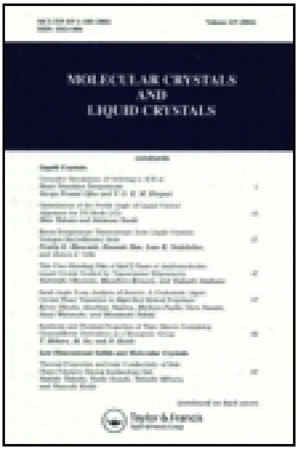

Molecular Crystals and Liquid Crystals

Synthesis and Properties of Liquid Crystalline 4,4″-Dialkoxy-2″-Methyl-P-Terphenyls

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SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALLINE 4,4″-DIALKOXY-2′-METHYL-p-TERPHENYLS

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A new series of laterally substituted terphenyl compounds, 4,4″-dialkoxy-2′-methyl-p-terphenyls ($n = 1$–12), were synthesized. Their liquid crystallinities were characterized by means of polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The influence of the length of the terminal alkoxy groups on the liquid crystalline behavior was investigated. It was found that the compounds with shorter end chains ($n \leq 8$) tended to form nematic mesophases. However, a smectic A mesophase is exhibited for those with longer end chains ($9 \leq n \leq 12$).

Keywords: liquid crystal; 4,4″-dialkoxy-2′-methyl-p-terphenyl; 2,5-bis(4′-alkoxyphenyl)toluene

INTRODUCTION

Terphenyls are excellent building blocks of liquid crystals [1]. Compared to other rigid-rod–like mesogenic units with two or three benzene rings linked together by polar groups—such as Shiff-base, azo, azoxy, ester, and amide groups, which are susceptible to moisture, temperature change, and ultraviolet radiation—terphenyls are chemically, electrochemically, and photochemically very stable [2]. In addition, the strong π–π interaction among terphenyls also favors the self-organization of these calamitic units. Thus terphenyls have attracted considerable interest in the past few years. They have been used to generate liquid crystals either independently [3–5] or in conjunction with other good units such as cyclohexane [6].

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The compound 4,4″-didecyloxy-2′-methyl-p-terphenyl (**I-10**) as well as its derivatives were first synthesized and characterized by Tschierske and coworkers [7–10]. Their initial work was intended to evaluate what would happen to liquid crystal properties when a hydrophilic group was not terminally but instead laterally attached to a rigid core. These facial amphiphiles were able to form well-defined thin films at the air-water interface. In the pure state they exhibit smectic and/or rectangular columnar mesophases. In solution up to three different rectangular columnar mesophases have been found, depending on the size of the lateral hydrophilic groups and solvents used. Recently a similar compound was used by us to prepare a new monomer for mesogen-jacketed liquid crystal polymers (MJLCPs) [11].

In low molecular weight liquid crystals, the terminal groups are important in determining the liquid crystalline nature of system. Unfortunately, little was known about the influence of the alkoxy chain length on the mesophase formation of this kind of laterally substituted terphenyl. In this article we shall report the synthesis and the characterization of a series of 4,4″-dialkoxy-2′-methyl-p-terphenyls ($n = 1-12$). The sizes of the terminal alkoxy groups were changed systematically, which allowed us to draw some conclusion about the influence of molecular structure on the occurrence of mesophases. In addition, the preparation of novel liquid crystalline monomers for MJLCPs and the formation of some supramolecular assemblies can also be achieved from these compounds or their derivatives.

EXPERIMENTAL SECTION

Materials

All solvents and reagents were used without further purification except as noted. Tetrahydrofuran (THF, Acros 99%) was heated under reflux over calcium hydride for at least 8 h and distilled before use.

Measurements

^{1}H spectra were obtained on a Varian Gemini2000 spectrometer (200 MHz) using $CDCl_3$ as solvent. Mass spectra were recorded on a Finnigan-MAT mass spectrometer. Elementary analyses were carried out on a Elementar Vario EL instrument. DSC curves were obtained using a TA DSC 2010 differential scanning calorimeter. Thermogravimetric analyses (TGA) were performed on a TA SDT 2960 instrument. Polarized optical microscopy (POM) observation was performed on a Leitz Laborlux 12 Pol microscope with Leitz 350 hot stage. Wide-angle X-ray diffraction was carried out on a Philips X′PERT (Cu-K_{α}, $\lambda = 0.154$ nm) with Anton Parr TTK 450 heating stage and Anton Parr TCU-100 thermal controller.

