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Synthesis and Properties of Reactive Liquid Crystal Monomers

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A new series of nematic liquid crystal (LC) monomers containing double bonds in the side chain were designed and synthesized via the Steglich esterification reaction. Length of the side groups varied from 1 to 2 methylene units. The molecular structures of the intermediates and the LC monomers were confirmed by Fourier transform infrared spectrum, elemental analysis, and nuclear magnetic resonance spectroscopy. The thermal phase behavior of the LC monomers was investigated by differential scanning calorimetry and polar optical microscopy coupled with hot stage. All of these LC monomers showed only one nematic mesophase at room temperature during the cooling process.

Keywords Liquid crystal; nematic; reactive liquid crystal; synthesis

1. Introduction

The use of liquid crystals (LCs) in active-matrix display devices has stimulated the development of synthetic approaches. Researchers have designed a number of functional LCs [1–10]. LCs with C═C are very important because of their low viscosity, low melting point, high clearing points, and good low-temperature stability. In addition, the reactivity of double bond in LCs is also very important. For example, it can be oxidized into epoxy groups to prepare LC adhesive or triggered to self-polymerize to produce LC polymers. Double bond can also be connected to the polymethylhydrosiloxane to form side-chain LC polymers through the hydrosilylation reaction [11–17].

The position of the double bond is usually in the main chain. A few studies have been conducted on LC monomer containing a double bond in the side chain. Patrick Keller et al. prepared an LC elastomer using the LC monomer containing a double bond in the side chain. The elastomer displayed a maximum reversible deformation amplitude of up to 40% [18,19]. Due to the location of double bond in LC, the thermal motions of the main chain have less interference in the organization of mesogenic units than it would have if the attachment was at one of the ends [20–24]. In this article, a new series of reactive LC monomers containing a double bond in the side chain were designed and synthesized.

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These monomers show liquid crystalline properties at room temperature. The influence of the side-chain length and main-chain groups on the phase transition behavior is discussed. Our approach has important implications for the synthesis of novel side-chain LC polymer.

2. Experimental Details

2.1. Instruments

Infrared (IR) spectra were recorded on a Fourier transform infrared (FT-IR) Bruker TENSOR27 spectrometer by using KBr pellets. The structures of the products were characterized by ^{1}H (400 MHz) and ^{13}C (400 MHz) nuclear magnetic resonance (NMR; Bruker Avance 400 MHz spectrometer) in $CDCl_3$ with tetramethylsilane as the internal standard. The purity of the products was evaluated by high-performance liquid chromatography (Shimadzu LC-10A). The liquid crystalline textures were observed by an Olympus BX51 polar optical microscope (POM) equipped with a Linkam THMS600 hot stage. The transformation temperature and associated enthalpy change were determined by differential scanning calorimetry (DSC; DSC 204 F1 Phoenix of NETZSCH) at a scanning rate of $10^{\circ}C \cdot min^{-1}$.

