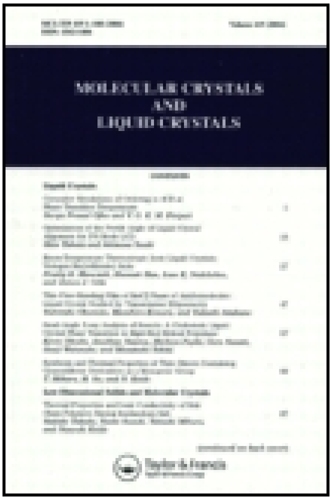

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DSC Study on Thermotropic Liquid Crystalline Compounds with Alkyl Substituents

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DSC Study on Thermotropic Liquid Crystalline Compounds with Alkyl Substituents

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A series of new liquid crystalline epoxy compounds with alkyl substituents from 1 to 15 carbon atoms were characterized by differential scanning calorimetry (DSC). The result showed the length of lateral alkyl substituents of liquid crystalline compounds was the dominant reason for the change of phase behavior. The result implied that $T_{N\text{-}I}$ *exhibited the odd–even effect when the length of lateral alkyl chains from 5 to 8 was approximately half of the fully extended length of mesogenic core with end polar epoxy groups.*

Keywords: differential scanning calorimetry; lateral substituents; liquid crystalline epoxides

INTRODUCTION

It was generally accepted that lateral substituents diminish the mesogeneity of a compound, and the extent of the effect depends on their molecular size. However, Weissflog and Demus found that compounds

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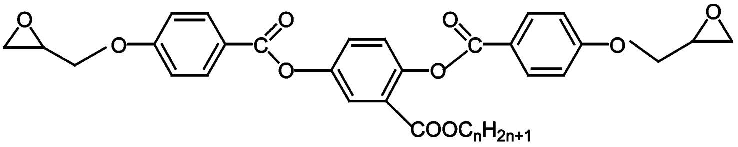
with large flexible lateral substituents exhibited liquid crystalline (LC) phases in the early 1980 s [1,2]. Compounds with large flexible lateral substituents, assuming that the lateral chains are oriented nearly parallel to the basic molecule, may be considered as variants of the classical rod-lid-like molecules [3]. Much of their works focused on relationship between the long and large lateral subsituents and the phase behavior of the LC compounds [1–5]. Few studies were reported about thermotropic LC compounds linked to end polar groups with lateral alkyl substituents.

Thermotropic LC compounds with lateral alkyl substituents were used for study of the LC thermosets [5] and LC elastomers [6], which had shape memory properties. In this present article, we have synthesized a series of LC epoxides with large and long substituents and investigated the effect of lengthening of flexible lateral sunstituents upon the LC phase behavior. Even though similar works of these compounds with lateral long-chain substituents have been done before [1–5], the study has not been carried out in a systematic fashion by mesogens linked to end polar groups like epoxy with substituent lengths from C1 to C15.



n = 1-15

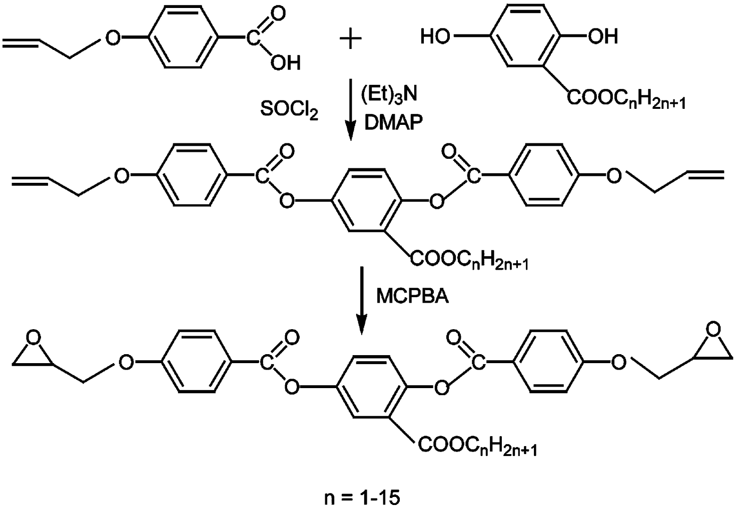
EXPERIMENTAL

Materials

2,5-Bihydroxy benzoic acid (gentistic acid) was purchased from Taizhou Candorly Sea Biochemical and Health Products Co., purified by recrystallization, and confirmed by ^{1}H NMR and thin-layer chromatography (TLC). n-Alkanol, 3-chloroperoxybenzoic acid (MCPBA), and 4-dimethylamin-pyridine (DMAP) were purchased from Flucka and used as received. All solvents were purified by standard procedures.

