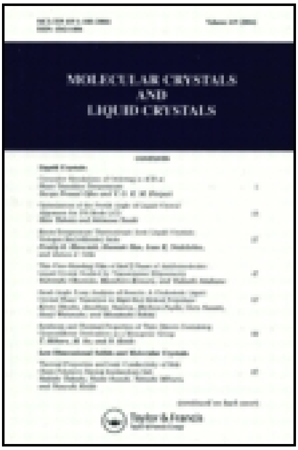

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The Synthesis and Property of Liquid Crystalline 4-Alkoxyl-4"-Cyano-*p*-Terphenyls

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The synthesis of some new 4-alkoxyl-4"-cyano-*p*-terphenyls is described. The preliminary characterization by means of polarized optical microscopy, differential scanning calorimetry and X-ray diffraction shows that all these compounds are thermotropically liquid-crystalline and can form both the nematic and smectic mesophases.

INTRODUCTION

Since the 4-alkyl-4'-cyanobiphenyls and 4-alkoxyl-4'-cyanobiphenyls were synthesized by George Gray more than 20 years ago[1,2] and used in liquid crystal display devices, the LCD market has shown continuous growth starting from simple TN applications including watches and calculators to high resolution displays such as large screen displays in notebook computers[3]. For most of the applications, LC materials were required for a fast response time, wide view angle, low power consumption and broad operating temperature range. In order to achieve these goals, LC materials must be of low viscosity, high optical and dielectric anisotropy and good thermal stability. At present the 4-alkyl-4'-cyanobiphenyl compounds were widely used in LCD technology because of their structural advantages. Their largely conjugated structure and high polarisability make them readily form liquid crystal phase. It is well known that the molecules of larger conjugation and higher polarisability form a more stable mesophase with a higher birefringence and other properties[4]. Thus, 4-alkyl-4"-cyano-*p*-ter-

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phenyls have been synthesized as components of LC-compositions for electro-optic devices because they are colorless, chemically and photochemically stable, ready to form simple eutectic nematic mixtures in wide temperature ranges, and of high optical anisotropy[5]. However, to our surprise, the 4-alkoxyl counterparts of the cyano-*p*-terphenyls have received little attention in LC studies.

The present work aims at investigation on the synthesis and the phase transition behavior of a series of 4-alkoxyl-4"-cyano-*p*-terphenyls ($C_nH_{2n+1}O \cdot C_6H_4 \cdot C_6H_4 \cdot C_6H_4 \cdot CN$, n = 1~7), which have a largely conjugated structure of terphenyl and a strong polar cyano terminal group as 4-alkyl-4"-cyano-*p*-terphenyls. The alkoxy homologues are expected to show similar or better properties than their alkyl counterparts because the alkoxy groups have higher polarisability than alkyl groups. In addition, a better understanding of the relationship between structure and property of these low molar mass liquid crystal compounds can also help us to design new liquid crystal polymers with such terphenyl moiety as mesogenic units, because little is known of liquid crystalline polymers having cyano-*p*-terphenyl as mesogenic units.

EXPERIMENTAL SECTION

Materials

4-Phenylphenol, n-butyl lithium, 4-bromobenzonitrile were purchased from Acros Inc., tetrakis(triphenylphosphine)palladium(0) was purchased from Aldrich Inc., and used without further purification.

Synthesis

The synthetic route (shown in Scheme 1) is based upon the palladium-catalyzed cross-coupling reaction. The procedures are described below with the synthesis of 4-n-hexyloxy-4"-cyano-*p*-terphenyl(Ter-6) as example.

Synthesis of 4-acetoxybiphenyl[6]

4-Phenylphenol(51.1g, 0.30mol) and acetic anhydride(42ml, 0.45mol) were placed in a 250ml round-bottom flask equipped with reflux condenser and magnetic stirrer. After the addition of a few drops of sulfuric acid, the reaction mixture was stirred at 60 °C for 3h. Then 200ml of water was added and the mixture was stirred until a white solid formed. The precipitate was washed with 200ml of water and recrystallized from 95% ethanol to give 54.8g (86%) of white crystals melting at 86–88 °C(literature[6]: 86–88 °C). ^{1}H-NMR: δ (ppm, in $CDCl_3$): 2.33(s, 3H), 7.14–7.60 (m, 9H).