2.2. Synthesis and Characterization of Monomers

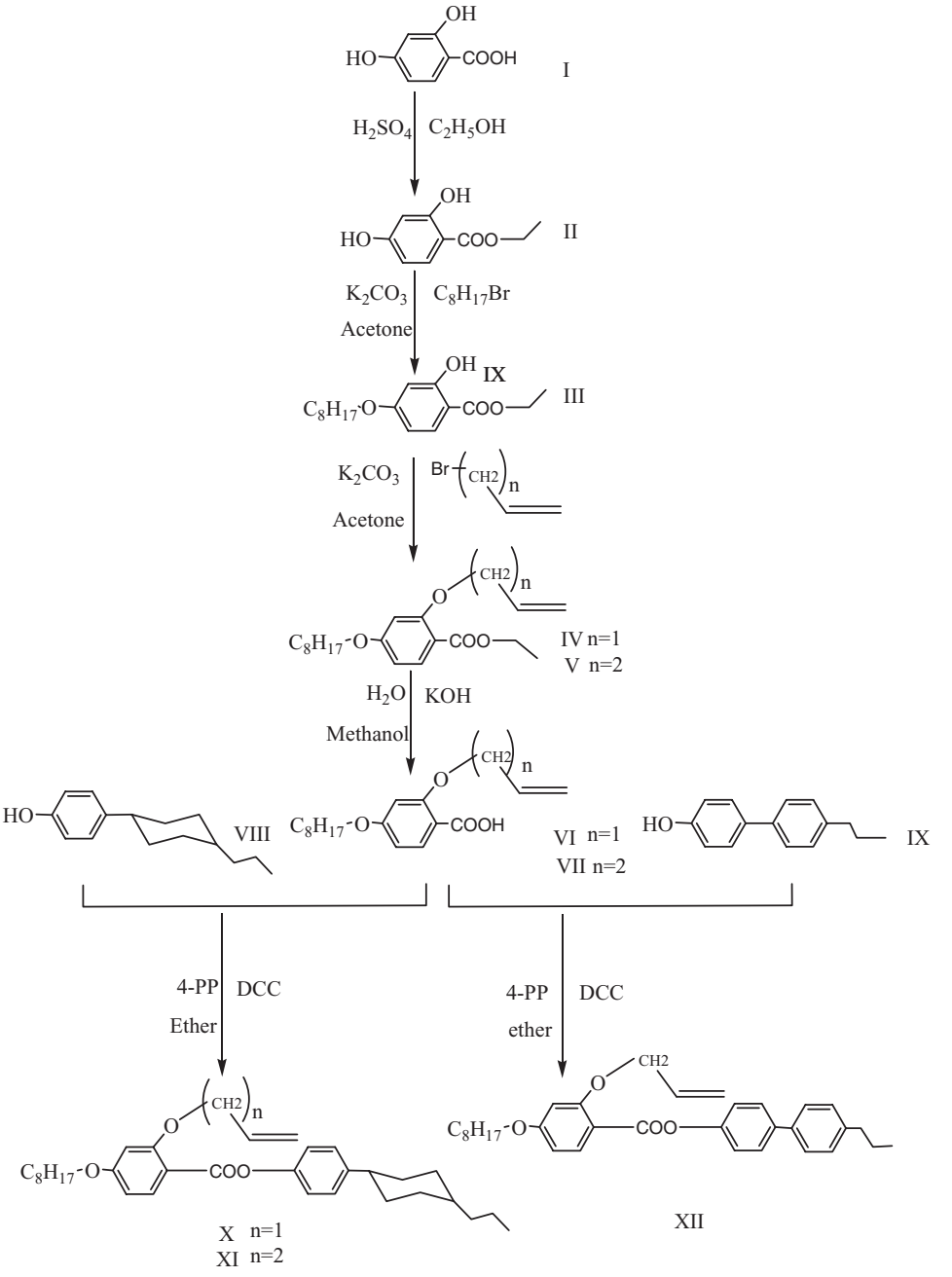
Allyl bromide and n-octyl bromide were purchased from Acros Organics and used with further purification. The purification methods of allyl bromide and n-octyl bromide are as follows. They were washed with 5% sodium bicarbonate solution three times and subsequently with distilled water three times and dried with anhydrous magnesium sulfate overnight. Finally, the purified allyl bromide and n-octyl bromide were obtained by filtration and vacuum distillation. All the other solvents and reagents were AR or CP grade and used without further purification. N,N′-dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine (4-PP) were purchased from J&K. 4-(trans-4-Propylcyclohexyl)phenol were obtained from Shijiazhuang Huarui Scientific and Technological Co. Ltd. The procedure of preparing a series of LC monomers is depicted in Scheme 1.

Compound ethyl 2,4-dihydroxybenzoate was synthesized as previously described in literature [25]. The synthesis conditions of the other compounds were experimentally determined.

Synthesis of Intermediates and Products.

