

SYNTHESIS AND CHARACTERIZATION OF SIDE CHAIN LIQUID CRYSTALLINE POLYSILOXANES CONTAINING BENZYL ETHER LINKING UNITS*

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Abstract Side chain liquid crystalline polysiloxanes containing benzyl ether linking units were synthesized by the hydrosilylation of poly(methylhydrosiloxane) with a series of 4-(4-alkoxybenzyloxy)-4'-allyloxybiphenyl monomers [4-(4-methoxybenzyloxy)-4'-allyloxybiphenyl (M_1), 4-(4-ethoxybenzyloxy)-4'-allyloxybiphenyl (M_2), 4-(4-propoxybenzyloxy)-4'-allyloxybiphenyl (M_3), 4-(4-butoxybenzyloxy)-4'-allyloxybiphenyl (M_4), 4-(4-pentoxybenzyloxy)-4'-allyloxybiphenyl (M_5), 4-benzyloxy-4'-allyloxybiphenyl (M_6)]. The phase behavior of monomeric and polymeric liquid crystals was characterized by differential scanning calorimetry and optical polarization microscopy where the groups are ranged from methoxy to pentoxy. Both the monomeric and polymeric liquid crystals exhibit liquid crystal behaviors.

Keywords Liquid crystal; Polysiloxane; Benzyl ether; Side chain; 4-Allyloxy-4'-hydroxybiphenyl

INTRODUCTION

The traditional pathway to synthesize low molecular weight liquid crystals is to interconnect two similar or dissimilar rings (e.g., aromatic, *trans*-cyclohexane, bicyclooctane, *trans*-cyclohexane, bicyclooctane, *trans*-2, 5-dioxane, -dithiane, or -dioxathiane), through rigid interconnecting groups (e.g., $-\text{C}\equiv\text{C}-$, $-\text{CH}=\text{N}-$, $-\text{N}=\text{N}-$, $-(\text{CH}=\text{CH})_n-$, $-\text{CH}=\text{N}-\text{N}=\text{CH}-$, ester group, ethane and methyleneoxy units). Ethane and methyleneoxy units are flexible and undergo free rotation, leading to a number of different conformational isomers^[1-3]. The benzyl mesogen was first employed in the polymeric liquid crystals by Hsu^[4] and Hsieh^[5,6] et al.

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We are very interested in the synthesis of liquid crystalline polymers containing this unit, because they are more thermally and chemically stable than liquid crystals containing other connecting groups mentioned above^[6]. The goal of this investigation is to present the synthesis and characterization of liquid crystalline polymers containing benzyl ether and biphenyl mesogen, which are potential gas chromatography stationary phases.

EXPERIMENTAL

Chemicals

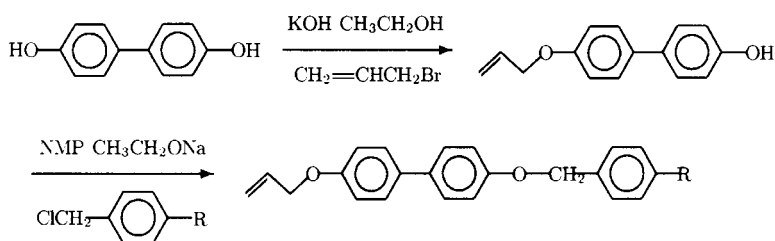
Poly(methylhydrosiloxane) (PMHS, $n = 35$) and 4, 4'-dihydrobiphenyl were obtained from Merck-Schuchardt Co. Other reagents were all analytical grade.

Methods

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions. The FTIR spectra were recorded with Perkin-Elmer FTIR-1600. $^1\text{H-NMR}$ spectra, 400 MHz, were recorded on a ARX 400 NMR spectrometer (ZHB-HS Co.). MS measurements (EI^+) were performed by VG 300 MS spectrometer (ZHB-HS Co.).