Synthesis of 4-acetoxy-4'-bromobiphenyl[7]

To a mixture of 4-acetoxybiphenyl(15.0g, 0.071mol) and anhydrous Na_2CO_3 (22.5g, 0.212mol) in 25 ml of 1,2-dichloroethane stirred at 50 °C was added dropwise (very slowly) a solution of Br_2(5.2ml, 0.100mol) in 25 ml of 1,2-dichloroethane. After the addition was complete, the reaction mixture was stirred overnight at the same temperature. Then the mixture was cooled and Na_2CO_3 was removed by filtration. The filtrate was evaporated on a rotary evaporator to yield a pale yellow solid. The solid was recrystallized from toluene to yield 17.4g(84.6%) of white crystals. M.p.: 132–134 °C (literature[7]: 128–130 °C). ^{1}H-NMR: δ (ppm, in $CDCl_3$): 2.33(s, 3H), 7.15–7.56(m, 8H).

Synthesis of 4-bromo-4'-hydroxybiphenyl[8]

4-Acetoxy-4'-bromobiphenyl(6.0g, 0.02mol) was added in a solution of 6.0g NaOH in 120ml of 80% aqueous ethanol and refluxed for 6 hours. The ethanol was removed on a rotary evaporator and the obtained solid was dissolved in 300ml of distilled water. The water solution was neutralized with dilute hydrochloric acid and the obtained solid was filtered, dried and recrystallized from a mixture ethanol/water (1/4) to yield 4.3g(83,8%) of white solid. M.p.: 158–159 °C). ^{1}H-NMR: δ (ppm, in deuterium substituted acetone): 6.92–7.59 (m, 8H), 8.57 (s, 1H).

Synthesis of 4-bromo-4'-n-hexyloxybiphenyl

4-Bromo-4'-hydroxybiphenyl(2.0g, 8.0mmol) was dissolved in 25ml of ethanol and the solution was heated to reflux. After the addition of 0.6g sodium hydroxide in 2.5ml water, n-hexyl bromide(3.5ml, 24mmol) was added. The mixture was refluxed for 1h and ethanol was distilled. The residue was washed with water. Recrystallization from ethanol yielded 2.338g (86,3%) of white crystals. M.p.: 124–125 °C. ^{1}H-NMR δ (ppm, in $CDCl_3$): 0.90(t, 3H), 0.31(m, 4H), 1.40(m, 2H), 1.7(m, 2H), 4.0(t, 2H), 6.9–7.5(m, 8H).

Synthesis of 4-n-hexyloxy-4'-biphenylboronic acid[9]

4-Bromo-4'-n-hexyloxybiphenyl(2.4g, 0.007mol) was dissolved in 20ml of anhydrous THF in a 50 ml three-neck flask equipped with a dropping funnel, thermometer, and nitrogen inlet- outlet. The solution was cooled to −78 °C with liquid nitrogen and ethanol. The n-BuLi (1.6M in hexane) 5.3 ml was added dropwise to the stirring mixture, maintaining the temperature below −65 °C. Then $B(OCH_3)_3$ (1.8ml) in 5ml of anhydrous THF was added dropwise to the stirring mixture, still maintaining the temperature below −65 °C. The reaction mixture was subsequently warmed to room temperature and stirred overnight. The dilute HCl(10ml) was added dropwise, and the mixture was stirred for 1 hour. The solution was extracted two times with Et_2O, washed with water, dried over $MgSO_4$ and filtered, and the solvent was evaporated to yield a white powder. The powder was dissolved in THF, precipitated in hexane, and filtered to yield a white powder 0.655g (yield 31.3%), which was used in the next step without further purification and characterization.

Synthesis of 4-n-hexyloxy-4"-cyano-p-terphenyl[9–11]

With the protection of nitrogen, 4-bromobenzonitrile (0.334g, 1.8 mmol), $Pd(PPh_3)_4$ (0.064g), 1M Na_2CO_3 (3ml) and toluene (4ml) were added to a 50ml three-neck flask. 4-n-Hexyloxy-4'-biphenyl-boronic acid (0.655g dissolved in 3ml 95% ethanol) was added dropwise at 80 °C. The reaction mixture was stirred at the same temperature overnight. Then the mixture was cooled to the room temperature and diluted with chloroform and water to form two phases. The organic layer was separated, dried over $MgSO_4$, and filtered and the solvent was distilled with a rotary evaporator. The resulting product was purified by column chromatography (silica gel, dichloromethane/hexane) to yield 0.360g (55.3%) of white powder. ^{1}H-NMR: δ (ppm, in $CDCl_3$): 0.9(m, 3H), 1.3(m, 4H), 1.5(m, 2H), 1.8(m, 2H), 4.0(m, 2H), 6.9–7.3(m, 12H).

