

SIDE CHAIN LIQUID CRYSTALLINE POLYSILOXANES CONTAINING CROWN ETHER AND BENZYL ETHER MOIETIES*

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Abstract Two kinds of side chain liquid crystalline polysiloxanes containing crown ether and benzyl ether were synthesized and characterized by optical polarization microscopy. Both the monomeric liquid crystals and polymeric liquid crystals show smectic phases.

Keywords Liquid crystalline polysiloxane; Side chain; Crown ether; Benzyl ether mesogens

INTRODUCTION

Crown ethers are well-known for their ability to form strong complexes with alkali metal and organic cations^[1]. This unique ability has led to numerous applications in synthetic and analytical chemistry^[2-4]. He et al. reported on some nematic liquid-crystal containing benzo-crown ether units^[5]. Percec et al. presented the synthesis and characterization of thermotropic, main chain, liquid crystalline polyesters, copolyesters and polysiloxanes containing crown ether units^[6-12]. Cowie et al. demonstrated the synthesis of a thermotropic, main-chain liquid crystalline, polyamide containing diaza-[18]-crown-6 ether units^[13]. Wen et al. investigated the synthesis of liquid crystalline polysiloxanes containing benzo-[15]-crown-5 ether and phenyl units^[14,15]. Huang et al. synthesized the liquid crystalline polysiloxanes containing benzo-[15]-crown-5 ether and biphenyl units^[16].

In our previous works, the chromatographic properties of liquid crystalline polysiloxane containing benzo-[15]-crown-5 ether and biphenyl units were studied^[17,18,19]. The goal of this paper is to describe the synthesis and characterization of side chain

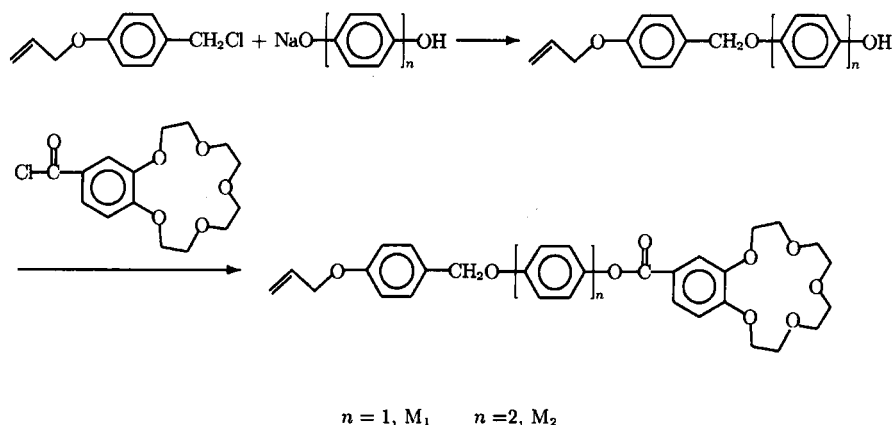
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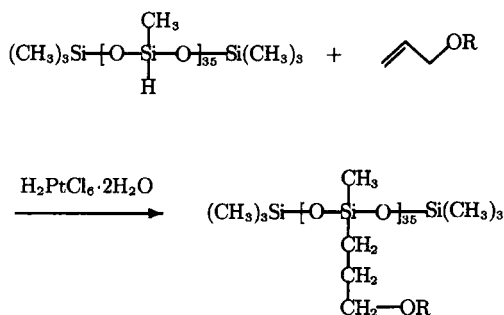
liquid crystalline polysiloxanes containing benzo-[15]-crown-5 ether, benzyl ether of biphenyl and phenyl. Their chromatographic properties will be studied in our later works.

EXPERIMENTAL

The synthesis of monomeric and polymeric liquid crystals were shown in Scheme 1 and Scheme 2.



Scheme 1 The synthesis of monomeric liquid crystals



Scheme 2 The synthesis of polymeric liquid crystals

Materials

Benzo-[15]-crown-5 ether was obtained from Neijiang Synthetic Material Factory (Sichuan Province, China). Polyhydromethylsiloxane and 4,4'-biphenol were obtained from Merck-Schuchardt. Other chemicals were all analytical reagents. 4'-Carboxybenzo-[15]-crown-5 ether was synthesized following the procedure described

in ref. [15].

Characterization

The phase transitions of monomeric and polymeric liquid crystals were examined on an optical polarization microscopy SG85 (Beijing Optical Instrument). 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 measurement was performed by VG 300 MS spectrometer (ZHB-HS Co.).

Synthesis of 4-(4-allyloxybenzyloxy)-phenol and 4-(4-Allyloxybenzyloxy)-biphenol

The two compounds were synthesized with the same procedure.

4-(4-Allyloxybenzyloxy)-biphenol was synthesized by the following procedure: 0.5 g (0.022 mol) freshly cut sodium was dissolved in 30 ml absolute ethanol. After the sodium was completely dissolved, 3.7 g (0.020 mol) 4, 4'-biphenol was added immediately under nitrogen. The ethanol was removed to form the sodium salt of 4, 4'-biphenol, and 50 ml dried N-methyl-2-pyrrolidone were added into the same flask. When the sodium salt was dissolved in N-methyl-2-pyrrolidone, 3.7 g (0.020 mol) 4-allyloxybenzyl chloride was added to the reaction mixture and was stirred at 110°C under nitrogen atmosphere for 5 h, cooled, and poured into water. The resulted precipitate was filtered, washed with dilute NaOH aqueous solution and water, then dried under vacuum. 4-(4-Allyloxybenzyloxy)-biphenol was purified by column chromatography using chloroform and petroleum ether as eluent solvent. Yield, 37.7%. m.p., 196.5°C . $^1\text{H-NMR}$ (400 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 (12H, aromatic protons). IR ($\bar{\nu}$, cm^{-1}): 3350, 2870, 2830, 1650, 1600, 1590, 1510, 1490, 1240. MS, (EI^+): 332, 186, 157, 147, 128, 107, 91, 77, 41.