Synthesis of Ethyl 2,4-Dihydroxybenzoate (II). 2,4-Dihydroxybenzoic acid (8.00 g, 51.90 mmol) was dissolved in 40 ml of ethanol (31.56 g, 686.08 mmol). The solution was heated to 60°C under stirring condition. Concentrated sulfuric acid (3 ml) was dropwise added to the reaction vessel in 30 min. Then the reaction mixture was refluxed for 12 h. After cooling, the pH of the solution was adjusted to 5–6 with the aqueous solution of sodium bicarbonate. After extracted with ether and distilled under reduced pressure, white crystals (5.24 g, 55.4%) were obtained (FT-IR [KBr, cm^{-1}]: 3500, 2960, 2930, 2870, 2850, 1650, 1450, 1280, 1150, 1086, 830, 794, 764, 718.)

Synthesis of Ethyl 2-Hydroxy-4-(octyloxy)benzoate (III). Ethyl 2,4-dihydroxybenzoate (8.00 g, 43.92 mmol) was dissolved in 40 ml of acetone. Potassium carbonate (20 g, 144.73 mmol) was added to the mixture and the mixture was heated to reflux under a nitrogen atmosphere. Acetone solution (32 ml) of n-octyl bromide (9.64 g, 50 mmol) was



Scheme 1.

dropwise added to the reaction vessel in 2 h and then refluxed for 15 h. After cooled to room temperature, the mixture was filtered and was washed with 3 × 5 ml of tetrahydrofuran. The filtrate was concentrated to produce yellow crystals. This crude product was recrystallized by using methanol and yielded ethyl 2-hydroxy-4-octyloxybenzoate (β, 12.91 g, 69.1%).

FT-IR (KBr, cm^{-1}): 3210, 3080, 2931, 2860, 2840, 1650, 1575, 1498, 1472, 1400, 1267, 1190, 1150, 1024, 832, 780, 755, 728, 697.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.80–7.73 (m, 1H), 6.49–6.39 (m, 2H), 4.39 (q, $J = 7.1$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 1.87–1.73 (m, 2H), 1.53–1.20 (m, 13H), 0.91 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.02, 14.70, 22.94, 26.49, 28.71, 28.96, 29.06, 31.65, 61.28, 69.64, 103.64, 106.48, 108.35, 133.26, 163.20, 166.01, 170.51.

Synthesis of Ethyl 2-(allyloxy)-4-(octyloxy)benzoate (IV). Compound III (8.0 g, 27.20 mmol) was dissolved in 40 ml of acetone. Potassium carbonate (18 g, 130.26 mmol) was added to the mixture. The solution was heated to reflux under a nitrogen atmosphere. Acetone solution (16 ml) of allyl bromide (3.63 g, 30 mmol) was dropwise added to the reaction vessel in 2 h and refluxed for 10 h. After cooled to room temperature, the mixture was filtered and the cake was washed with 3 × 5 ml of tetrahydrofuran. The filtrate was concentrated to give yellow liquid. The crude product was washed with methanol/water (1:1) to give yellow liquid compound IV (9.09 g, 90.1%).

FT-IR (KBr, cm^{-1}): 3080, 2931, 2850, 1740, 1610, 1501, 1250, 1120, 1000, 930, 834, 756.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.5$ Hz, 1H), 6.46 (dd, $J = 8.5$, 1.9 Hz, 2H), 6.19–5.83 (ddt, $J = 17.2$, 10.5, 3.0 Hz, 1H), 5.54 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.29 (dd, $J = 10.6$, 1.4 Hz, 1H), 4.57 (dd, $J = 3.0$, 1.7 Hz, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 3.95 (t, $J = 6.5$ Hz, 2H), 1.92–1.57 (m, 2H), 1.54–1.04 (m, 13H), 0.88 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.10, 14.36, 22.66, 25.98, 29.11, 29.34, 31.80, 60.34, 68.18, 69.35, 100.58, 105.41, 112.82, 117.35, 132.64,133.77,160.21, 163.59.