Characterization

The thermal stability was studied by a TGA (TA SDT 2960) with a heating rate of 20 °C min^{-1} in nitrogen. The phase transition temperatures were obtained using DSC (TA 2010) at the 10 °C min^{-1} in nitrogen for both the heating and the cooling cycles (Figures 1, 2 and 3; Table II). The liquid crystallinity was also studied by means of the polarizing optical microscopy (POM) using a Leitz Laborlux 12 Pol instrument and a Leitz 350 heating stage (Figure 4). Because these new compounds all form one or two smectic phases the x-ray diffraction (Philips PW 1700, CuKα radiation) was applied to deduce the type of each smectic phase (Figures 5 and 6 ; Table III).

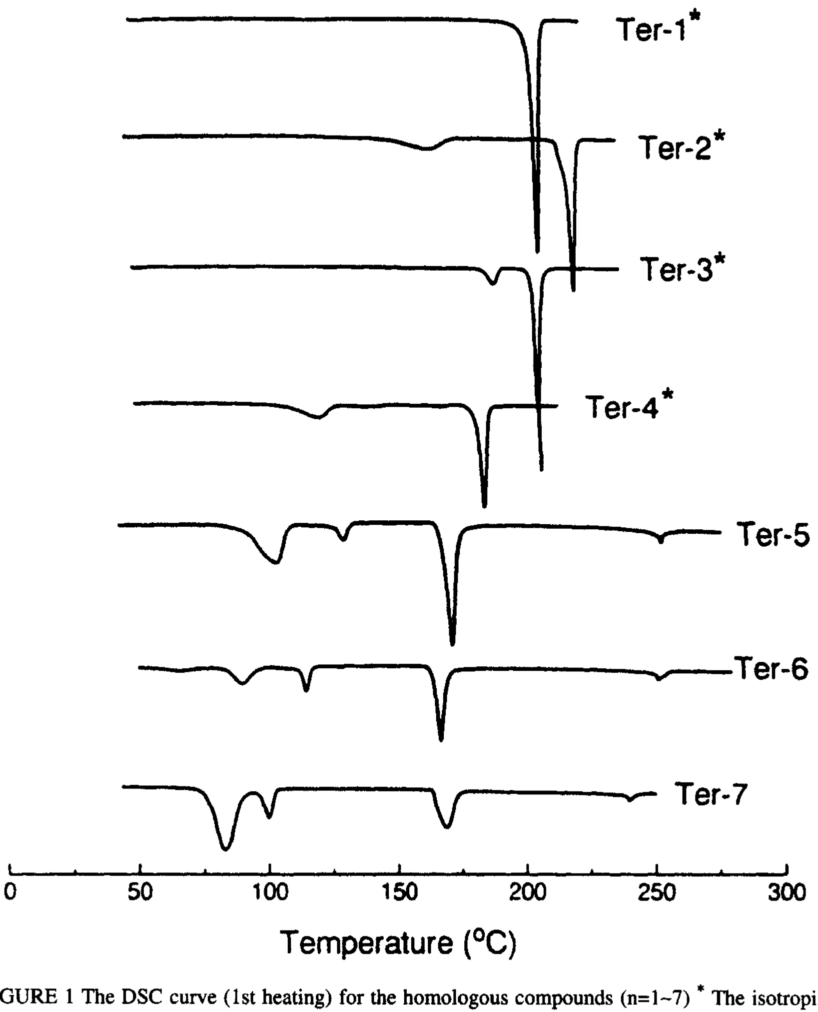


FIGURE 1 The DSC curve (1st heating) for the homologous compounds (n=1~7) * The isotropization endotherm is not shown because Ti is higher than the Td (refer to the text)

RESULTS AND DISCUSSION

Among the seven 4-alkoxyl-4”-cyano-*p*-terphenyls, only 4-methoxyl-4”-cyano-*p*-terphenyl (Ter-1) was briefly reported in a patent[12]. Even for this compound, no detailed description was given for its synthesis and property as a liquid crystal.