Synthesis of monomers and polymers

The synthesis of monomeric and polymeric liquid crystals are outlined in Scheme 1 and Scheme 2, respectively



Monomer	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆
R	CH ₃ O	CH ₃ CH ₂ O	CH ₃ (CH ₂) ₂ O	CH ₃ (CH ₂) ₃ O	CH ₃ (CH ₂) ₄ O	H

Scheme 1 The synthesis of monomeric liquid crystals

4-Alkoxybenzyl chloride 0.055 mol of 4-alkoxybenzyl alcohol was dissolved in 180 ml methylene chloride, and 10 ml (0.137 mol) of SOCl_2 were added dropwise. After the addition, the reaction mixture was again stirred for 1 h, washed with water, a 2% NaHCO_3 aqueous solution, and water, then dried over anhydrous sodium sulfate. The water-free solution was passed through a silica gel column, and the solvent was evaporated to yield an oily product. The 4-alkoxybenzyl chloride was characterized by $^1\text{H NMR}$ (60 Hz, δ , ppm, CCl_4):

4-propoxybenzyl chloride, 1.07 (3H, $-\text{CH}_3$), 1.87 (2H, MeCH_2-), 3.36 (2H, $\text{EtCH}_2\text{O}-$), 3.96 (2H, $\text{PhCH}_2\text{Cl}-$), 6.76—7.16 (4H, aromatic protons)

4-butoxybenzyl chloride, 1.05 (3H, $-\text{CH}_3$), 1.33—2.14 (4H, $\text{MeCH}_2\text{CH}_2-$), 3.36 (2H, $\text{PrCH}_2\text{O}-$), 3.98 (2H, $\text{PhCH}_2\text{Cl}-$), 6.80—7.19 (4H, aromatic protons)

4-pentoxybenzyl chloride, 1.06 (3H, $-\text{CH}_3$), 1.13—2.04 (6H, $\text{MeCH}_2\text{CH}_2\text{CH}_2-$), 3.36 (2H, $\text{EtCH}_2\text{O}-$), 3.98 (2H, $\text{PhCH}_2\text{Cl}-$), 6.80—7.19 (4H, aromatic protons)

4-Allyloxy-4'-hydroxybiphenyl A mixture of 3.0 g of KOH, 10 g of 4, 4'-dihydroxybiphenyl, and 50 ml ethanol was stirred until the solid was dissolved, and heated to refluxing. 8.5 ml (0.11 mol) of allyl bromide was added to the mixture dropwise. The reaction mixture was refluxed for 10 h. The solvent was removed and the crude product was recrystallized several times from a 10 wt.% aqueous sodium hydroxide solution to remove 4, 4'-dihydroxybiphenyl. The batch was then redissolved in 500 ml of a 2 wt.% aqueous solution of sodium hydroxide, heated up to about 90°C and filtered off the insoluble diether, which is a by-product of the reaction. The filtrate was neutralized with hydrochloric acid at $60-70^\circ\text{C}$ yielding the desired product 4.6 g (34.0%).

$^1\text{H NMR}$ (60 Hz, δ , ppm, CCl_4): 3.67 (2H, $-\text{CH}_2\text{Ph}$), 5.17—5.67 (2H, $=\text{CH}_2$), 5.86—6.58 (1H, $=\text{CH}-$), 6.90—8.40 (8H, aromatic protons)

Liquid crystal monomers The monomeric liquid crystals were synthesized by etherification of the corresponding sodium phenolate with 4-alkoxybenzyl chloride. An example of preparation is presented below. To a sodium ethoxide solution prepared by dissolving 0.15 g (6.5×10^{-3} mol) of freshly cut sodium in 30 ml absolute ethanol, 1.0 g (5.0×10^{-3} mol) of 4-allyloxy-4'-hydroxybiphenyl was added at once. The ethanol was evaporated to form the sodium salt of 4-allyloxy-4'-hydroxybiphenyl, and 50 ml of dried N-methyl-2-pyrrolidone were added into the same flask. When the sodium salt was completely dissolved, 1.0 g (5.4×10^{-3} mol) 4-alkoxybenzyl chloride was added to the mixture. The mixture was reacted at 110°C for 5 h, cooled to room temperature, and poured into water. The solid was filtered