The procedures of preparing ethyl 2-(but-3-enyloxy)-4-(octyloxy)benzoate (V) were similar to the procedure of compound IV. The final crude product was purified by column chromatography (silica gel, methylene chloride/petroleum ether = 12:7) to yield compound V (yield: 45.1%).

FT-IR (KBr, cm^{-1}): 3032, 2930, 2854, 1750, 1600, 1505, 1250, 1105, 101, 930, 835, 758.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, $J = 6.7$ Hz, 1H), 6.47 (d, $J = 2.2$ Hz, 1H), 6.46 (dd, $J = 8.6$, 2.2 Hz, 1H), 6.44 (d, $J = 2.1$ Hz, 1H), 5.17 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.09 (dd, $J = 10.2$, 0.9 Hz, 1H), 4.37–4.23 (m, 2H), 4.03 (t, $J = 6.7$ Hz, 2H), 3.95 (t, $J = 6.5$ Hz, 2H), 2.59 (m, 2H), 1.83–1.68 (m, 2H), 1.49–1.38 (m, 2H), 1.38–1.18 (m, 13H), 0.93–0.81 (m, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.11, 14.37, 22.65, 25.97, 29.11, 29.21, 29.23, 29.32, 31.79, 33.58,53.76, 60.39, 65.80, 68.16, 68.24, 69.47, 100.25, 105.29, 112.68, 117.06, 133.72, 134.37,160.45, 163.58, 165.89, 210.78.

Synthesis of 2-(Allyloxy)-4-(octyloxy)benzoic acid (VI). A solution of compound IV (8.0 g, 23.95 mmol), methanol (40 ml), and sodium hydroxide (4 g, 100 mmol) was heated to reflux for 8 hours while stirring. Then the methanol was removed under reduced pressure and 100 ml of deionized water was added. After cooling, the solution was adjusted to pH 1–2 with concentrated HCl. The precipitate was filtered and recrystallized from methanol/petroleum ether (1:4) to give white crystals of compound VI (7.33 g, 92.3%).

FT-IR (KBr, cm^{-1}): 3470, 2920, 2850, 2560, 1680, 1600, 1508, 1462, 1280, 1200, 1150, 1088, 937, 849, 753, 722, 671, 652.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.15 (d, $J = 8.8$ Hz, 1H), 6.66 (dd, $J = 8.8$, 1.9 Hz, 1H), 6.54 (d, $J = 1.8$ Hz, 1H), 6.19–6.05 (m, 1H), 5.49 (dd, $J = 5.8$ Hz, 2H),

4.78 (d, $J = 5.6$ Hz, 2H), 4.03 (t, $J = 6.5$ Hz, 2H), 1.90–1.75 (m, 2H), 1.47 (d, $J = 7.8$ Hz, 2H), 1.42–1.20 (m, 8H), 0.91 (t, $J = 6.6$ Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.14, 22.79, 25.87, 29.04, 29.23, 29.31, 31.74, 68.62,70.74, 100.13, 107.36, 110.35, 120.68, 130.83, 135.58, 158.51, 164.61,165.25.

The procedures for the preparation of 2-(but-3-enyloxy)-4-(octyloxy)benzoic acid (VII, a yield of 91.5%) were similar to the procedure of compound VI.

FT-IR (KBr, cm^{-1}): 3430, 2930, 2852, 2560, 1650, 1600, 1506, 1452, 1250, 1200, 1150, 1088, 937, 849, 753, 722, 668, 654.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88–10.38 (m, 1H), 8.14 (d, $J = 8.8$ Hz, 1H), 6.65 (dd, $J = 8.8$, 2.3 Hz, 1H), 6.53 (d, $J = 2.2$ Hz, 1H), 5.88 (d, $J = 6.9$ Hz, 1H), 5.31 (d, $J = 1.5$ Hz, 1H), 5.29–5.21 (m, 1H), 4.28 (t, $J = 6.2$ Hz, 2H), 4.03 (t, $J = 6.5$ Hz, 2H), 2.69 (d, $J = 6.6$ Hz, 2H), 1.88–1.75 (m, 2H), 1.48 (s, 2H), 1.42–1.23 (m, 8H), 0.91 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.15, 22.65, 25.96, 29.05, 29.23, 29.31, 31.80, 33.40, 68.59, 68.62, 99.67, 107.08, 110.10, 119.09, 132.94, 135.57, 158.67, 164.58, 165.34.

