(20) Matsuzaki, K.; Kanai, T.; Matsubara, T.; Matsumoto, S. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1475.

(21) Persistence ratio $\rho = 2(m)(r)/(mr)$

(22) Elias, H.-G. *Macromolecules*; Plenum; New York, 1977; p 584.

(23) Khan, I. M.; Hogen-Esch, T. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1986**, 27(1), 159.

(24) Okamoto, Y.; Suzuki, K.; Yuki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3043.

(25) Yuki, H.; Ohta, K.; Okamoto, Y.; Hatada, K. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 589.

Liquid Crystalline Compounds and Polymers from Promesogens

James C. W. Chien,* Renmo Zhou, and C. Peter Lillya*

Department of Polymer Science and Engineering, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

Received February 24, 1987

ABSTRACT: Alkyl 4-[(4-alkoxybenzoyl)oxy]benzoates (with C_1–C_{10} alkyl and alkoxy groups) are monotropic compounds which melt directly to isotropic liquids. Twin liquid crystalline compounds, TLCC's of [(alkoxybenzoyl)oxy]benzoic acid have been synthesized. The TLCC with methoxy end groups and trioxyethylene spacer is weakly mesogenic, but replacement of the methoxy with an *n*-butoxy end group results in a smectic mesophase. With the decamethylene spacer, the TLCC with a methoxy end group shows a nematic mesophase, whereas the compound with *n*-butoxy end groups exhibits both smectic and nematic mesophases. The latter has much higher ordered liquid crystalline states than the former. The polymeric TLCC's with *n*-butoxy end groups and $\bar{M}_n$ = 650 poly(THF) and $\bar{M}_n$ = 725 poly(propylene oxide) spacers display weak liquid crystalline order with only one mesophase transition. Decreasing the $\bar{M}_n$ of the poly(propylene oxide) spacer to 425 resulted in much stronger liquid crystalline order, exhibiting both smectic and nematic phases. It is suggested the microphase separation due to dissimilar solubility parameters can be an important contributing factor toward mesophase formation.

Introduction

Several types of twin liquid crystalline compounds (TLCC's) have been synthesized and characterized recently.[1-6] Most were prepared by coupling two mesogenic units with an aliphatic spacer, usually $(CH_2)_n$ (n = 2–12). The thermodynamic data show an even–odd effect for n. The purpose of this work is 2-fold. First, we demonstrate that coupling of two promesogenic (PM) units with either monodisperse $(CH_2)_n$ or $(CH_2CH_2O)_n$ spacers yielded TLCC's. Second, we show that twin liquid crystalline polymers (TLCP's) can be obtained by coupling the same PM cores with α,ω-dihydroxy-terminated poly(THF) and poly(propylene oxide) (poly(PPO)).

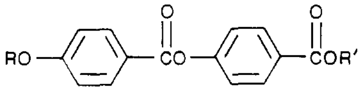
Experimental Section

Materials. 4-Methoxybenzoyl chloride, 4-butoxybenzoyl chloride, 4-hydroxybenzoic acid, ethanol, propanol, decanediol, and triethylene glycol were all obtained from Aldrich Chemical Company. 4-Methoxybenzoyl chloride was distilled at 117–118 °C/14 mm, 4-butoxybenzoyl chloride was distilled at 160 °C/8 mm, and 4-hydroxybenzoic acid was dried at 85 °C in vacuo for 1 h, mp 215–217 °C. Ethanol and propanol were refluxed with magnesium and distilled. Decanediol was vacuum dried at 60 °C for 5 h. Triethylene glycol was dried over anhydrous $MgSO_4$ and distilled at 137 °C/0.5 mm. α,ω-Dihydroxy-terminated poly(THF) (MW 650) and poly(PPO) (MW 425 and 725) were obtained from Polyscience, Inc.

4-[(4-Alkoxybenzoyl)oxy]benzoic acids were prepared by reaction of the appropriate 4-alkoxybenzyl chloride with 4-hydroxybenzoic acid in pyridine at 0 °C for 20 h. The products were precipitated with dilute aqueous HCl, washed to neutrality with distilled water, and recrystallized. The compounds have the literature thermotropic transitions: 4-[(4-methoxybenzoyl)oxy]benzoic acid ($T_{K\text{-}L}$ = 210 °C, $T_{L\text{-}I}$ = 270 °C);[7] 4-(4-butoxybenzoxy)benzoic acid ($T_{K\text{-}L}$ = 160 °C, $T_{L\text{-}I}$ = 260 °C).[8]

4-[(4-Alkoxybenzoyl)oxy]benzyl chloride was obtained by refluxing the corresponding acid in an excess of purified thionyl chloride. After vacuum removal of all volatile substances, the products were used without further purification. Their melting points are in agreement with literature values: [(4-methoxybenzoyl)oxy]benzoyl chloride (T_m = 140 °C); [(4-butoxybenzoyl)oxy]benzoyl chloride (T_m = 78 °C).