Synthesis

Synthesis of 4-bromophenol

This compound was synthesized following the method of Adams and Marvel [12]. Yield: 75%.

Syntheses of 4-alkoxy-1-bromobenzenes

4-Bromoanisole and 1-bromo-4-ethoxybenzene were prepared according to the procedures in the literature [13]. Other 4-alkoxy-1-bromobenzenes were synthesized using the method of Allen and Gates [14]. The yields of the products were 50–70%.

Synthesis of 4-alkoxyphenylboronic acids

4-Alkoxyphenylboronic acids were prepared in the same manner as the above example of 1-bromo-4-pentoxybenzene. To a rapidly stirred solution of 12.15 g (0.050 mol) of 1-bromo-4-pentoxybenzene and 150 mL of dry THF cooled to −78°C under an argon atmosphere was added 50 mL solution of n-butyllithium (1.2 M in hexane) dropwise over 30 min. The mixture was stirred for 2.5 h. A solution of 14 mL of commercial trimethyl borate in 30 mL of THF was added dropwise to the mixture (bath temperature was kept below −65°C). The solution was allowed to warm to room temperature and stirred for 8 h, and 30 mL of 10% aqueous HCl was added. The mixture was stirred for 1 h and then extracted with three portions of 80 mL of diethyl ether. The combined ethereal extract was washed with brine three times and dried over $MgSO_4$. Removal of the solvents under reduced pressure was followed by purification by recrystallization from hexane. The yield of the product was 55%.

Synthesis of 4,4″-dibutoxy-2′-methyl-p-terphenyl(I-4)

To a stirred solution of 10.23 g (0.053 mole) of 4-butoxyphenylboronic acid, 5.50 g (0.022 mole) of 2,5-dibromotoluene, and 1.2 g (0.001 mole) of tetrakis(triphenylphosphine)palladium in 55 mL of benzene under argon atmosphere was added 33 mL of ethanol and 25 mL of aqueous Na_2CO_3 (2 M). The mixture was heated to reflux with stirring for 40 h and then allowed to cool to room temperature. The layers were separated and the aqueous layer was extracted with three portions of 80 mL of chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel using CH_2Cl_2/light petroleum (1/6) as eluant. The yield was 79%. ^1H NMR (δ, ppm) 0.96–1.03 (t, $-O(CH_2)_3-CH$, 6H), 1.40–1.70(m, $-O(CH_2)_2\underline{CH}_2-$, 4H), 1.70–1.90(m, $-OCH_2-\underline{CH}_2-$, 4H), 2.34 (s, $-CH_3$, 3H), 3.98–4.04(t, $-OCH_2-$, 4H), 6.95–7.60(m, phenyl ring, 11H). Mass Spectrum (m/e): 388(parent, base), 332, 276, 247, 202. Elemental analysis calculated for $C_{27}H_{32}O_2$: C, 83.46; H, 8.30. Found: C, 83.27; H, 8.49.

4,4″-dimethoxy-2′-methyl-p-terphenyl(I-1). ^1H NMR (δ, ppm) 2.35(s, $-CH_3$, 3H), 3.86(s, $-OCH_3$, 6H), 6.95–7.59(m, phenyl ring, 11H). Mass Spectrum (m/e): 304(parent, base), 289, 261, 202, 152. Elemental analysis calculated for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.54; H, 6.62.

4,4″-diethoxy-2′-methyl-p-terphenyl(I-2). ^1H NMR (δ, ppm) 1.41–1.48(t, $-OCH_2-\underline{CH}_3$, 6H), 2.34(s, $-CH_3$, 3H), 4.03–4.14(q, $-OCH_2-$, 4H), 6.93–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 332(parent, base), 303, 276, 247, 202. Elemental analysis calculated for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.75; H, 7.24.

4,4″-dipropoxy-2′-methyl-p-terphenyl(I-3). ^1H NMR (δ, ppm) 1.02–1.10(t, $-O(CH_2)_2\underline{CH}_3$, 6H), 1.82–1.86(m, $-OCH_2-\underline{CH}_2-$, 4H), 2.34 (s, $-CH_3$, 3H), 3.94–4.00(t, $-OCH_2-$, 4H), 6.93–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 360(parent, base), 318, 276, 247, 202. Elemental analysis calculated for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.11; H, 7.82.