Synthesis of 4-(4-Propylcyclohexyl)phenyl 2-(allyloxy)-4-(octyloxy)benzoate (X). A solution of compound VI (8.0 g, 26.14 mmol), 4-(trans-4-propylcyclohexyl)phenol (6.0 g, 27.5 mmol), DCC (7.0 g, 33.4 mmol), 4-PP (0.3 g, 2.03 mmol), and ether (60 ml) was heated to reflux for 30 h under stirring. After cooling, the precipitate was filtered and washed with ether. The filtrate was merged and concentrated to give crude product. The final crude product was purified with column chromatography (silica gel, methylene chloride/petroleum ether = 12:7) to yield compound X (10.61 g, 80.2%).

FT-IR (KBr, cm^{-1}): 3015, 2938, 2850, 1720, 1600, 1580, 1515, 1459, 1380, 1250, 1200, 1127, 1010, 870, 837, 801, 700, 663.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J = 8.7$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.16–7.08 (m, 2H), 6.61–6.47 (m, 2H), 6.09 (ddt, $J = 17.2$, 10.5, 4.7 Hz, 1H), 5.59 (dq, $J = 17.2$, 1.6 Hz, 1H), 5.30 (dd, $J = 10.6$, 1.5 Hz, 1H), 4.64 (dt, $J = 4.6$, 1.6 Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 2.65–2.31 (m, 1H), 1.86 (m, 6H), 1.64–1.18 (m, 17H), 1.15–0.98 (m, 2H), 0.92 (m, 6H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.16,14.45, 20.07, 22.71, 25.99, 29.12, 29.36, 33.58, 36.99, 39.73, 44.12, 68.35, 69.40, 100.66, 105.59, 111.48, 117.56, 121.62, 127.64, 132.38, 134.47,145.07, 149.01, 160.99, 164.08, 164.28.

Elemental analysis: $C_{33}H_{46}O_4$ requires C78.26, H 9.09; found: C 78.12, H 9.14.

The procedures for the preparation of 4-(4-propylcyclohexyl)phenyl 2-(but-3-enyloxy)-4-(octyloxy)benzoate (XI) and 4-(2-allyloxy-4-octyloxy benzoate)-4′-propylbiphenyl (XII) were similar to the procedure of compound X.

4-(4-Propylcyclohexyl)phenyl 2-(but-3-enyloxy)-4-(octyloxy)benzoate (XI). Yield: 76.8%.

FT-IR (KBr, cm^{-1}): 3025, 2924, 2860, 1735, 1690, 1601, 1510, 1456, 1360, 1250, 1200, 1150, 1008, 868, 835, 806, 705, 660.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.7$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.52 (d, $J = 2.0$ Hz, 2H), 6.09–5.87 (m, 1H), 5.23–5.13 (m, 1H), 5.13–5.05 (m, 1H), 4.10 (t, $J = 6.7$ Hz, 2H), 4.03 (s, 2H), 2.62 (d, $J = 6.7$ Hz, 1H), 2.54–2.39 (m, 2H), 1.90 (m, 4H), 1.63–1.18 (m, 19H), 1.14–1.02 (m, 2H), 0.90 (m, 6H)

^{13}C NMR (400 MHz, $CDCl_3$) δ 14.10, 14.42, 20.04, 22.66, 25.99, 29.12, 29.22, 29.33, 31.80, 33.50, 34.43, 37.02, 39.73, 44.11, 68.34, 68.45, 100.41, 105.54, 117.16, 121.49, 121.56, 127.64, 131.04, 134.37, 142.23, 144.99, 158.92, 161.29, 164.29.

Elemental analysis: $C_{34}H_{48}O_4$ requires C78.46, H 9.23; found: C 78.41, H 9.30.