Synthesis. Promesogens were prepared by reaction of 1 equiv of the appropriate 4-[(4-alkoxybenzoyl)oxy]benzoyl chloride dissolved in dry dioxane with 1.5 equiv of alcohol. The reaction mixture containing excess pyridine was refluxed overnight and then was poured into stirred distilled water. The precipitated product was washed in succession with 3% aqueous HCl, aqueous $NaHCO_3$, and water and was purified by preparative thin-layer chromatography on silica. Samples used for optical and thermal studies were homogeneous on thin-layer chromatography. These compounds exhibit intense infrared absorptions at 1730 and 1715 cm^{-1} for the aryl benzoate and alkyl benzoate carbonyls, respectively, and at least five bands in the C–O stretch region from 1000 to 1300 cm^{-1}. The structures of the four promesogens are



I

a, R = methyl, R′ = *n*-propyl
b, R = *n*-butyl, R′ = ethyl
c, R = *n*-butyl, R′ = *n*-propyl
d, R = *n*-butyl, R′ = *n*-decanyl

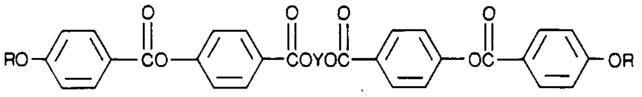
The procedure described above for promesogens was also used here with the α,ω-diols (decane-1,10-diol and triethylene glycol),

0024-9297/87/2220-2340$01.50/0

Table I
Monotropic Exotherms of Monoesters during Cooling from Melt

	I-a		I-b		I-c		I-d	
cooling rate, °C/min	$T_{I\text{-}L}$	$T_{L\text{-}K}$	$T_{I\text{-}L}$	$T_{L\text{-}K}$	$T_{I\text{-}L}$	$T_{L\text{-}K}$	$T_{I\text{-}L}$	$T_{L\text{-}K}$
40	23.1	18.0	66.0	62.1	54.7	43.4		
20	35.5	32.7	70.6	68.5	58.6	50.2		
10		41.0	72.8	70.3	60.0	52.0	47.3	28.1
5		43.0	75.8	74.6	61.0	53.4	48.1	30.6
2		44.2			62.3	54.8	48.3	34.0

poly(THF), and PPO to obtain twin liquid crystalline compounds (TLCC's) and to obtain twin liquid crystalline polymers (TLCP's). Products were purified by using preparative thin-layer chromatography on silica, and samples used for optical and thermal studies were homogeneous to thin-layer chromatography. The structures for the TLCC's are



II

a, R=methyl; Y=$CH_2(CH_2OCH_2)_2CH_2$
b, R=n-butyl; Y=$CH_2(CH_2OCH_2)_2CH_2$
c, R=methyl; Y=$-(CH_2)_{10}-$
d, R=n-butyl; Y=$-(CH_2)_{10}-$

The structures for the TLCP's are as follows: III-a, R = n-butyl, Y = $-(CH_2CH_2CH_2CH_2O)_{7.9}CH_2CH_2CH_2CH_2-$; III-b, R = n-butyl, Y = $-(CH_2CHMeO)_{10.7}CH_2CHMe-$; III-c, R = n-butyl, Y = $-(CH_2CHMeO)_{5.2}CH_2CHMe-$.

End group analysis by ^{1}H NMR yielded the following experimental values for the average number of repeat units in the polymeric spacers: III-a, $n = 8.9 \pm 0.1$ (nominal value 8.8); III-b, $n = 11.7 \pm 0.1$ (nominal value 12.2); and III-c, $n = 6.2 \pm 0.2$ (nominal value 7.0).

Methods. Elemental analyses were carried out by the Microanalytical Lab of the University of Massachusetts. Infrared spectra were recorded with a Perkin-Elmer 1420 IR spectrophotometer. ^{1}H NMR spectra were obtained with Varian XL-300 and XL-200 spectrometers using deuteriochloroform as solvent and TMS as an internal standard.

The observed (calculated) analyses are as follows. I-a: C, 68.31 (68.78); H, 6.0 (5.78). I-b: C, 70.32 (70.16); H, 6.34 (6.48). I-c; C, 70.73 (70.78); H, 6.71 (6.79). I-d: C, 73.81 (73.98); H, 8.07 (8.43). II-a: C, 65.70 (65.65); H, 5.15 (5.20). II-b: C, 67.74 (67.91); H, 6.33 (6.24). II-c: C, 70.17 (70.37); H, 5.85 (6.20). II-d: C, 72.24 (72.04); H, 7.22 (7.10).