Synthesis

All synthetic procedures of liquid crystalline epoxides (LCEs) with different lateral substituents were similar (Scheme 1). A typical example using C-8 LCE was given as follows: 2,5-Didydroxybenzoate octanol ester was prepared by esterfication of gentistic acid with octanol catalyzed by sulfuric acid. 4-(2-Propenyloxy) benzoic acid was prepared according to the procedure proposed by Broer *et al.* [7].



SCHEME 1 Synthetic scheme of substituted liquid crystalline epoxides.

2,5-bis[4-(2,3-Diallypropoxy)-oxy]benzoic Acid Octanol Ester

Into a 250-ml round-bottomed flask equipped with a magnetic stir bar, were 3.6 g [4-(2-propenyloxy)benzoic acid], 10 ml of benzene, 3 ml thoinyl choride placed. The flask was equipped with a condenser and heated to reflux with an oil bath. After 2 h, the benzene and excess thionyl chloride were removed by distillation under and reduced pressure. Under an N_2 atmosphere, the product was placed into the flask with an ice bath. A solution (0.1 g DMAP in 10 ml of THF and 10 ml of triethyl amine) was then added over a period of 10 min. The reaction was kept for 8 h, then at 25°C for 2 days. The reaction mixture was poured into 500 ml of acidified aqueous solution. The solid was filtered and washed with 500 ml of water and 500 ml of ethanol twice in sequence. The solid product was dried in a vacuum oven at 40°C. Yield: 55%. ^{1}H NMR [$CDCl_3$/TMS, δ (ppm)]: 0.84 (3H, t, CH_3) 1.23 (10H, m, CH_2), 1.46 (2H, m, CH_2), 4.13 (2H, t, $-CH_2-OOC-$), 4.62 (4H, s, CH_2), 5.32 (2H, d,$-CH{=}CH_2$), 5.43 (2H, d, $-CH{=}CH_2$), 6.07 (2H, m, $-CH{=}CH_2$),7.00 (4H, dd, aromatic),7.23 (1H, s, aromatic), 7.43 (1H, d, aromatic), 7.87 (1H, s, aromatic), 8.15 (4H, dd, aromatic).

2,5-bis [4-(2,3-Epoxypropoxy)-oxy]benzoic Acid Octanol Ester

Diallyl mononer (2,5-bis[4-(2,3-diallypropoxy)-oxy]benzoic acid octanol ester) was oxidized with MCPBA in dichloromethane at 25°C for 7 days. After filtration, the filtrate was washed successively with

5% Na_2SO_3 solution, 5% Na_2CO_3 solution, and concentrated NaCl solution and dried over $MgSO_4$, and the solvent was evaporated. A pure product was obtained after recrystallization from ethyl acetate. Yield: 60%. ^{1}H NMR [$CDCl_3$/TMS, δ (ppm)]: 0.84 (3H, t, CH_3), 1.23 (10H, m, CH_2), 1.46 (2H, m, CH_2), 2.78 (2H, m, CH_2 of epoxy), 2.93 (2H, dd, CH_2 of epoxy), 3.38 (2H, t, CH of epoxy), 4.01 (2H, m, $-O-CH_2$), 4.12 (2H, t, $-CH_2-OOC-$), 4.32 (2H, m, $-O-CH_2$), 7.00 (4H, dd, aromatic), 7.23 (1H, s, aromatic), 7.43 (1H, d, aromatic), 7.87 (1H, s, aromatic), 8.15 (4H, dd, aromatic).

RESULTS AND DISCUSSION

The phase transition of the C-n compounds have been studied by differential scanning calorimetry (Perkin-Elmer DSC II, USA) at heating/cooling rate of 10°C min^{-1} as given in Table 1. The changes in entropies were calculated from the enthalpy changes obtained during phase transitions. For comparison, a plot of the transition temperatures against the number of methylene groups in the lateral substituents is exhibited in Fig. 1 and shows a very large decrease in $T_{N\text{-}I}$ values with an increasing number of methylene groups.