4,4″-dipentyloxy-2′-methyl-p-terphenyl(I-5). ^1H NMR (δ, ppm) 0.91–0.98(t, $-O(CH_2)_4\underline{CH}_3$, 6H), 1.43–1.54(m, $-O(CH_2)_2-\underline{CH}_2-\underline{CH}_2-$, 8H), 1.76–1.82(m, $-OCH_2-\underline{CH}_2-$, 4H), 2.34(s, $-CH_3$, 3H), 3.97–4.04(t, $-OCH_2-$, 4H), 6.93–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 416(parent, base), 346, 276, 247. Elemental analysis calculated for $C_{29}H_{26}O_2$: C, 83.61; H, 8.71. Found: C, 83.43; H, 8.63.

4,4″-dihexyloxy-2′-methyl-p-terphenyl(I-6). ^1H NMR (δ, ppm) 0.92–1.82(m, $-OCH_2(\underline{CH}_2)_4\underline{CH}_3$, 22H), 2.34(s, $-CH_3$, 3H), 3.97–4.04(t, $-OCH_2-$, 4H), 6.93–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 444(parent, base), 360, 276, 247. Elemental analysis calculated for $C_{31}H_{40}O_2$: C, 83.74; H, 9.07. Found: C, 83.52; H, 8.89.

4,4″-diheptyloxy-2′-methyl-p-terphenyl(I-7). ^1H NMR (δ, ppm) 0.91–1.81(m, $-OCH_2(\underline{CH}_2)_5\underline{CH}_3$, 26H), 2.34(s, $-CH_3$, 3H), 3.97–4.03(t, $-OCH_2-$, 4H), 6.95–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 472(parent, base), 374, 276, 247. Elemental analysis calculated for $C_{33}H_{44}O_2$: C, 83.85; H, 9.38. Found: C, 83.71; H, 9.29.

4,4″-dioctyloxy-2′-methyl-p-terphenyl(I-8). ^{1}H NMR (δ, ppm) 0.89–1.81(m, $-OCH_2(\underline{CH}_2)_6\underline{CH}_3$, 30H), 2.34(s, $-CH_3$, 3H), 3.98–4.03(t, $-OCH_2-$, 4H), 6.95–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 500(parent, base), 388, 276, 247. Elemental analysis calculated for $C_{35}H_{48}O_2$: C, 83.95; H, 9.66. Found: C, 83.86; H, 9.56.

4,4″-dinonyloxy-2′-methyl-p-terphenyl(I-9). ^{1}H NMR (δ, ppm) 0.89–1.81(m, $-OCH_2(\underline{CH}_2)_7\underline{CH}_3$, 34H), 2.34(s, $-CH_3$, 3H), 3.97–4.03(t, $-OCH_2-$, 4H), 6.95–7.57(m, phenyl ring, 11H). Mass Spectrum (m/e): 528(parent), 402, 276(base), 247. Elemental analysis calculated for $C_{37}H_{52}O_2$: C, 84.04; H, 9.91. Found: C, 83.90; H, 9.81.

4,4″-didecyloxy-2′-methyl-p-terphenyl(I-10). ^{1}H NMR (δ, ppm) 0.89–1.81 (m, $-OCH_2(\underline{CH}_2)_8\underline{CH}_3$, 38H), 2.34(s, $-CH_3$, 3H), 3.97–4.03(t, $-OCH_2-$, 4H), 6.93–7.57 (m, phenyl ring, 11H). Mass Spectrum (m/e): 556(parent, base), 416, 276, 247. Elemental analysis calculated for $C_{39}H_{56}O_2$: C, 84.12; H, 10.14. Found: C, 83.97; H, 10.11.

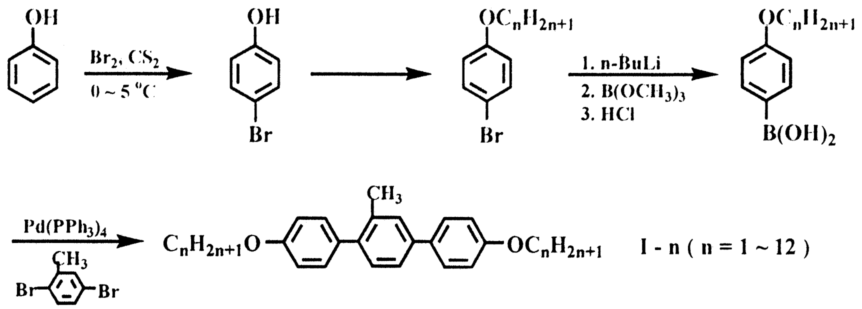
4,4″-diundecyloxy-2′-methyl-p-terphenyl(I-11). ^{1}H NMR (δ, ppm) 0.85–1.85 (m, $-OCH_2(\underline{CH}_2)_9\underline{CH}_3$, 42H), 2.34(s, $-CH_3$, 3H), 3.97–4.03 (t, $-OCH_2-$, 4H), 6.93–7.57 (m, phenyl ring, 11H). Mass Spectrum (m/e): 584(parent), 430, 276(base), 259, 231. Elemental analysis calculated for $C_{41}H_{60}O_2$: C, 84.19; H, 10.34. Found: C, 84.12; H, 10.34.