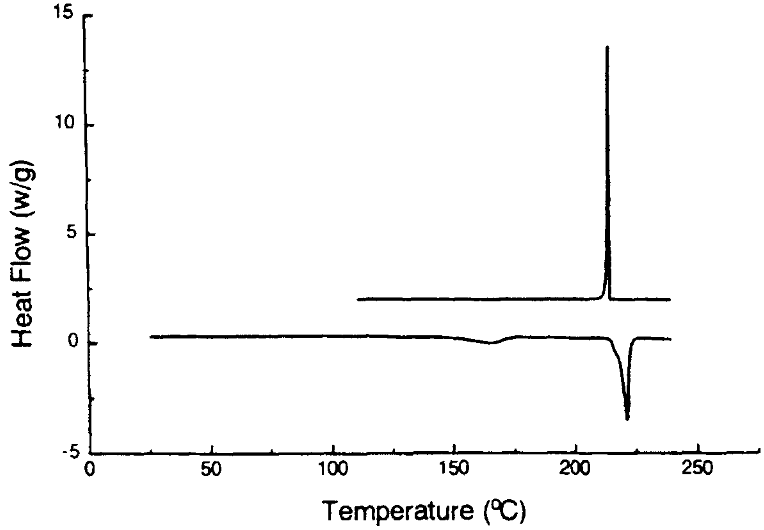


FIGURE 2 The DSC curve for Ter-2 The upper was cooling curve and the lower was heating curve

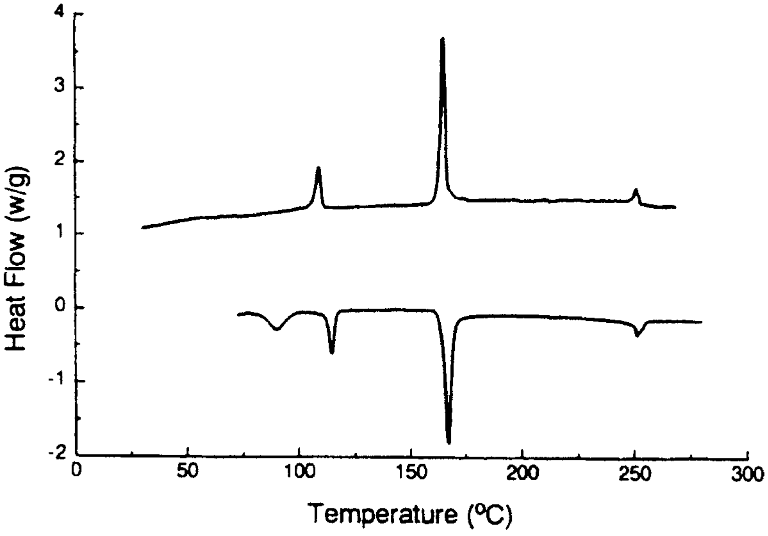
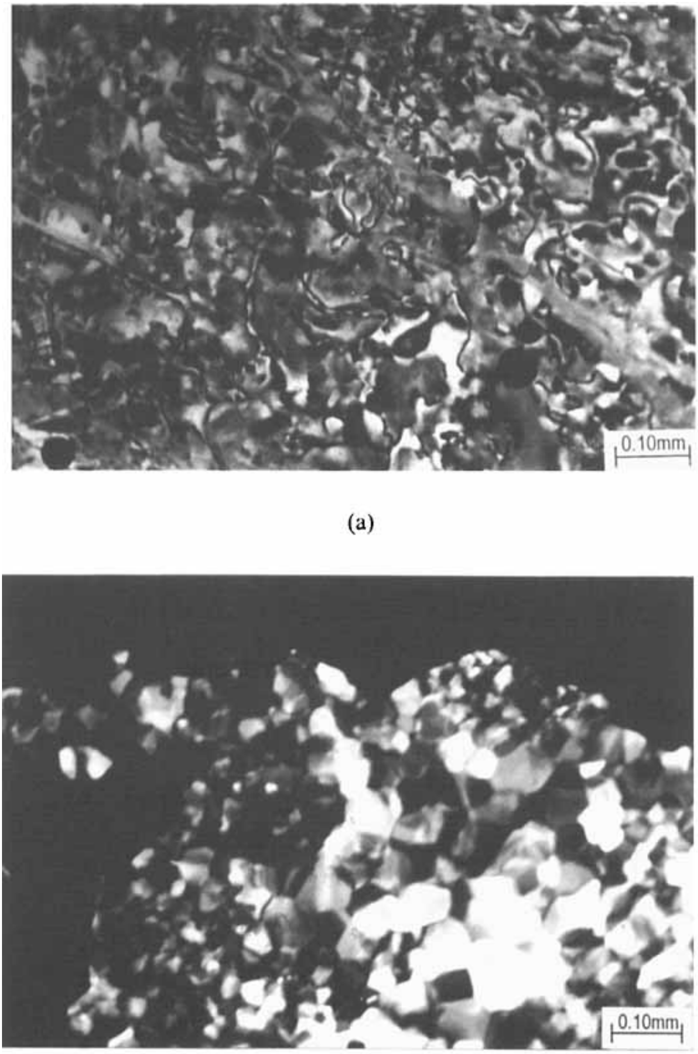