The ^{1}H NMR results for promesogens ($CDCl_3$) are as follows: I-a: δ 1.08 (t, 3 H, CH_3),[9] 1.75 (m, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 4.30 (t, 2 H, OCH_2), 6.92–7.37 (m, 4 H, $H_{3,5}$-oxybenzoate), 8.07–8.26 (t, 4 H, $H_{2,6}$-oxybenzoate). I-b: δ 0.99 (t, 3 H, butyl CH_3), 1.40 (t, 3 H, ethyl CH_3), 1.56 (s, 2 H, CH_2), 1.81 (quin., 2 H, CH_2), 4.05 (t, 2 H, butyl OCH_2), 4.37 (q, 2 H, ethyl OCH_2), 6.98 (d, 2 H, $H_{3,5}$-oxybenzoate), 7.29 (d, 2 H, $H_{3,5}$-oxybenzoate), 8.12 (q, 4 H, $H_{2,6}$-oxybenzoate). I-c: δ 1.02 (2t, 6 H, $2CH_3$'s), 1.51 (sextet, 2 H, CH_2), 1.80 (m, 4 H, CH_2), 4.04 (t, 2 H, butyl OCH_2), 4.28 (t, 2 H, propyl OCH_2), 6.97 (d, 2 H, $H_{3,5}$-oxybenzoate), 7.28 ($H_{3,5}$-oxybenzoate), 8.12 (q, 4 H, $H_{2,6}$-oxybenzoate).

The TLCC NMR are as follows: II-a: δ 3.7–3.9 (two apparent singlets, 8 H, analyzed as OCH_3, H_β), 4.45 (m, 4 H, H_α), 6.95–7.40 (m, 8 H, $H_{3,5}$-oxybenzoate), 8.16 (d, 8 H, $H_{2,6}$-oxybenzoate). II-b: δ 0.96 (t, 6 H, CH_3), 1.49 (m, 4 H, butyl CH_2), 1.77 (m, 4 H, butyl CH_2), 3.70 (apparent s, 4 H, H_δ), 3.80 (apparent s, 4 H, H_β), 4.01 (t, 4 H, butyl OCH_2), 4.45 (apparent s, 4 H, H_α), 6.94 (d, 4 H, $H_{3,5}$-oxybenzoate), 7.26 (d, 4 H, $H_{3,5}$-oxybenzoate), 8.10 (d, 8 H, $H_{2,6}$-oxybenzoate). II-c: δ 1.34 (m, 12 H, $H_{\gamma-\epsilon}$), 1.77 (quin., 4 H, H_β), 3.90 (s, 6 H, OCH_3), 4.33 (t, 4 H, H_α), 6.98 (d, 4 H, $H_{3,5}$-oxybenzoate), 7.30 (d, $H_{3,5}$-oxybenzoate), 8.13 (q, 8 H, $H_{2,6}$-oxybenzoate). II-d: δ 1.00 (t, 6 H, CH_3), 1.31 (m, 16 H, CH_2), 1.78 (m, 8 H, butyl and decamethylene H_β), 4.06 (t, 4 H, butyl OCH_2), 4.32 (t, 4 H, H_α), 6.96 (d, 4 H, $H_{3,5}$-oxybenzoate), 7.30 (d, 4 H, $H_{3,5}$-oxybenzoate), 8.13 (q, 8 H, $H_{2,6}$-oxybenzoate).

The ^{1}H NMR results for TLCP are as follows: III-a: δ 1.00 (t, 6 H, CH_3), 1.63 (m, 39 H, butyl H_γ), 1.84 (m, 8 H, butyl H_β), 344 (m, 31 H, THF CH_2), 4.06 (t, 4 H, butyl H_α), 4.35 (t, 4 H, CH_2 ester), 6.99 (d, 4 H, 3,5-oxybenzoate), 7.3 (d, 4 H, 3,5-oxybenzoate), 8.13 (t, 8 H, 2,6-oxybenzoate). III-b: δ 0.98 (t, 6 H, CH_3), 1.10 (d, 30 H, PPO CH_3), 1.34 (d, 6 H, PPO α,ω-CH_3), 1.50 (m, 4 H, butyl H_γ), 1.79 (m, 4 H, butyl H_β), 3.53 (m, 34.6, PPO CH_2CH), 4.03 (t, 4 H, butyl H_α), 5.26 (m, 2 H, CH ester), 6.93 (d, 4 H, 3,5-oxybenzoate), 7.24 (d, 4 H, 3,5-oxybenzoate), 8.06 (t, 8 H, 2,6-oxybenzoate). III-c: δ 0.98 (t, 6 H, butyl CH_3), 1.20 (s br, 15 H, PPO CH_3), 1.33 (apparent t, 6 H, PPO α,ω-CH_3), 1.50 (apparent quin, 4 H, γ-CH_2), 1.80 (apparent q, 4 H, β-CH_2), 3.3–3.75 (br, 16.7 H, PPO CH_2CH), 4.04 (apparent q, 4.2 H, OCH_2 of butyl and α,ω-CH_2's of PPO), 5.25 (br, 1.8 H, α- and ω-OC*H*Me of PPO), 6.93 (d, 5 H, 3,5-oxybenzoate), 7.25 (d, 4 H, 3,5-oxybenzoate), 8.09 (br s, 8 H, 2,6-oxybenzoate).