4,4″-didodecyloxy-2′-methyl-p-terpheyl(I-12). ^{1}H NMR (δ, ppm) 0.88–1.81 (m, $-OCH_2(\underline{CH}_2)_{10}\underline{CH}_3$, 46H), 2.34(s, $-CH_3$, 3H), 3.97–4.03 (t, $-OCH_2-$, 4H), 6.93–7.55(m, phenyl ring, 11H). Mass Spectrum (m/e): 612(parent, base), 522, 443, 276, 186. Elemental analysis calculated for $C_{43}H_{64}O_2$: C, 84.26; H, 10.52. Found: C, 84.30; H, 10.50.

RESULTS AND DISCUSSION

Synthesis

The title compounds were synthesized according to the synthetic route shown in Scheme 1. p-Bromophenol was prepared following the method described by Adams and Marvel [12]. 4-Methoxybromobenzene and 4-ethoxybenzene were obtained by etherification of p-bromophenol with dimethyl sulfate and diethyl sulfate, respectively. Other 4-alkoxy-1-bromobenzenes were synthesized by etherification of p-bromophenol with the corresponding alkyl bromides. The obtained 4-alkoxy-bromobenzenes were treated with n-BuLi in dry THF at −78°C under argon, followed by



SCHEME 1 Synthetic route.

reaction with trimethyl borate, and finally hydrolysis with hydrochloric acid to form 4-alkoxyphenylboronic acids. The final step was the palladium-catalyzed Suzuki cross-coupling reaction of 4-alkoxyphenylboronic acids with 2,5-dibromotoluene [15,16].

The resulting products were purified by column chromatography (silica gel, dichloromethane/petroleum ether) followed by recrystallization from the mixture of petroleum ether and dichloromethane. The structures were confirmed with proton NMR, mass spectrometry, and elemental analysis.

Thermal Behavior

The thermotropic properties of I-n were characterized by DSC, POM, and XRD. Some of the results are listed in Table 1.

TABLE 1 Properties of 4,4″-dialkoxy-2′-methyl-p-terphenyl (I-n)

	Phase transitions (°C) and corresponding enthalpy changes (KJ/mol)	
Terphenyls	Heating	Cooling
I-1	K128.2(35.2)N158.6(1.15)I	I157.4(1.28)N81.6(33.1)K
I-2	K142.0(39.6)N180.6(1.75)I	I179.5(1.71)N90.9(29.5)K
I-3	K113.5(40.9)N137.5(0.93)I	I136.5(0.67)N85.8(28.6)K
I-4	K106.1(37.6)N143.1(1.43)I	I142.4(1.10)N85.3(30.1)K
I-5	K87.8(29.3)N125.5(0.95)I	I124.6(1.02)N63.2(24.9)K
I-6	K71.4(38.6)N121.9(1.54)I	I121.2(1.70)N51.3(31.3)K
I-7	K73.8(33.9)N116.2(1.09)I	I115.4(1.14)N56.6(33.0)K
I-8	K73.6(36.3)N116.2(1.66)I	I115.3(1.76)N51.1(37.4)K
I-9	K74.6(56.5)S99.9(0.79)N108.9(1.51)I	I108.0(1.64)N99.1(0.89)S57.5(48.8)K
I-10	K77.6(59.1)S103.5(1.20)N109.0(1.74)I	I108.1(1.70)N102.7(1.08)S66.3(52.0)K
I-11	K82.2(65.9)S102.6(1.66)N104.5(1.55)I	I103.8(1.64)N101.9(1.54)S73.6(62.1)K
I-12	K82.7(71.4)S103.1(7.32)I	I102.0(7.75)S70.7(63.1)K