Remarkably, the difference in the T_M and $T_{N\text{-}I}$ depends on whether the flexible spacer contains an even or odd number of methylene

TABLE 1 Thermal Propertiess of LC Epoxides

Samples	T_M (°C), first heating	ΔH_M (kJ · mol^{-1}), first heating	ΔS_M (J.mol^{-1} · K^{-1}), first heating	$T_{N\text{-}I}$ (°C), second heating	$\Delta H_{N\text{-}I}$ (kJ · mol^{-1}), second heating	$\Delta S_{N\text{-}I}$ (J · mol^{-1}·K^{-1}), second heating
C-1	125.4	29.46	73.9	155.0	1.60	3.7
C-2	134.2	33.81	83.0	142.2	1.52	3.6
C-3	117	27.75	71.1	124.7	1.45	3.6
C-4	96.6	25.45	68.8	118.4	1.16	2.9
C-5	83.3	19.43	54.5	84.8	0.72	2.0
C-6	86.9	26.67	74.1	99.3	1.29	3.4
C-7	59.8	22.39	67.2	76.5	0.88	2.5
C-8	77.4	36.95	105.4	87.6	1.27	3.5
C-9	70.8	34.66	100.8	86.8	1.11	3.1
C-10	89.9	21.86	60.2	74.9	0.91	2.6
C-11	56.8	21.28	64.5	63.5	0.79	2.3
C-12	58.4	34.51	104.1	61.3	0.98	2.9
C-13	69.7	39.20	114.3	63.6	0.79	2.3
C-14	52.8	41.43	127.1	69.0	0.72	2.1
C-15	52.6	28.91	88.7	48.4	0.55	1.7

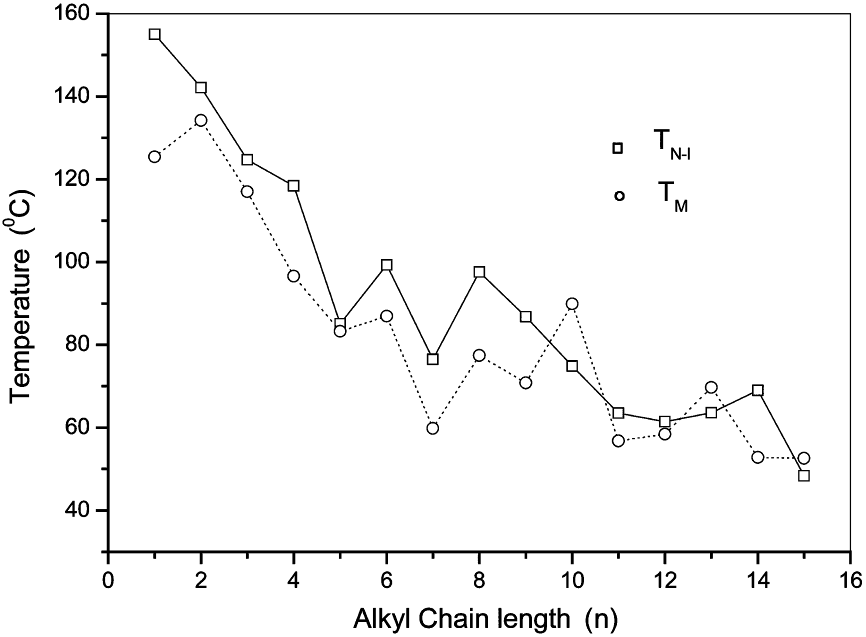


FIGURE 1 Transition temperature in the homologous of the LC epoxides.

groups. The plot of $T_{N\text{-}I}$ versus the number of carbon atoms in the alkyl chain exhibited the odd–even effect between the fourth member and eighth member of the series.

The lateral alkyloxycarbonyl chains linked to mesogens acted as a diluent, increasing the mean space between molecules; this in turn prevented the regular stacking of layers and reduced the anisotropy of the intermolecular forces, and so made the mesophase less stable. It has been previously reported that the identity and position of terminal substituent groups could strongly influence the LC properties of resulting compounds. For phenylene alkoxybenzoate there was mutual conjunction between the alkyl and carboxy groups; this should increase the negativity of the carbonyl oxygen and so help to stabilize the mesophase. However, the presence of polar groups at the ends of molecule increased the intermolecular attractive forces and decreased the usual tendency of rod-shaped molecules to form LC phases. Because the epoxy groups in these LC eopxides were low, they had a small negative effect on LC phase stability [8].