The actual molecular weight of Y in TLCP can be calculated from the intensity ratios. For III-a, the average value of $n = 8.9 \pm 0.1$, as compared to calculate value of 8.8 from poly(THF) MW. For III-b, the average value of $n = 11.7 \pm 0.1$ from NMR intensity ratios; it is 12.2 for the MW of poly(PPO). For III-b, the average value of $n = 6.9 \pm 0.1$ from NMR intensity ratios; it is 7.0 for the MW of poly(PPO).

Thermal behavior was determined with a Perkin-Elmer DSC-4 instrument under a nitrogen atmosphere. The heating rate was 20 °C/min, and the cooling rate was 10 °C/min. The values of ΔH_i and ΔS_i were calculated from the endothermic peak areas in the thermogram and the weight of the sample. Indium (ΔH_m = 6.8 cal/g) was the standard.

A Leitz polarizing microscope with a Mettler FP-2 hot stage was used for optical studies of phase changes and mesophase textures.

Results and Discussion

Promesogens. The promesogens are all crystalline compounds. The T_m's as found by microscopy were 76–78, 87–89, 77–79, and 62–63 °C for I-a, I-b, I-c, and I-d, respectively; the corresponding T_m's according to DSC were 83, 93, 83, and 66 °C. The compounds exhibit intense absorptions at 1730 and 1715 cm^{-1} for the carbonyl vibration in the phenyl benzoate and alkyl benzoate, respectively, and at least five bands in the C–O stretching region from 1000 to 1300 cm^{-1}.

When heated under a polarizing microscope, the promesogens melt to clear liquids within 1–2 deg, and they have only one very sharp DSC transition. Compound I-a has been reported as monotropic. Such a substance has metastable mesophase existing just below T_m; its existence may be seen upon supercooling of the isotropic melt before crystallization occurs, where behavior varies with the cooling rate. This monotropic characteristic was observed for I-b and I-c as well (Table I). In the case of I-a, only one exotherm was seen at slow cooling rates, <10 °C min^{-1}. At more rapid cooling rates and for all cooling rates in the cases of I-b–d, there are two exotherms assigned to isotropic-to-LC and LC-to-crystalline transitions. The temperature range $\Delta T = T_{I\text{-}L} - T_{L\text{-}K}$ is larger for higher cooling rates. However, ΔT is only a few degrees for compounds I-a–c; it is much greater for I-d ($\Delta T = 16 \pm 2$ °C) as shown in Figure 1.

When compounds I-a–c were examined by polarizing microscope, only crystal-to-isotropic changes were observed upon heating and vice versa upon cooling. Under certain conditions, one might have a fleeting glance of mesophase. The incorporation of decanyl end group in I-d resulted in

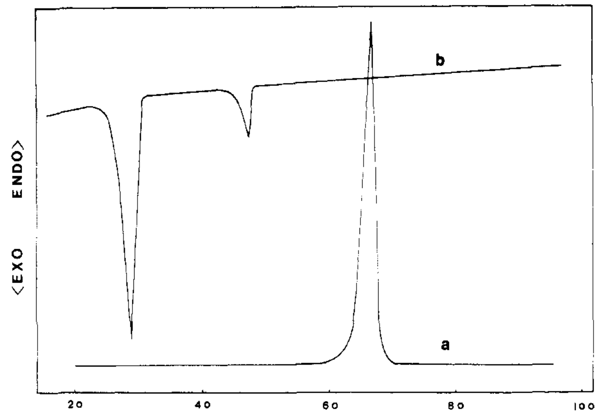


Figure 1. DSC thermograms of promesogen I-d: (a) heating scan; (b) cooling scan. First and subsequent heating give identical results.

the appearance of mesophase 14 °C below T_m and substantial temperature separation between T_{I-L} and T_{L-K}. Therefore the mesophase was readily observed by microscopy for this compound with the classical fan texture.