All terphenyl derivatives are white crystals at room temperature and exhibit mesophases at elevated temperature before clearing into isotropic liquid. The compounds with shorter terminal groups ($n \leq 8$) exhibited only one mesophase. The DSC thermograms of **I-1** to **I-8** are shown in Figure 1. The DSC curves during heating scans displayed at least two endothermic peaks. POM studies showed that the first peak at lower temperature was due to melting transition and the second peak at higher temperature corresponded to the transition from an anisotropic phase to the isotropic liquid phase. Supercooling of the crystallization temperature occurred with all compounds investigated, but this was not significant for the transition of the isotropic state to mesophase. The enthalpy values corresponding to the

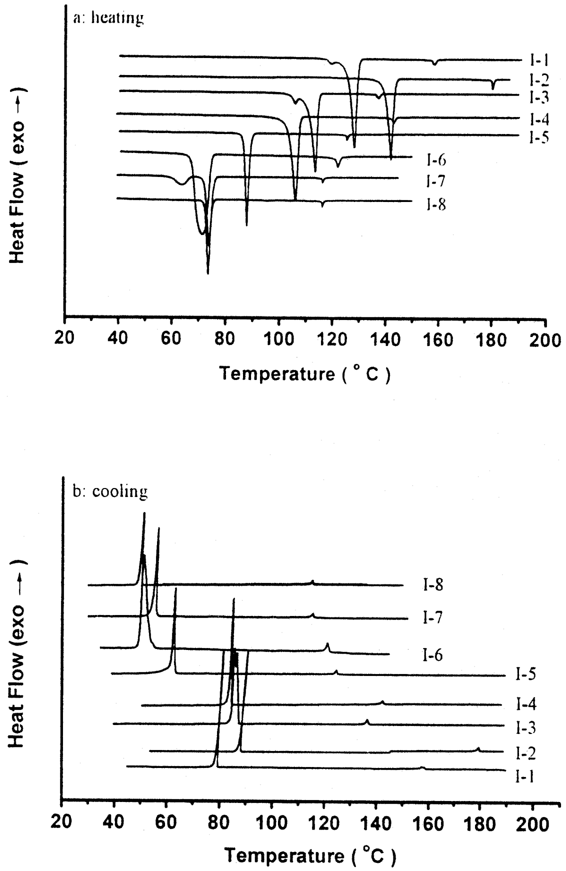


FIGURE 1 DSC thermograms of the compounds **I-1** to **I-8** obtained on (a) heating and (b) cooling scans.

second transition were very small (< 1.7 kJ/mol), which were in the same order of phase changes from nematic state to isotropic state [17]. The DSC curves of **I-1**, **I-3**, and **I-7** showed another small endothermic peak at the temperature below melting point, which may be due to a crystal-crystal transition.

Figure 2 was a representative polarized optical micrograph of **I-6**, showing a Schlieren texture. The point singularities with values of *s* equal to one half as well as one were observed. Both the Schlieren texture with *s* of ½ and the small enthalpy change indicated the formation of the nematic mesophase.

The molecules with longer terminal groups (n = 9, 10, and 11) were capable of forming either smectic or nematic mesophase according to thermal studies and texture observation. Figure 3 shows the DSC spectra of **I-9**, **I-10**, and **I-11** on both heating (a) and cooling (b) scans. Besides the melting transition, each compound also displayed two other endothermic peaks, which meant there might be two different mesophases formed. On cooling from isotropic liquid state, the typical Schlieren texture of nematic liquid crystal occurred first. But on further cooling a transition to another mesophase, which exhibited a focal-conic texture (Fig. 4 for **I-9**), was found. Therefore the formation of smectic phase for **I-9**, **I-10**, and **I-11** were suggested, although we could not figure out which smectic state they were using only by DSC and POM studies.

In Figure 5 were shown the DSC spectra of the compound **I-12**. Both heating and cooling curves displayed two peaks. This compound melted into a birefrigent liquid at 82.7°C and turned clear at 103.1°C. The enthalpy of the transition from the anisotropic state to the isotropic state was rather

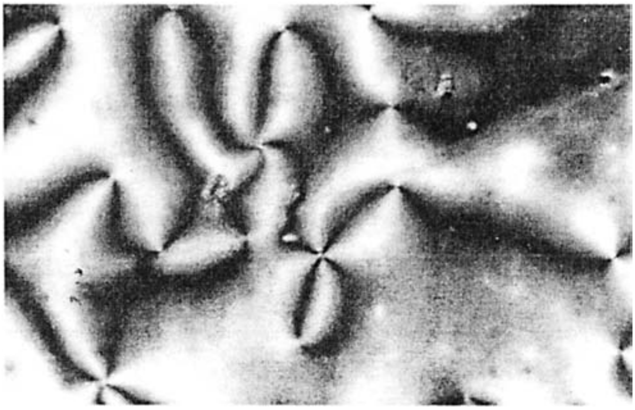


FIGURE 2 Polarized optical micrograph of the compound **I-6** taken at 102°C.