FIGURE 3 The DSC curve for Ter-6 The upper was cooling curve and the lower was heating curve



(a)

(b)

FIGURE 4 The polarizing optical microscopic textures of compounds Ter-6. a) at 167 °C – b) at 143 °C (See Color Plate IV at the back of this issue)

The syntheses of this series of 4-alkoxyl-4”-cyano-*p*-terphenyls were described in the experimental section with Ter-6 as example. Although the syntheses were difficult and time-consuming, the reactions were known and straightforward

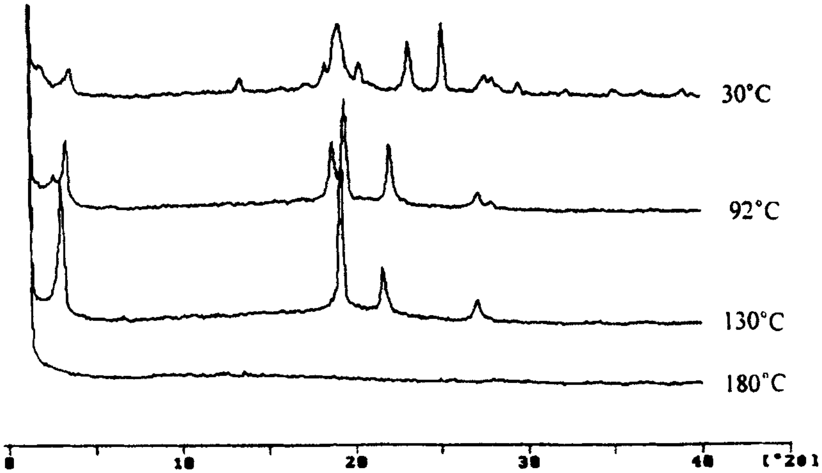


FIGURE 5 X-ray diffraction pattern of Ter-6

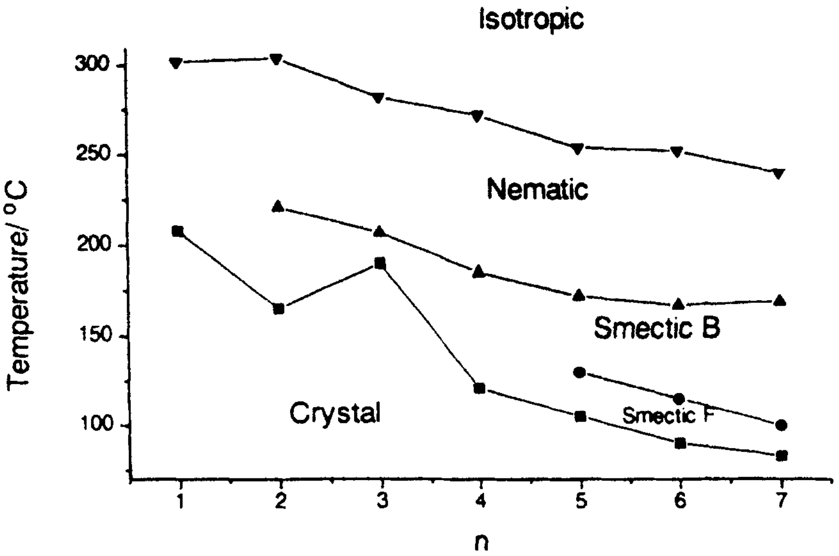
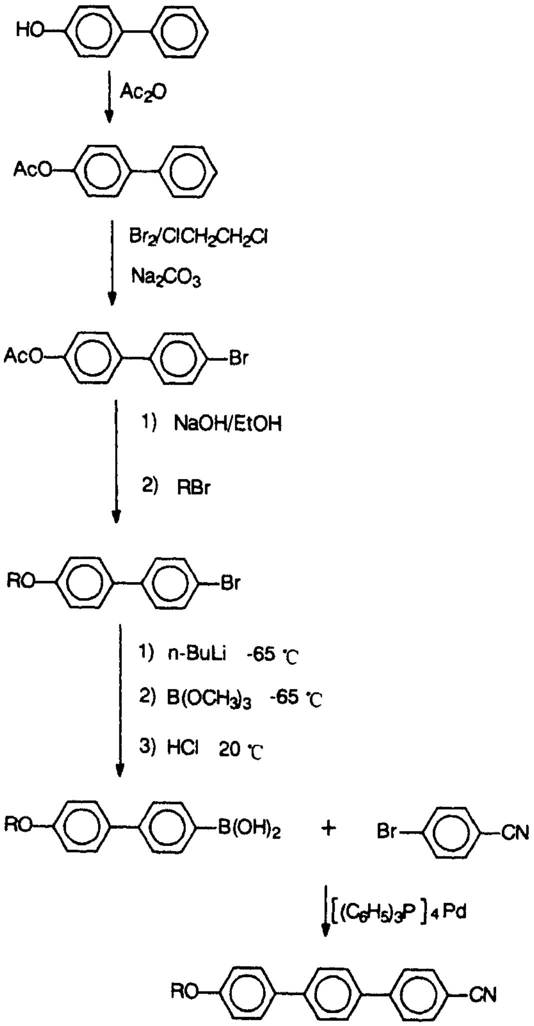


FIGURE 6 Phase transition temperature versus length of the alkoxy group(n) for the homologous compounds(n=1~7)

(Scheme 1). The yields of the reactions were usually above 80% and the purity of the products was high. The NMR (with a Bruker ARX 400Mhz instrument) analytical data of the seven final products were collected in Table I, showing the successful syntheses.



Ter-n