4-(2-Allyloxy-4-octyloxybenzoate)-4′-propylbiphenyl (XII). Yield: 82.1%.

FT-IR (KBr, cm^{-1}): 3020, 2920, 2857, 1728, 1690, 1601, 1510, 1456, 1360, 1250, 1200, 1150, 1008, 868, 835, 806, 705, 660.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J = 8.7$ Hz, 1H), 7.54–7.63 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.22–7.33 (m, 4H), 6.44–6.57 (m, 2H), 6.07 (ddt, $J = 16.1$, 9.8, 6.1 Hz, 1H), 5.58 (dq, $J = 16.1$, 1.6 Hz, 1H), 5.28 (dd, $J = 9.8$, 1.5 Hz, 1H), 4.64 (dt, $J = 6.1$, 1.6 Hz, 2H), 4.03 (t, $J = 6.2$ Hz, 2H), 2.62 (t, $J = 7.8$ Hz, 2H), 1.74–1.85 (m, 2H), 1.67–1.72 (m, 2H), 1.41–1.52 (m, 2H), 1.2–1.40 (m, 8H), 0.94–1.03 (m, 3H), 0.84–0.92 (m, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 12.98, 14.01, 22.93, 24.48, 26.49, 28.71, 28.96, 29.06, 31.64, 38.11, 69.64, 71.17, 104.65, 107.03, 113.63,117.52, 122.06, 127.25, 127.99, 130.21, 133.98, 134.46, 134.74, 139.07, 141.84, 153.11, 162.31, 165.05, 167.58.

Elemental analysis: $C_{32}H_{46}O_4$ requires C79.2, H 8.0; found: C 79.14, H 8.02.

3. Results and Discussion

These new reactive LC monomers were synthesized as shown in Scheme 1. The purities of these compounds and the reaction time were verified by thin layer chromatography (TLC). From the FT-IR, compound X at 3085 cm^{-1} might be a result of the existence of the double bond group, because it might be –C=C–H stretching bands. The characteristic absorption of the target compound X at 1720 cm^{-1} can attributed to the stretching bands of the carbonyl group (C=O). The peak at 2938 cm^{-1} corresponds to the methyl group and the peak at 2850 cm^{-1} might be a result of the existence of methylene group. Compared with compound X, the characteristic absorptions of the target compounds XI and XII could be find in the FT-IP spectra (3025, 2924, 2860, and 1735 cm^{-1} for the target compound XI; 3020, 2920, 2857, and 1728 cm^{-1} for the target compound XII).

In the ^{1}H NMR (400 MHz, $CDCl_3$) of compound X, the chemical shifts at δ 6.09 (ddt, $J = 17.2$, 10.5, 4.7 Hz–CH=C), δ 5.59 (dq, $J = 17.2$, 1.6 Hz, –C=CH2), and δ 5.30 ppm (dd, $J = 10.6$, 1.5 Hz,–C=CH2) verify the double bond in the molecular structure of compound X. In the ^{13}C NMR (400 MHz, $CDCl_3$) of compound X, the chemical shifts at δ 164.28 ppm are attributed to the carbonyl carbon. Compared with compound X, similar chemical shifts could be found in the ^{1}H NMR and ^{13}C NMR of compounds XI and XII.

Based on the above analysis, we confirm that the reactive LC monomers (compounds X, XI, and XII) have been successfully synthesized.

The mesomorphic properties of the target products (compounds X, XI, and XII) were investigated with a POM equipped with a heating stage and differential scanning calorimeter. The results (during the first heating–cooling run) of the target products (compounds X, XI, and XII) are shown in Fig. 1.