Twin Liquid Crystalline Compounds. Compounds II-b–d all exhibit definite liquid crystalline transitions. TLCC II-a is the exception; it becomes cloudy between 64 and 72 °C and forms a clear liquid at 115 °C. Polarizing microscopy at 99 °C showed mesophase formation but without well-defined textures. DSC of this compound is extremely sensitive to heating and cooling rates as well as annealing conditions. Up to five endothermic peaks were found at ca. 53, 59, 64, 67, 78 °C; their relative peak areas are quite variable. The compound shows a very weak endotherm at about 20 °C or none at all in other DSC scans. One might expect annealing to have a significant effect on the thermotropic transitions of II-a. Increasing the annealing temperature shifts the multiple entotherms to slightly higher temperatures, like in slowly cooled specimens. All evidence indicates II-a to be marginally liquid crystalline substances.

The DSC behavior of compounds II-b–d is less sensitive to thermal history and is more reproducible on repeated heating and cooling cycles. In general, at the highest temperature transition, there is a single endotherm corresponding to the transition from a liquid crystal phase to the isotropic phase. Transitions from crystal-to-liquid crystal are marked by one or more endotherms. When multiple peaks were observed, the highest temperature one was attributed to the crystal–mesophase transition. Hot-stage polarizing microscopy yielded no evidence for fluidity below this transition. The lower temperature peak must represent undefined crystal–crystal transitions; the peaks are broad and separated by relatively small temperature differences. Identification of the nature of these phase changes will be difficult. It is possible that these diesters are polymorphic; multiple melting peaks are not uncommon for polyesters.[10]

DSC scans of compound II-b are shown in Figure 2 for heating (a) and cooling (b); the first and subsequent heatings give identical results. The liquid crystal-to-isotropic transition is a broad one centered at 104 °C; the crystal to liquid crystal transition occurs at 74 °C. In a Mel-Temp apparatus, the melt transition was observed between 50 and 80 °C; at 130 °C, the melt is clear. There is a crystal-to-crystal transition at 59 °C. The cooling scan (Figure 2b) has two broad exotherms at 103 and 70 °C. Under polarizing microscope, II-b has a fanlike or focal conic texture at 86 °C, suggesting strongly a smectic morphology.

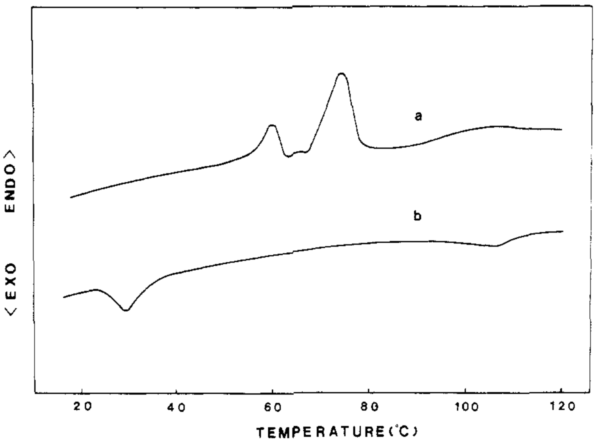


Figure 2. DSC thermograms of TLCC II-b: (a) heating scan; (b) cooling scan. First and subsequent heating give identical results.

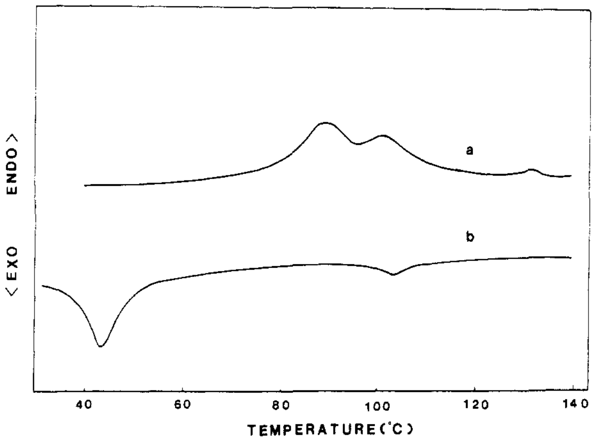


Figure 3. DSC thermograms of TLCC II-c: (a) second and subsequent heating scans; (b) cooling scan.

The first heating of TLCC II-c gives broad unresolved transitions in the 80–100 °C region. The DSC curves for all subsequent heatings (Figure 3) resembled that for II-b (Figure 2). Crystal–crystal, crystal–nematic, and nematic–isotropic transitions are centered at 90, 101, and 129 °C, respectively. On cooling, isotropic-to-liquid crystal and liquid crystal-to-crystal transitions are found at 104 and 43 °C, respectively. In the melting point apparatus, the material becomes a cloudy fluid at 94–97 °C and is clear at 132 °C. A photomicrograph at 95 °C revealed a classic Schlieren texture, suggesting a nematic mesophase. Above 100 °C, polarizing microscope showed coexistence of isotropic and nematic mesophases. Cooling from the isotropic state to 70 °C produced a mixture of spherulites in a nematic–liquid crystal phase.