Table 1 The characterization of monomeric liquid crystals

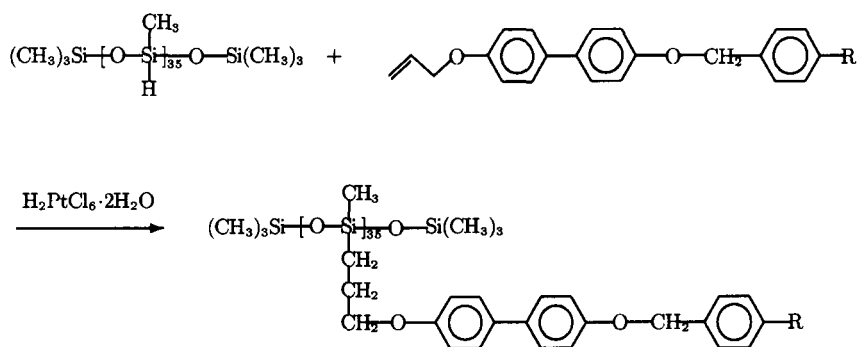
Compound	$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm)	IR (cm^{-1})	MS (EI^+)	Elemental analysis
M_1	3.82 (3H, $-\text{OCH}_3$),	2900, 2850, 1650,	346, 305,	C:79.65
	4.46—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	1610, 1580, 1520	225, 185,	H:6.75
	5.01 (2H, PhCH_2O),	1500, 1270, 1230	128, 121,	
	5.29—5.32 and 5.40—5.46 (2H, $=\text{CH}_2$),		91, 78,	
	6.03—6.11 (1H, $=\text{CH}$),		41	
	6.92—7.48 (12H, aromatic protons)			
M_2	1.40—1.43 (3H, $-\text{CH}_3$),	2980, 2860, 1650,	360, 319,	C:80.01
	4.02—4.07 (2H, MeCH_2O),	1610,	185, 157,	H:6.93
	4.56—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	1600, 1590, 1520,	135, 128,	
	5.10 (2H, $\text{Ph}-\text{CH}_2\text{O}$),	1500, 1270, 1230	107, 77,	
	5.29—5.32 and 5.41—5.46 (2H, $=\text{CH}_2$),		41	
	6.03—6.13 (1H, $=\text{CH}$),			
M_3	6.90—7.48 (12H, aromatic protons)			
	1.01—1.06 (3H, $-\text{CH}_3$),	3050, 2970,	374, 333,	C:80.19
	1.79—1.84 (2H, MeCH_2),	2870, 1650, 1610,	226, 197,	H:7.21
	3.91—3.95 (2H, EtCH_2O),	1600, 1570,	185, 157,	
	4.56—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	1520,	149, 128,	
	5.10 (2H, $\text{Ph}-\text{CH}_2\text{O}$),	1500, 1270,	107, 90	
M_4	5.29—5.32 and 5.41—5.46 (2H, $=\text{CH}_2$),	1230	77, 41	
	6.03—6.13 (1H, $=\text{CH}$),			
	6.90—7.48 (12H, aromatic protons)			
	0.96—0.99 (3H, $-\text{CH}_3$),	3050, 2960,	388, 226,	C:80.27
	1.45—1.54 (2H, MeCH_2),	2860, 1650,	185, 163,	H:7.244
	1.73—1.81 (2H, EtCH_2),	1610, 1590,	157, 128	
M_5	3.95—3.99 (2H, PrCH_2O),	1570, 1520,	107, 77, 41	
	4.56—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	1500, 1270, 1230		
	5.01 (2H, $\text{Ph}-\text{CH}_2\text{O}$),			
	5.29—5.32 and 5.41—5.46 (2H, $=\text{CH}_2$),			
	6.03—6.13 (1H, $=\text{CH}$),			
	6.90—7.48 (12H, aromatic protons)			
M_6	0.91—0.95 (3H, $-\text{CH}_3$),	3050, 2950,	402, 361,	C:80.43
	1.37—1.46 (2H, MeCH_2),	2860, 1650, 1610,	291, 226,	H:7.47
	1.77—1.81 (4H, EtCH_2CH_2),	1590,	185, 177,	
	3.94—3.98 (2H, BuCH_2O),	1520, 1500,	157, 128,	
	4.56—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	1270, 1230	107, 77, 41	
	5.00 (2H, $\text{Ph}-\text{CH}_2\text{O}$),			
M_6	5.29—5.32 and 5.41—5.46 (2H, $=\text{CH}_2$),			
	6.03—6.13 (1H, $=\text{CH}$),			
	6.91—7.48 (12H, aromatic protons)			
	4.56—4.58 (2H, $=\text{C}-\text{CH}_2\text{O}$),	3050, 2930,	316, 275,	C:83.37
	5.10 (2H, $\text{Ph}-\text{CH}_2\text{O}$),	2860, 1650, 1610,	185, 157,	H:6.39
	5.28—5.32 and 5.41—5.46 (2H, $=\text{CH}_2$),	1570,	138, 128	
M_6	6.03—6.13 (1H, $=\text{CH}$),	1500, 1270, 1230	71, 85, 41	
	6.91—7.48 (13H, aromatic protons)			