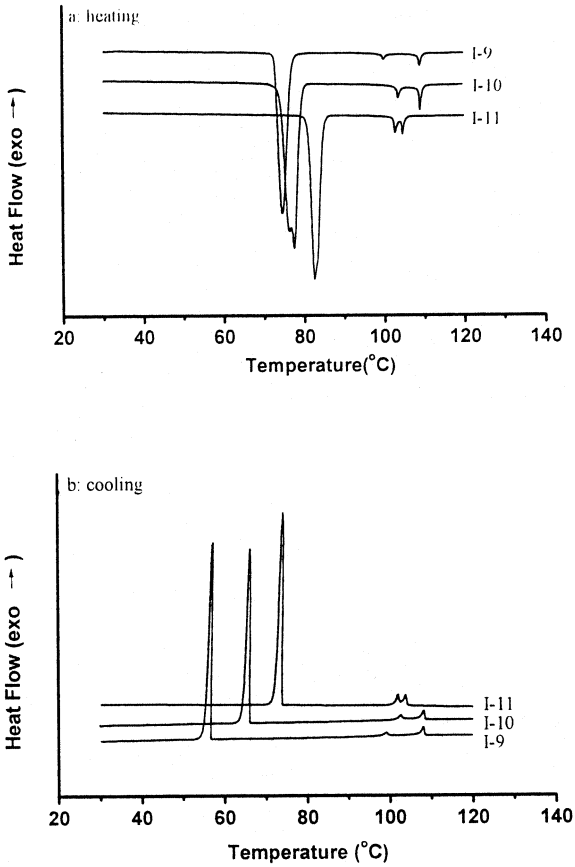


FIGURE 3 DSC thermograms of the compounds **I-9**, **I-10**, and **I-11** obtained on (a) heating and (b) cooling scans.

high and amounted to 7.75 kJ/mol. Figure 6 showed the focal-conic texture of **I-12** on cooling from the isotropic liquid state. The smectic mesophase was indicated.

The mesomorphic properties of the obtained compounds were also investigated by wide-angle X-ray diffraction. The X-ray diagrams of the representative compounds **I-6**, **I-9**, and **I-12** at variable temperatures were shown in Figures 7, 8, and 9, respectively. All three of these compounds gave a series of sharp peaks of crystalline structure at room temperature. After being melted, **I-6** exhibited two weak diffused scatterings at $2\theta = 3.16°$ and $19.77°$. This was the typical feature of the nematic mesophase [18]. The former corresponded to the molecular

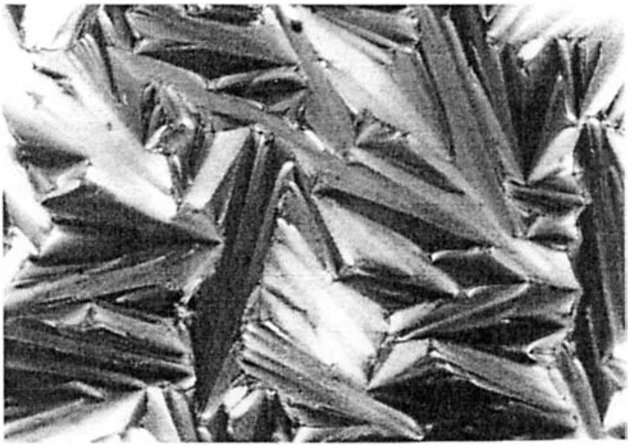


FIGURE 4 Polarized optical micrograph of the compound **I-9** taken at 90°C.

length of 2.79 nm, which was almost the same with the value calculated from standard bond lengths and angles under the assumption of a planar, all *trans* conformation of the molecule, and the latter to the interchain spacing of approximately 0.45 nm. The X-ray spectra of **I-9** changed as a function of temperature in a somewhat different way to that of **I-6**. At 90°C, it showed a strong, sharp reflection at $2\theta = 2.56°$ and a secondary diffraction peak at $2\theta = 5.11°$, in addition to a diffused wide-angle scattering at $2\theta = 18.48°$. The higher degree of order for the