Figure 1 shows that the target products display two exothermic peaks during the cooling, which should be attributed to phase transition (as confirmed by the POM images in Fig. 2). From Fig. 2, it can be seen that the final products show optical texture characteristics of the nematic phase. However, compounds X and XI display two endothermic peaks during the heating and they do not show the optical texture characteristics of LC phase. The colors of compounds X and XI changed from white to yellow at the first endothermic peak temperature, suggesting that their first endothermic peaks may be the crystal-to-crystal transition peaks induced by the conformational reorganization of molecules into a more stable crystalline configuration. The target products melt at the second endothermic peaks. Therefore, the second endothermic peaks correspond to the melting points of the target products. The phase transition temperatures of compounds X, XI, and XII are shown in Table 1.

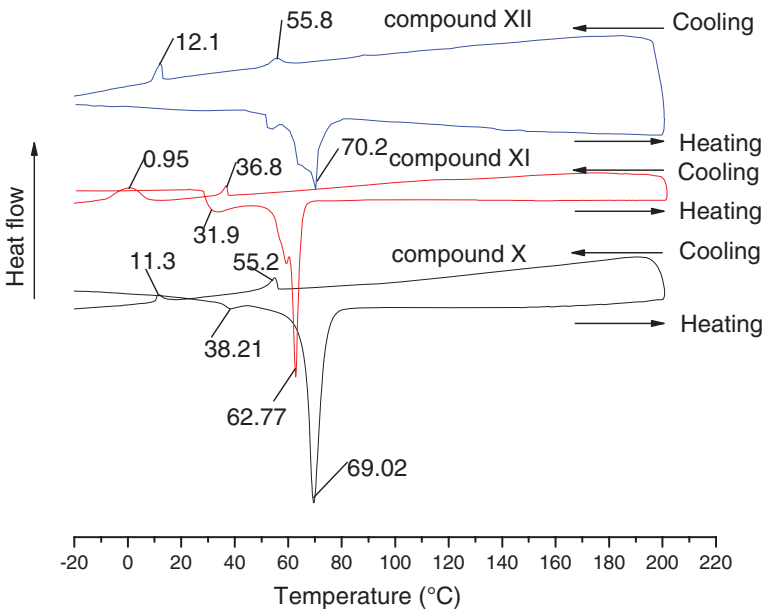


Figure 1. DSC curves of the target product (compounds X, XI, and XII) during the first heating-cooling run.

Figure 1 shows that the phase-transition temperature of compound XI shifts to a temperature lower than that of compound X. This is due to the two methylene groups in the side chain of the compound XI. The flexibility of compound XI is higher than that of compound X, especially for the side-chain flexibility. So molecules of compound XI may close more easily to form the orientation to exhibit a monotropic nematic mesophase. Therefore a slight change of the side chain has big effect on liquid crystalline behavior.

Compared with compound X, compound XII has more phenyl groups and little changes were found in the LC interval. But it can still be seen that the increased rigidity of the main chain makes the LC interval shift to a higher temperature region. So a slight change of the polarity of the main chain has little effect on liquid crystalline behavior.

From the above analysis, the flexibility of side chains affects more than that of the main chain on liquid crystalline behavior.

However, the target products (compounds X, XI, and XII) do not show LC phase during the heating process, which can be attributed to the steric hindrance that makes it difficult for the molecules to be active during the heating process. The steric hindrance is easy to overcome during the cooling process, since the molecules move more easily in the liquid

Table 1. Phase transition temperatures of compounds X, XI, and XII. Enthalpy values in $J \cdot g^{-1}$ are given in parentheses

Compound	Phase transition temperatures on cooling	Melting point
X	Cr 11.3 (5.31) N 55.2 (1.72) I	69.02 (44.18)
XI	Cr 0.95 (9.40) N 36.8 (1.65) I	62.77 (58.72)
XII	Cr 12.1 (6.85) N 55.8 (1.37) I	70.20 (38.15)