out, washed with dilute NaOH aqueous solution and then with water, and dried in vacuum. The product was purified by column chromatography (silica gel, CH_2Cl_2), and recrystallized from methanol to yield 1.6 g (83.2%) of white platelets. Table 1 summarized the results of the characterization for all the synthesized monomeric liquid crystals. Table 2 presents the phase transition of the same compounds.

Table 2 The phase transitions of monomeric liquid crystals

Compound	Phase transitions ($^{\circ}\text{C}$)	
	Heating	Cooling
M ₁	k178.8(37.6)s184.0(37.6)i	k128.8(−17.2)s135.9(−13.0)n176.1(−13.1)i
M ₂	k165.6(26.1)s189.7(19.5)n191.3(19.5)i	K149.8 (−12.2)n184.5(−14.4)i
M ₃	k162.4(18.4)s189.1(21.8)n191.6(21.8)i	k149.2(−8.3)s184.7(−17.2)i
M ₄	k145.4(16.7)s181.0(2.56)n190.9(14.5)i	k102.3(−5.4)s119.3(−6.3)s178.4(−16.0)n184.9 (−16.0)i
M ₅	k138.7(17.1)s180.5(3.18)n190.2(19.2)i	k91.5(−16.5)s100.7(−16.5)s177.7(−2.3)n185.0(12.0)i
M ₆	k161.5(11.52)s175.3(24.8)i	k130.2(−3.9) s167.7(−20.31)i

Polysiloxanes The procedure of synthesis was shown in Scheme 2. A general synthetic procedure is shown below. 0.2 g of M₁ was dissolved in 30 ml of dry, fresh,



Scheme 2 The synthesis of polymeric liquid crystals

toluene together with 0.15 g of polymethylhydrosiloxane. The reaction mixture was heated to 110°C under nitrogen, and $50\text{ }\mu\text{g}$ of hydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$) was added as a solution in tetrahydrofuran (1 mg/ml). The reaction mixture was refluxed under nitrogen for 20 h. After this reaction time, the remained Si—H groups were reacted with ethylene until IR analysis showed that the hydrosilylation reaction was complete. The white polymer products were separated by precipitation in methanol, purified by reprecipitation from chloroform solutions

with methanol, and then dried under vacuum.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of monomeric liquid crystals. As described in the experimental part, each reaction step was accomplished with pretty high yield and the monomers were obtained in high purity as determined by ^1H -NMR spectroscopy and thin layer chromatography. The synthesized compounds were characterized by ^1H -NMR, MS(EI⁺), IR and elemental analysis, the results of which are shown in Table 1. Table 2 lists the phase transitions and thermodynamic parameters of monomeric liquid crystals. All of the monomers exhibit liquid crystalline behaviors. The alkyl group (R in the liquid crystals) affects the phase transition of the monomeric liquid crystals. The monomeric liquid crystal having longer tail exhibits wider mesophase transition range. The alkyl groups have no evident influence on the clear point of the monomeric liquid crystals, but show strong influence on the melting point. The monomeric liquid crystal having longer alkyl group exhibits lower melting point.