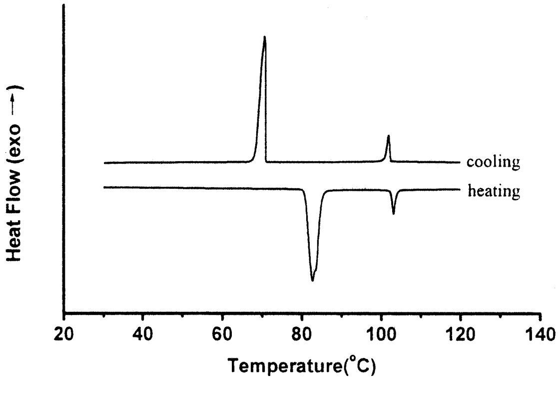


FIGURE 5 DSC thermograms of the compound **I-12** observed on (a) heating and (b) cooling scans.

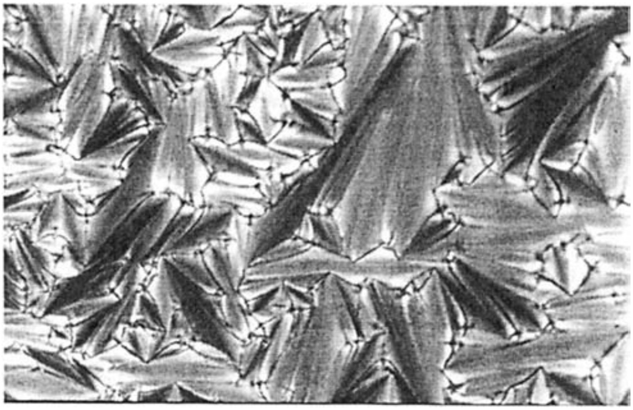


FIGURE 6 Polarized optical micrograph of the compound **I-12** taken at 90°C.

smectic phase was clearly seen. At a higher temperature that was still below its clearing point of 108.9°C, the diffraction pattern of the nematic mesophase was again displayed (see Fig. 8). As shown in Figure 9, the X-ray spectrum of **I-12** at 90°C was similar to that of **I-9** in smectic phase. Therefore, the formation of smectic mesophase was also suggested. This was coincident with the results educed from DSC and POM studies.

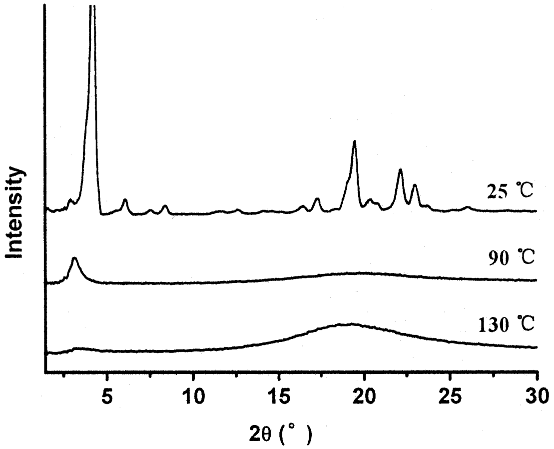


FIGURE 7 X-ray diffraction spectra of **I-6** in crystalline, nematic, and isotropic states.

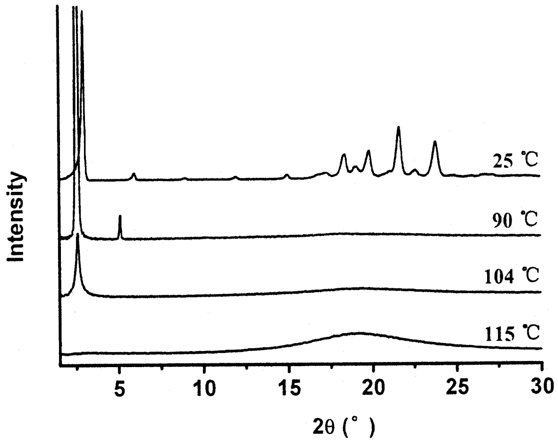


FIGURE 8 X-ray diffraction spectra of **I-9** in crystalline, smectic A, nematic, and isotropic states.

The interlayer spacing of **I-9** and **I-12** in smectic state obtained from XRD spectra at 90°C were 3.45 and 4.05 nm, respectively. Compared to the full length calculated by CS Chem3D Pro software, which was 3.54 nm for **I-9** 4.27 nm for **I-12**, it could be concluded that the long axes of the molecules **I-9** and **I-12** were almost perpendicular to their layer plane in smectic state. Thereafter smectic A state was implied.