SCHEME 1 Synthesis of Ter-n (n = 1~7, RO are normal-alkoxy groups with n carbon atoms)

TABLE I ^{1}H-NMR Data for the Compounds

Compounds	*RO-*	*δ (ppm, in $CDCl_3$)*
Ter-1 *	methoxy	3.9 (s, 3H), 7.0–7.7 (m, 12H)
Ter-2	ethoxy	1.4 (m, 3H), 4.0–4.1 (m, 2H), 6.9–7.7 (m, 12H)
Ter-3	n-propoxy	1.0 (m, 3H), 1.8 (m, 2H), 3.9 (m, 2H), 6.9–7.7 (m, 12H)
Ter-4	n-butoxy	1.0 (m, 3H), 1.5 (m, 2H), 1.7–1.8 (m, 2H), 4.0 (m, 2H), 6.9–7.7 (m, 12H)
Ter-5	n-pentyloxy	1.0 (m, 3H), 1.4–1.5 (m, 4H), 1.8 (m, 2H), 4.0 (m, 2H), 6.9–7.7 (m, 12H)
Ter-6	n-hexyloxy	0.9 (m, 3H), 1.3 (m, 4H), 1.5 (m, 2H), 1.8 (m, 2H), 4.0 (m, 2H), 6.9–7.7 (m, 12H)
Ter-7	n-heptyloxy	0.9 (m, 3H), 1.3–1.4 (m, 6H), 1.5 (m, 2H), 1.8 (m, 2H), 4.0 (m, 2H), 6.9–7.7 (m, 12H)

*. The compound has been reported[12].

Although the compounds have a cyano-*p*-terphenyl structure, the thermal stability is only moderate probably because of the presence of the alkoxyl substitution. The TGA experiments showed that the samples started to loss weight at 250 °C or so (Table II). Therefore the successive experiments by DSC and POM were all run within the limit of decomposition.