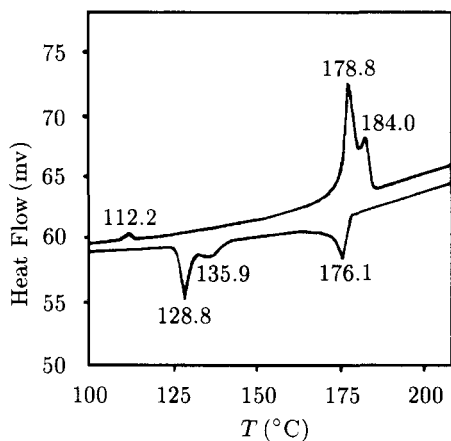


Fig.1 The DSC scan of M_1 ($10^\circ\text{C}/\text{min}$)

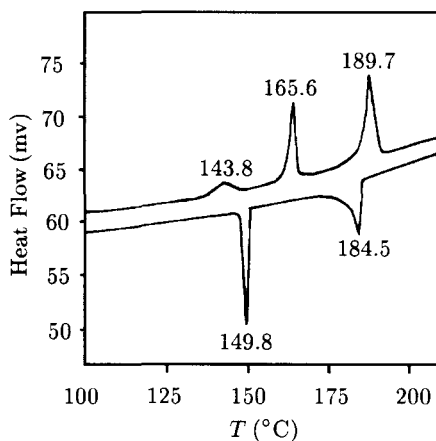
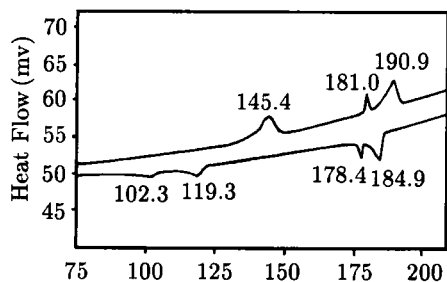


Fig.2 The DSC scan of M_2 ($10^\circ\text{C}/\text{min}$)

Fig.1-6 illustrated the DSC scan of monomeric liquid crystals. M_1 is smectic from 178.8°C to 184.0°C on heating, and becomes isotropic liquid above 184.0°C , but it is smectic from 128.8°C to 135.9°C , and nematic from 135.9°C to 176.1°C on cooling. M_2 is smectic from 165.6°C to 189.7°C on heating, and isotropic above 189.7°C , but it is nematic 149.8°C to 184.5°C on cooling. M_3 is smectic from 162.4°C to 189.1°C , nematic from 189.1°C to 191.6°C on heating, and it is smectic from 149.2°C to

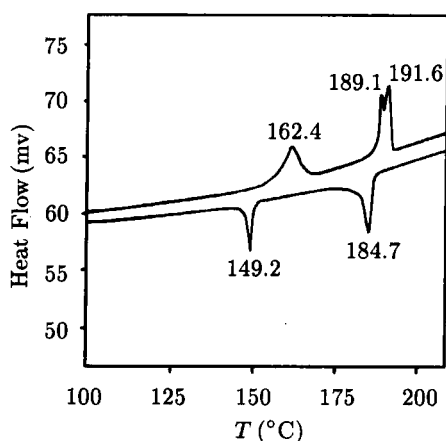
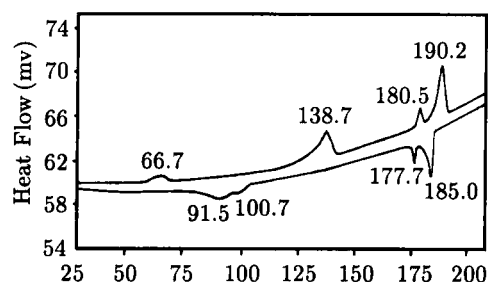
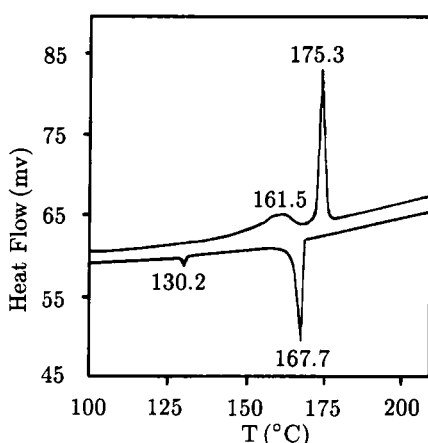
184.7°C on cooling. M_4 is smectic from 145.4°C to 181.0°C, and nematic from 181.0°C to 190.9°C on heating. But it is smectic from 102.3°C to 178.4°C, and nematic from 178.4°C to 184.9°C on cooling. M_5 exhibits the differences in thermal behavior between liquid crystals. It has a solid-solid phase transition at 66.7°C on the heating scan. This is caused by the "pentyl tail" of M_5 ,