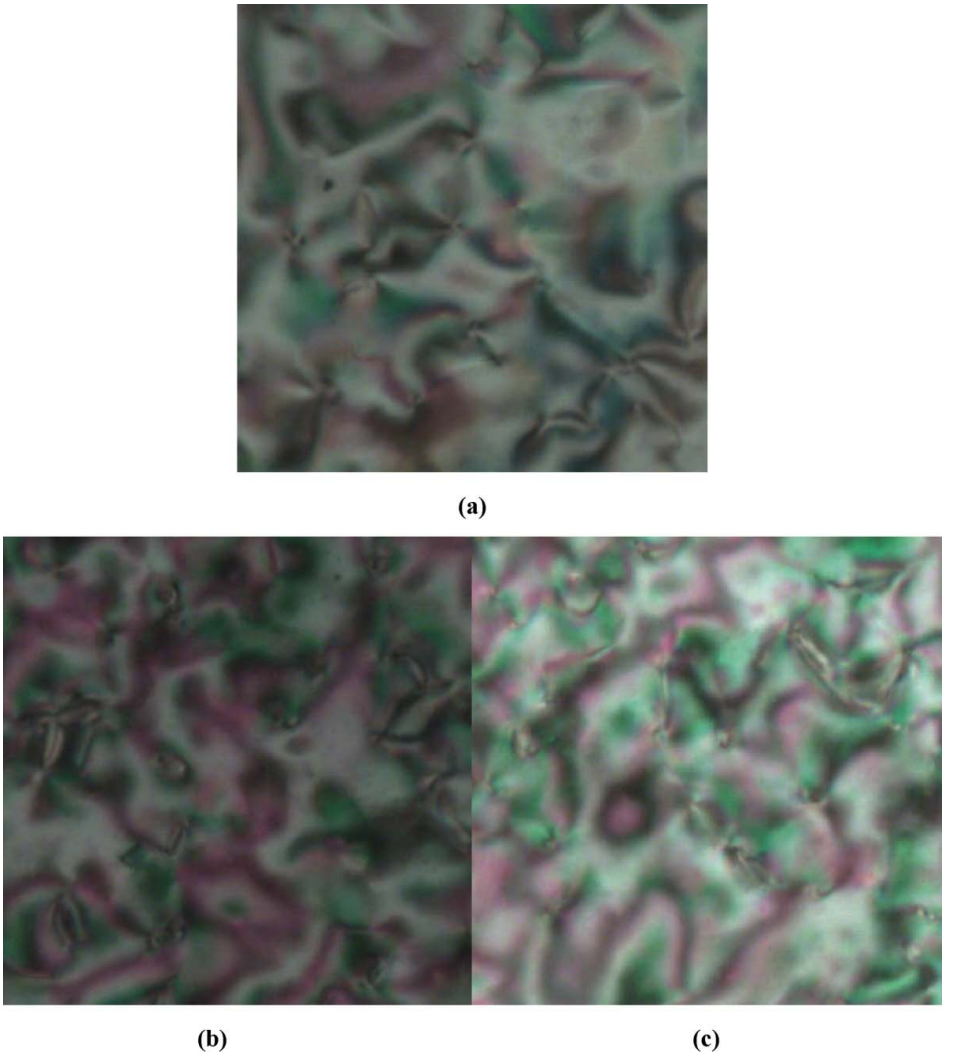


Figure 2. POM images of compounds X, XI, and XII on cooling. (a) Polarizing optical textures of compound X at 24.7°C. (b) Polarizing optical textures of compound XI at 7.8°C. (c) Polarizing optical textures of compound XII at 35.4°C.

state than in solid state. Therefore, the steric effect can be overcome by molecular motion and polymer molecules arrange to form the LC phase.

4. Conclusions

A series of novel ester LC monomers with double bonds in the side chains were successfully synthesized and their structures were characterized by elemental analysis, NMR, and FT-IR spectrum. The effect of the side-chain length on the phase transition behavior was studied. The LC range of 4-(4-propylcyclohexyl)phenyl 2-(but-3-enyloxy)-4-octyloxybenzoate

shifts to lower temperatures region in comparison with 4-(4-propylcyclohexyl)phenyl 2-allyloxy-4-octyloxybenzoate. When the phase transition takes place, the change in the side chains is more significant than that in the main chains. Our novel ester LC monomers with double bonds in the side chains are important for extending the applications of LCs.

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