DSC heating scans for II-d remain substantially unchanged from the first heating to subsequent heatings. The compound exhibits both smectic and nematic mesophase in passage from the crystal to the isotropic state.[11,12] Polarizing microscopy showed well-defined elliptical focal conic texture for the smectic mesophase and the Schlieren texture for the nematic mesophase.[13,14] The DSC scans (Figure 4) showed crystal-to-crystal, crystal-to-smectic, smectic-to-nematic, and nematic-to-isotropic transitions at 73, 80, 107, and 115 °C, respectively. There are, upon cooling, three exotherms at 109, 104, and 47 °C.

The thermal properties of TLCC's are summarized in Table II.

Twin Liquid Crystalline Polymers. Thermal behavior of TLCP's III-a–e is simpler than that of the low molecular weight twins. Both III-a and III-b exhibited two

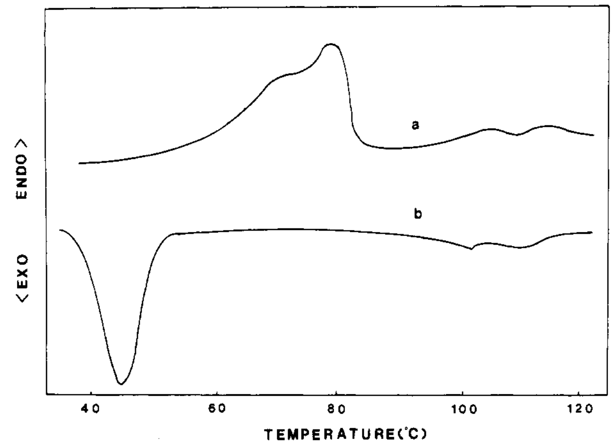


Figure 4. DSC thermograms of TLCC II-d: (a) second heating scan; (b) cooling scan.

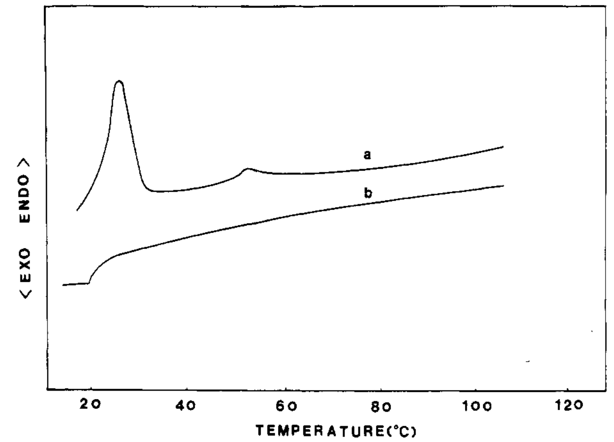


Figure 5. DSC thermograms of TLCP III-a: (a) heating scan after rapid quench from isotropic state; (b) cooling scan.

Table II
Thermal Properties of TLCC's

compd	transitions[a]	thermodynamic parameters
II-a	$K \xrightarrow[72\ ^\circ C]{\sim 64\ ^\circ C} M \xrightarrow{\sim 115^\circ C} I$	
II-b	$K_1 \xrightarrow{59\ ^\circ C} K_2 \xrightarrow{74\ ^\circ C} S \xrightarrow{104\ ^\circ C} I$	$\Delta H_{S\text{-}I}$ = 757 cal mol^{-1} $\Delta S_{S\text{-}I}$ = 2.0 cal mol^{-1} K^{-1}
II-c	$K_1 \xrightarrow{90\ ^\circ C} K_2 \xrightarrow{101\ ^\circ C} N \xrightarrow{129\ ^\circ C} I$	$\Delta H_{N\text{-}I}$ = 53 cal mol^{-1} $\Delta S_{N\text{-}I}$ = 0.13 cal mol^{-1} K^{-1}
II-d	$K_1 \xrightarrow{73\ ^\circ C} K_2 \xrightarrow{80\ ^\circ C} S \xrightarrow{107\ ^\circ C}$ $N \xrightarrow{115\ ^\circ C} I$	$\Delta H_{N\text{-}I}$ = 307 cal mol^{-1} $\Delta S_{N\text{-}I}$ = 0.79 cal mol^{-1} K^{-1}
III-a	$K \xrightarrow{26\ ^\circ C} M \xrightarrow{48\ ^\circ C} I$	$\Delta H_{M\text{-}I}$ = 434 cal mol^{-1} $\Delta S_{M\text{-}I}$ = 1.35 cal mol^{-1} K^{-1}
III-b	$K \xrightarrow{27\ ^\circ C} M \xrightarrow{55\ ^\circ C} I$	$\Delta H_{M\text{-}I}$ = 27 cal mol^{-1} $\Delta S_{M\text{-}I}$ = 0.08 cal mol^{-1} K^{-1}
III-c	$K \xrightarrow{49\ ^\circ C} S \xrightarrow{67\ ^\circ C} N \xrightarrow{80\ ^\circ C} I$	$\Delta H_{N\text{-}I}$ = 377 cal mol^{-1} $\Delta S_{N\text{-}I}$ = 1.07 cal mol^{-1} K^{-1}