Fig.4 The DSC scan of M_4 (10°C/min)

which is flexible and undergoes free rotation about $-\text{CH}_2-\text{CH}_2-$ bond leading to a number of different conformational isomers. On the heating scan, M_5 is smectic from 138.7°C to 180.5°C, nematic from 180.5°C to 190.2°C. On the cooling scan, it is smectic from 91.5°C to 177.7°C, and nematic from 177.7°C to 185.0°C. M_6 is smectic from 161.5°C to 175.3°C on heating, and it is smectic from 130.2°C

to 167.7°C on cooling. The texture of M_3 on cooling and the texture of PM_3 on heating are shown in Figs.7-8.

Scheme 2 outlines the synthesis of polymeric liquid crystals, the FTIR spectra

Fig.3 The DSC scan of M_3 (10°C/min)Fig.5 The DSC scan of M_5 (10°C/min)Fig.6 The DSC scan of M_6 (10°C/min)

showed the absence of Si—H adsorption. Table 3 summarizes the phase transitions of polymeric liquid crystals. Their phase transitions were characterized by optical polarization microscopy. The polymeric liquid crystals exhibit wider mesophases than the monomeric liquid crystals. The alkyls of liquid crystals show no evident influence

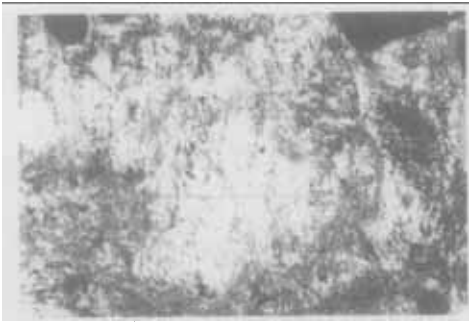


Fig.7 The texture of M₃ on cooling at 170°C (magnification: 200x)



Fig.8 The texture of PM₃ on heating at 180°C (magnificant: 200x)

Table 3 The phase transitions of polymeric liquid crystals*

Polymer	PMHS: monomer, mol:mol	Phase transitions (°C)	Δ <i>T</i> (°C)
PM ₁	1:35	g171.9s260.4i	88.5
	1:9.8	g147.8s220.6i	78.2
	1:6.5	g140.5s207.4i	66.9
	1:4.4	g134.4s196.5i	62.1
PM ₂	1:35	g169.8s261.5i	91.7
	1:9.1	g144.5s213.6i	69.1
	1:6.4	g130.6s197.8i	67.2
PM ₃	1:35	g168.3s259.5i	91.2
	1:8.8	g145.5s220.3i	74.8
	1:6.2	g129.8s197.6i	67.8
PM ₄	1:35	g166.7s260.5i	93.8
	1:8.5	g140.5s218.8i	78.3
	1:5.8	g130.3s199.5i	68.9
PM ₅	1:35	g164.8s259.4i	94.6
	1:8.2	g139.8s215.8i	76.0
	1:5.6	g128.7s199.9i	71.1
PM ₆	1:35	g169.8s203.5i	33.7
	1:9.8	g150.7s170.7i	20.0
	1:5.9	g130.5s140.6i	10.1

on the polymeric liquid crystals. In order to obtain the polymers that can be dissolved in organic solvent, the monomeric liquid crystals were allowed to react with poly(methyl-hydrosiloxane) of different ratios. If all of the Si—H bond were re-

acted with the monomeric liquid crystals, the obtained polymers will not dissolve in cool organic solvent, such as chloroform, dichloromethane, toluene, etc. With the decreasing of ratio of monomeric liquid crystals, mesophases of the polymeric liquid crystals become narrower. The phase transitions of polymeric liquid crystals were listed in Table 3. The application of these materials in gas chromatography will be published elsewhere.

CONCLUSION

All of the synthesized liquid crystals present mesomorphism, and the polymeric liquid crystals exhibit wider mesophase than the corresponding monomeric liquid crystals. The alkyl group of monomeric liquid crystals have an evident influence on their liquid crystalline behavior. With the alkyl group becomes longer, the monomeric liquid crystals show wider mesophase.

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