TABLE II Phase Transition of the Compounds from DSC studies

Compounds	*RO –*	*Phase transition Temperature(°C) / ΔH (J/g)*	*Td^{**} (°C)*
Ter-1	methoxy	C 208/91 N 302* I (199/58)	225
Ter-2	ethoxy	C 165/15 S_B 221/56 N 304* I (215/55)	230
Ter-3	n-propoxy	C 190/9.0 S_B 207/61 N 282* I (169/6.7) (204/59)	239
Ter-4	n-butoxy	C 121/15 S 185/36 N 272* I (183/35)	215
Ter-5	n-pentyloxy	C 104/21 S_F 130/3.5 S_B 172/36 N 253/4.01 (127/4.0) (170/33) (252/3.6)	265
Ter-6	n-hexyloxy	C 90/6.9 S_F 115/6.3 S_B 167/25 N 251/3.3 I (109/6.5) (165/25) (251/3.0)	280
Ter-7	n-heptyloxy	C 83/54 S_F 100/11 S_B 169/26 N 240/3.3 I (167/26) (238/1.8)	250

Notes: Data in parentheses were from cooling cycles.
* The temperature was obtained by POM because of sample's decomposition.
** Temperature at which the TGA curve started to deviate.

The first heating curves obtained from DSC are shown in Fig. 1. As mentioned above, the experiments were run to temperatures below decomposition so that some phase transitions are missing in the curves. We found with POM that the nematic-to-liquid transition temperatures (Ti) of the four samples from Ter-1 to Ter-4 were all higher than their TGA-found decomposition temperatures. Thus there must be one more endothermic peak in the DSC heating curves of these four compounds. The transition temperatures obtained from DSC (supplemented by POM) were collected in Table II.

The DSC curve of Ter-1 showed only one endothermic peak at 208 °C. However, when examined on POM, the sample melted at 208 °C and formed a birefringent mesophase with nematic schlieren textures as would have expected from the rigid rod structure with a short terminal methoxyl substituent. The sample slowly turned yellow when heated to temperatures higher above its decomposition, but the isotropization could still be determined to be at 302 °C by careful experiments with fast observation using pre-heated stages. The nematic-to-liquid transition temperature of the samples Ter-2 to Ter-4 were found similarly, and these data were also collected in Table II but asterisked.

The thermal decomposition of the samples from Ter-1 to Ter-4 precluded the determination of their enantiotropic nature of the nematic-to-liquid transitions. With these exceptions, the enantiotropic nature of all other phase transitions of these compounds was studied by DSC as well as POM. The results are represented by Figure 2 of Ter-2 and Figure 3 of Ter-6. Again, because of the thermal decomposition of Ter-2 at higher temperatures the isotropic peak was missing in Figure 2, but the heating and cooling curves showed that the smectic-to-nematic transition was enantiotropic. The endothermic peak at 221 °C in the heating curve was of the smectic-to-nematic transition, while the reverse transition was shown by the exothermic peak at 215 °C in the cooling curve. A super-cooling of 6 degrees was observed in this experiment. The melting peak was at 165 °C in the heating curve of Ter-2. There was no corresponding exothermic peak shown in its cooling curve for crystallization when the sample was cooled to about 100 degrees below its melting temperature. This is probably because of the high viscosity of the smectic phase and the slow crystallization in the experimental conditions. For Ter-6, four endothermic peaks were shown in the heating curve and three exothermic peaks were shown in the cooling curve (Figure 3). The three enantiotropic transitions (with certain degrees of super-cooling) were the nematic-to-liquid, the smectic-to-nematic, and that from one smectic phase to another smectic phase. The crystallization of the lowest-temperature smectic phase was again not shown when the sample was cooled to room temperature.

Thus, all the compounds were found to be liquid crystalline and most of the transitions were enantiotropic within the limit of chemical decomposition as well as the experimental conditions. Ter-1 showed one nematic phase, Ter-2 to Ter-4 each showed one smectic phase and one nematic phase, and Ter-5 to Ter-7 each showed two smectic phases and one nematic phase.

The Highest temperature mesophase of every compound was found to be nematic by means of polarizing optical microscopy. The typical schlieren textures of nematic phase were found for this phase. Figure 4a of Ter-6 is one example of the nematic textures which was taken when the sample was cooled to 167 °C before the nematic phase was transformed to the smectic phase. When the sample was further cooled, it formed a smectic phase. Figure 4b was taken at 143 °C showing that the sample Ter-6 had formed a smectic B phase with the typical mosaic texture[13].