[a] Phases are K = crystal, M = mesophase of unspecified nature, N = nematic, S = smectic, I = isotropic.

transitions, one near room temperature and the second near 50 °C on the first heating and all subsequent heatings (Figures 5 and 6). The values of $\Delta H_{K\text{-}M}$ are typically higher on the first heating. TLCP III-c with a relatively short spacer exhibits more complex behavior. The first heating gave a single transition at ca. 50 °C; two were observed on the second heating, while the third and all subsequent heatings produced three reproducible transitions (Figure 7, Table II). Optical polarizing microscopy confirmed the formation of fluid, birefringent phases, and even of two different liquid crystalline phases in the case of III-c. Optical birefringence of these phases is weak, probably owing to dilution of mesogen by long spacers, and no characteristic texture was observed. Thus, while it is reasonable that the two mesophases exhibited by III-c are smectic and nematic, no evidence for this is at hand.

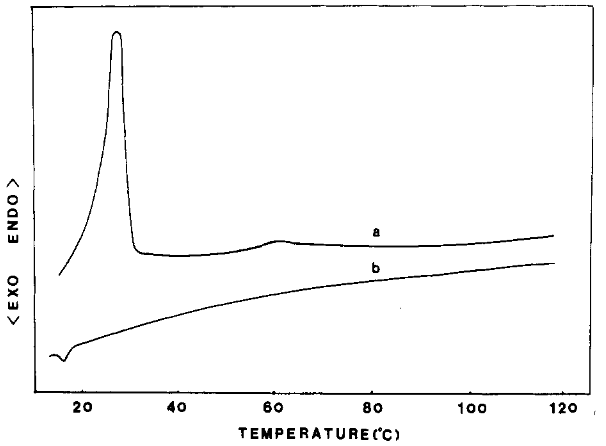


Figure 6. DSC thermograms of TLCP III-b: (a) heating scan after rapid quench from isotropic state; (b) cooling scan.

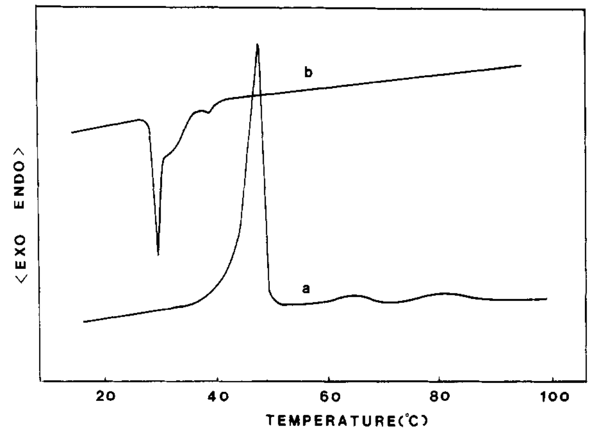


Figure 7. DSC thermogram of TLCP III-c: (a) heating scan after rapid quench from isotropic states; (b) cooling scan.

Conclusions

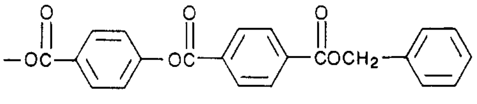
Replacing the short methoxy group at the mesogen terminus with a longer flexible *n*-butoxy group noticeably enhances mesophase formation and results in higher ordering. For example, II-a appears to be a borderline liquid crystalline material, while its butyl analogue II-b exhibits a well-defined smectic mesophase. Only the butoxy compounds exhibit the more highly ordered smectic-type mesophases. Clearing entropies suggest that the nematic phase of II-d (ΔS_C = 0.79 cal M^{-1} K^{-1}) is more highly ordered than that of II-c (ΔS_c = 0.13 cal M^{-1} K^{-1}). This effect of linear alkyl groups enhancing liquid crystallinity is well-known and may be manifest in the effects observed when the triethylene glycol spacer is changed to the stiffer decamethylene spacer. The decamethylene derivatives exhibit higher temperature crystal-to-mesophase and clearing transitions as expected from greater spacer rigidity. The decamethylene compounds exhibit either more pronounced liquid crystallinity, II-a vs. II-c or an enhanced mesophase temperature domain, II-b vs. II-d.