When the length of lateral alkyl chains was from 5 to 8, it was approximately half of the fully extended length of mesogenic core with end polar epoxy groups. T_{NI} increased when *n* was even, but decreased when *n* was odd because of the increased size of the protruding group. One possible reason was the changes in orientation of the lateral alkyl group with the long axis of the basic molecule. When the number of lateral methyl groups was odd, the terminal methyl group of lateral substituents was off-axis and the interaction between the neighbor molecules might be strong. This made it difficult for the molecules to pack neatly in the parallel arrangement needed for an LC phase. Consequently, this effect greatly decreased the $T_{N\text{-}I}$ value and enthalpy ($\Delta H_{N\text{-}I}$). However, when *n* was even, the terminal methyl group of lateral substituents was on-axis and the interaction between the neighbor molecules might be weak. This effect greatly increased the $T_{N\text{-}I}$ value and enthalpy ($\Delta H_{N\text{-}I}$).

An orientation of fully extended all-trans-conformation lateral aliphatic chain nearly parallel to the long axis of the basic molecule (Fig. 2) is assumed. When the lateral chain length was shorter than the half length of fully extended mesogenic core, its effects have been rationalized in terms of a reduction in anisotropic polarisability and an increased axial separation, thus giving a reduction in intermolecular attraction forces. The changes of T_M and $T_{N\text{-}I}$ and the increased isotropic entropies in Table 1 resulted from that lateral groups functioned as a bulge enhancing positional correlation and short range order in nematic phase (by an interlocking effect) [9].

For the same lateral substituents linked to 1,4-phenylene bis (4-n-octyloxybenzoates), the nematic–isotropic transition points have simply decreased with increasing length of the lateral aliphatic substituents without end polar groups [5]. Even though the presence of polar

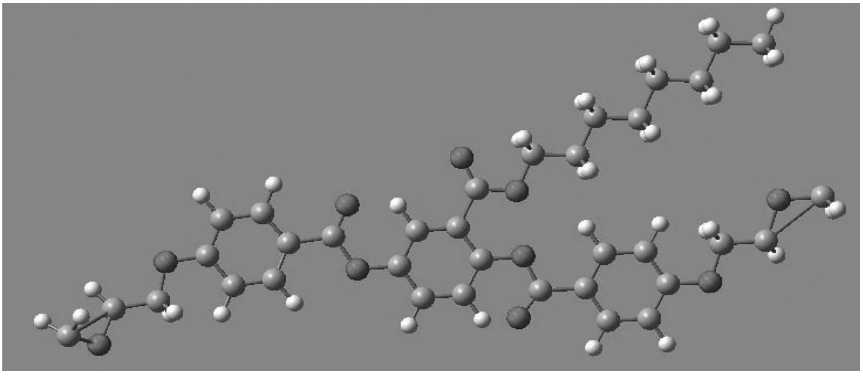


FIGURE 2 Model of the C-8 LC epoxides compounds with long alteral chains through GaussView 2.1.

end groups increased the intermolecular attractive forces and decreased the usual tendency of rod-shaped molecules to form LC phases, the intermolecular attractive could make odd–even effects through protruding the lateral alkyl groups turn up.

When the lateral chain length continued to increase to longer than the half-length of fully extended mesogenic core with end polar epoxy groups, the increase in length would lead to increase its geometrical anisotropy. Lateral chains were oriented nearly parallel to the basic molecule and might be considered as variants of the classical rod-like molecules [3,4]. The effect of lateral alkyloxycarbonyl chains in the middle of three-ring moiety acted as a diluent, and the intermolecular attractive might continually be relatively weak. This combination of effects could simply result in the decrease of T_M and $T_{N\text{-}I}$.

The relationship between the length of lateral substituents and length of three-ring mesogenic core indicated that the trans-conformation lateral substituents nearly paralleled the long axis of the basic molecule. The length of lateral alkyl substituents of LC compounds was the dominant reason for the change of phase behavior. $T_{N\text{-}I}$ decreased largely as the increasing number of lateral alkyl groups. Even though the presence of polar groups at the ends of molecule increased the intermolecular attractive forces and decreased the usual tendency of rod-shaped molecules to form LC phases, the intermolecular attractive could make odd–even effects through protruding the lateral alkyl groups. When the length of lateral alkyl chains was from 5 to 8, T_{NI} increased when n was even but decreased when n was odd.

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