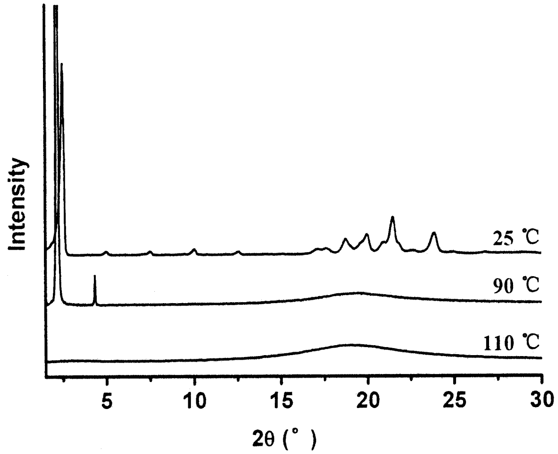


FIGURE 9 X-ray diffraction spectra of **I-12** in crystalline, smectic A, and isotropic states.

Transition Temperatures versus Spacer Length

Based on the discussion above, it was obvious that there was a strong dependence of the mesomorphic properties of the compounds **I-n** on the chain length of the terminal n-alkoxy groups. In Figure 10 are plotted the melting and clearing temperatures of **I-n** as a function of length of the end groups. The clearing points of **I-n** decreased regularly in a zig-zag fashion, but with a diminishing amplitude, as the number of methylene groups (n) increased. The smectic-nematic transition temperatures lay on a rising curve that eventually leveled off to merge into the T_i curve and gave direct smectic-isotropic transition. As is commonly observed, the molecules with an even number of methylene groups in the spacer had higher clearing points than those with odd numbers of methylene groups.

An interesting feature of the plots of transition temperature versus spacer length was the melting point on spacer length and the clearing point. The melting points of **I-n** decreased regularly as the number of methylene groups (n) increased to 6, after which the melting temperatures seemed to increase at longer flexible spacer lengths. As a result, the compound **I-6** not only had lower melting temperature than others but also had a wider temperature range of mesophase.

Another effect of increasing flexible spacer length was the change from compounds having a nematic mesophase to those having a smectic mesophase. The longer the alkoxy end chain, the more marked the smectic phase. Smectic properties increased at the expense of nematic phases as the chain length was increased. Evidently, the longer terminal groups favored the organization of the molecules, and thus more ordered smectic structures could be formed. In this series of compounds, the necessary end

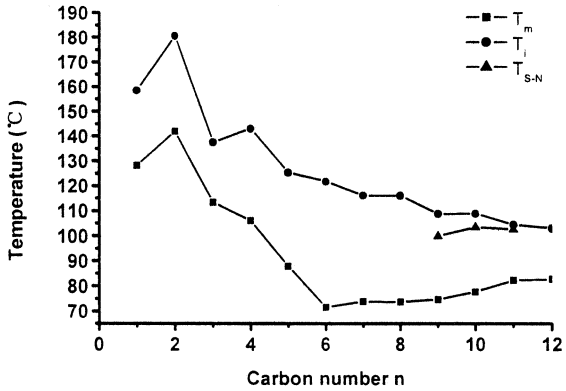


FIGURE 10 Dependence of the phase transitions of **I-n** on the number of the methylenic units in the n-alkyloxy end groups.

chain length for forming smectic phase is n = 9. These results were consistent with the ground rule brought out by Gray and coworkers in their studies on the series of 4-p-n-alkoxybenzylideneaminobiphenyl [19,20].

CONCLUSIONS

As we have shown, a series of 4,4″-dialkoxy-2′-methyl-p-terphenyls have been synthesized. All these compounds were reported for the first time with the exception of 4,4″-didecyloxy-2′-methyl-p-terphenyl. The preliminary characterization by means of POM, DSC, and wide-angle X-ray diffraction showed that the nematic and/or smectic mesophases could be formed depending on the length of the terminal n-alkoxy chains. Extension of the terminal n-alkoxy chain gave rise to regular trends in liquid crystal transition temperature. Smectic properties were found to become more marked as the chain lengthened. Because the lateral methyl group is easily functionized by many methods such as bromination, they are very good precursors of many systems. With the advances in new-material development efforts, their potential in research and application will be largely exploited in the future.

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