Of the greatest significance is the behavior of TLCP (III-a–c) with polymeric spacers. The possibility that the 26 °C transition of III-a is simply a melting of the poly(THF) spacer is belied by the almost identical behavior of III-b which has a noncrystallizable PPO spacer with a very low intrinsic glass transition temperature. These samples consist of two promesogens joined by flexible poly(THF) and poly(PPO) chains.

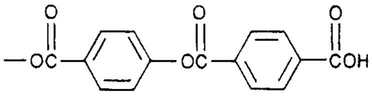
In III-c, promesogens are connected by a flexible chain that averages 18.6 backbone atoms, and only 64 wt % promesogen is present. Compounds III-b and -a have spacers which average 35 and 44.5 backbone atoms, respectively, and are only 52 and 50 wt % promesogen. The vol % promesogen in these samples will be even lower than wt %. Nevertheless, liquid crystalline behavior is clear with a mesophase which is stable over a 22–31 °C temperature range. Clearing entropies exceed those observed for TLCC's in several cases, indicating well-ordered mesophases.

Decreasing T_{K-M} and clearing temperatures as the same promesogen is separated by longer polyether spacers, compare II-b, III-c and III-a or -b, suggest that longer spacers may lead to TLCP's which are liquid crystalline at room temperature. PPO or a similar amorphous spacer would be the best choice. Crystallization of longer poly(THF) spacers could prevent low-temperature liquid crystallinity.

Our results invite comparison with the observations of Lenz et al.[6] who investigated long-chain diols capped with mesogens IV and V



IV



V

Derivatives of V probably owe their enhanced liquid crystalline properties to formation of carboxylic acid dimers which doubles the axial ratio and volume of each mesogen. However, those of mesogen IV should be closely analogous to our III-a. Lenz studied poly(ethylene oxide), poly(THF), polybutadiene, and hydrogenated polybutadiene spacers both longer and shorter than ours. Poly(THF) of either $\bar{M}_n$ = 650 or 1650 failed to give liquid crystalline derivatives. In fact, only one of seven compounds, that with a poly(ethylene oxide) spacer, $\bar{M}_n$ = 1760, exhibited a mesophase, and that was stable over a range of only five degrees.

We feel that an important factor favoring mesophase formation in our compounds in which two small promesogens are connected by a long flexible chain is that the aromatic end groups and the poly(THF) or poly(PPO) spacer possess very different solubility parameters, leading to a strong tendency toward microphase separation of mesogen from spacer. This would be analogous to the well-known phenomenon of phase separation in block copolymers. We suggest that phase separation can be an important contributing factor toward mesophase formation in these and related materials which possess relatively low-volume percentages of mesogen.

Acknowledgment. This work is supported by a grant from the Office of Naval Research.

Registry No. I-9, 50649-67-7; I-6, 90233-54-8; I-c, 110015-72-0; I-d, 110015-73-1; II-a, 110015-74-2; II-b, 110015-75-3; II-c, 110015-76-4; II-d, 110015-77-5; III-a, 110015-78-6; III-b, 110015-79-7.

References and Notes

(1) Griffin, A. C.; Britt, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 4957.
(2) Blumstein, R. B.; Stickles, E. M.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 205.
(3) Jin, J. I.; Park, J. H. *Mol. Cryst. Liq. Cryst.* **1983**, *149*, 92.
(4) Buglione, J. A.; Roviello, A.; Sirigu, A. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 169.
(5) Emsley, J. W.; Luckhurst, G. R.; Shilstone, G. N.; Sage, I. *Mol. Cryst. Liq. Cryst.* **1984**, *102*, 223.
(6) Hoshio, H.; Jin, J. I.; Lenz, R. W. *J. Appl. Polym. Sci.* **1984**, *29*, 547.
(7) Beguin, A.; Dubois, J. C.; LeBarry, P.; Billard, J.; Bonamy, F.; Buisine, J. M.; Cavelier, P. *Mol. Cryst. Liq. Cryst.* **1984**, *115*, 1.
(8) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Basel, 1980.
(9) The NMR multiplet descriptions are s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet.
(10) vanMeter, J. P.; Klanderman, B. H. *Mol. Cryst. Liq. Cryst.* **1973**, *22*, 271.
(11) Lader, H. J.; Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1661.
(12) Brown, G. H. *Chem Eng. New.* **1983**, *24* (Jan.), 31.
(13) Strzelecki, L.; VanLugen, D. *Eur. Polym. J.* **1980**, *16*, 299.
(14) Domus, D.; Richter, L. *Texture of Liquid Crystal*; Verlag Chemie: WeinHeim, 1978.