The liquid crystalline phases were also characterized by means of x-ray diffraction. Before each scanning, the powder samples were heated to a pre-set temperature and be held at that temperature for 5 or 10 minutes so as to ensure the formation of any expected phase. Again we take the results of Ter-6 as examples because Ter-6 has one crystal and three mesomorphic phases. The resulted four diffraction curves were shown in Figure 5. As showed by the figure, the sample was in its crystalline state at 30 °C, in a smectic phase at 92 °C, in another smectic phase at 130 °C and in a nematic phase at 180 °C. The scattering at 180 °C was very diffused and did not show any Bragg type diffraction. With this and the results of DSC (Figure 3) and POM (Figure 4a) we conclude that the phase of Ter-6 at 180 °C is nematic. As for the smectic phases, our calculations seem to have suggested that the phase at 92 °C fits the molecular arrangement in an $S_F$phase, while that at 130 °C fits an S_B phase. In both the S_F and the S_B phases, the packing of the molecules in the layers is hexagonal, but in S_F the molecules are packed with their long axes tilted with respect to the layer planes, while in S_B the molecules are orthogonal to the planes[13]. The tilt angle was found to be 112° for the S_F phase of Ter-6. Because it was in the same temperature range (from 115 to 167 °C) that the sample showed a typical mosaic texture of S_B (compare Figure 4b with plate 7 in reference 13) and gave the x-ray diffraction of the S_B phase, this assignment of S_B must have been convincing. On the other hand, although it is rare that the S_F phase is formed by cooling from an S_B phase, such a transition has indeed already been observed[13]. The x-ray diffraction results of this study were collected in Table III, with the indices of the reflection planes of the smectic phase of Ter-4 left to be deduced.

Thus, we have shown that the title compounds 4-alkyloxyl-4"-cyano-*p*-terphenyls are liquid crystalline with phase behavior changed with the number of carbon atoms in the normal alkoxyl group (n). With n=1 the compound (Ter-1) exhibited only a nematic phase. With higher n, the compound had not only one nematic phase but also one (n = 2, 3, 4) or more smectic phases (n = 5, 6, 7). To show this, the phase transition temperatures were plotted against n in Figure 6.

TABLE III X-ray diffraction results

Compounds	*Temp (°C)*	*Average d-spacing(Å) and (index)*	*phase type*
Ter-2	200	20.2(001) 9.8(002) 4.7(110) 4.0(111) 3.3(020)	S_B
Ter-3	197	21.4(001) 10.2(002) 4.9(110) 4.6(111) 4.1(020)	S_B
Ter-4	150	22.8( ) 4.8( ) 4.6( ) 4.1( ) 3.3( ) 3.2( )	S
Ter-5	150	25.5(001) 4.6(110) 4.1(111) 3.2(020)	S_B
	116	23.7(001) 4.7(010) 4.5(110) 4.0(111) 3.3(020)	S_F
Ter-6	130	28.2(001) 4.6(110) 4.1(111) 3.3(020)	S_B
	92	26.1(001) 4.7(010) 4.6(110) 4.0(111) 3.3(020)	S_F
Ter-7	130	29.7(001) 4.6(110) 4.1(111) 3.3(020)	S_B
	92	27.6(001) 4.7(010) 4.6(110) 4.0(111) 3.3(020)	S_F

In comparison with the property of 4-alkyl-4"-cyano-*p*-terphenyl reported by others[14], we see that the alkyl homologous with the alkyl group being n-hexyl or shorter tend to form only nematic liquid crystals. The heptyl homologue has also only one stable liquid crystalline phase that is nematic, though it does have a meta-stable smectic phase. In contrast, all the 4-alkoxyl-4"-cyano-*p*-terphenyls but the methoxyl derivative have not only a nematic phase but also smectic phases. In addition, the clearing temperatures of the nematic phases of these alkoxyl derivatives are higher than that of the alkyl homologues. Therefore the replacement of the terminal alkyl group by the more polarizable alkoxyl group helps the cyano-*p*-terphenyls to form more stable and more ordered liquid crystalline phases. These results are in good agreement with the classical reports by, e.g., Gray[15] on the terminal group effect of liquid crystals

In conclusion, we have synthesized a series of 4-alkoxyl-4"-cyano-*p*-terphenyls. With the exception of 4-methoxyl-4"-cyano-*p*-terphenyl, all are new liquid crystalline compounds forming nematic and smectic phases. Because of the large conjugation in structure and the large polarisability, these compounds should have high values of Δn and $\Delta\varepsilon$ similar to 4-alkyl-4"-cyano-*p*-terphenyls and be useful in liquid crystal compositions for display or other applications.

Acknowledgements

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