4-(4-Allyloxybenzyloxy)-phenol was purified by the following procedure: the crude product was crystallized and recrystallized several times from a 10 wt.% aqueous NaOH solution to remove hydroquinone. The batch was then dissolved in 500 ml of a 2 wt.% aqueous solution of NaOH, heated to about 90°C and filtered off the insoluble diether, which is a byproduct of the reaction. Neutralization of the filtrate with hydrochloric acid at 60°C gave 4-(4-allyloxybenzyloxy)-phenol. Yield: 48.1%; m.p.: $113.5\text{--}114.0^\circ\text{C}$. IR ($\bar{\nu}$, cm^{-1}): 3300, 2900, 1640, 1580, 1500, 1240. $^1\text{H-NMR}$ (400 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). MS, (EI^+): 256, 181, 147, 129, 107, 91, 78, 55, 41.

Synthesis of monomeric liquid crystals

1-(4-Allyloxybenzyloxy)-4-(4'-carboxybenzo-15-crown-5) phenyl (M_1). To a mix-

ture of 1.0 g (3.2×10^{-3} mol) 4'-carboxybenzo-15-crown-5 in 30 ml water-free benzene, 1.0 ml thionyl chloride was added dropwise. The mixture was refluxed for 3 h, followed by removal of solvent and excess thionyl chloride under vacuum. The obtained acid chloride was dissolved in 10 ml benzene and added dropwise to 4-(4-allyloxybenzyloxy)-phenol (0.8 g, 3.3×10^{-3} mol) and triethylamine (10 g, 0.01 mol) in 30 ml benzene at 0°C. After the solution was refluxed for 5 h, benzene was removed under vacuum and the remaining white solid was washed with water, and recrystallized from ethanol, yield 1.5 g (83.1%) of white crystals, phase transition temperature, 113.5—198.7°C. IR ($\bar{\nu}$, cm^{-1}): 2850, 1720, 1610, 1510, 1500, 1270, 1230, 1190, 1170. ^1H NMR (400 Hz, δ , ppm, CDCl_4): 3.77—4.22 (16H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 4.54—4.56 (2H, $=\text{C}-\text{CH}_2\text{O}-$), 4.99 (2H, $-\text{CH}_2\text{O}-$), 5.44—5.45 and 5.46—5.47 (2H, $=\text{CH}_2$), 6.10—6.11 (1H, $=\text{CH}-$), 6.90—7.66 (11H, aromatic protons). Elemental analysis (%): C, 67.59; H, 6.29 [calcd. values: C, 67.62; H, 6.22]. MS (FB): 626, 573, 426, 290, 154, 77.

1-(4-Allyloxybenzyloxy)-4-(4'-carboxybenzo-15-crown-5) biphenyl (M_2). The monomeric liquid crystal was synthesized according to the procedure used in the synthesis of 1-(4-Allyloxybenzyloxy)-4-(4'-carboxybenzo-15-crown-5) phenyl (M_1): yield: 77.8%; phase transition temperature: 166.0—194.2°C. IR ($\bar{\nu}$, cm^{-1}): 2930, 2820, 1720, 1600, 1510, 1270, 1230, 1190. ^1H NMR (400 Hz, δ , ppm, CDCl_4): 3.77—4.22 (16H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 4.54—4.56 (2H, $=\text{C}-\text{CH}_2\text{O}-$), 4.99 (2H, $-\text{CH}_2\text{O}-$), 5.44—5.45 and 5.46—5.47 (2H, $=\text{CH}_2$), 6.10—6.11 (1H, $=\text{CH}-$), 6.88—7.46 (15H, aromatic protons). Elemental analysis (%): C, 70.88; H, 6.19 [calcd. values: C, 70.91; H, 6.11]. MS (FB): 550, 428, 325, 217, 109.

Synthesis of polymeric liquid crystals

The synthesis procedure was shown in Scheme 2. A general synthetic procedure is shown below. 0.2 g (M_1 , 3.6×10^{-4} mol; M_2 , 3.2×10^{-4}) monomeric liquid crystal was dissolved in 30 ml dry, freshly distilled toluene together with 0.15 g (6.6×10^{-5} mol) polymethylhydrosiloxane. The reaction mixture was heated to 110°C under nitrogen, and 50 μg 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 that reaction time, the remaining Si—H groups were reacted with ethylene until IR analysis showed that the hydrosilylation reaction was completed. The white polymer products were separated by reprecipitation several times with methanol, purified by several reprecipitation from chloroform solutions into methanol, and then dried under vacuum.

PM_1 , IR ($\bar{\nu}$, cm^{-1}): 1950, 1730, 1600, 1500, 1420, 1260, 1180, 1090, 1020, 760.

PM_2 , IR ($\bar{\nu}$, cm^{-1}): 3020, 2950, 1730, 1600, 1510, 1490, 1270, 1230, 1160, 1080,

1020, 920, 810.

RESULTS AND DISCUSSION

The structure of monomers was confirmed by elemental analysis, MS, ^1H NMR and IR. The IR spectra data of polymers illustrated that the Si—H bonds were completely reacted with monomers and ethylene. The phase transition temperature of monomers and polymers were measured using optical polarization microscopy, and were listed in Table 1. On the heating scanning, M_1 is smectic from 113.5°C to 198.4°C, M_2 is smectic from 166.0°C to 194.5°, PM_1 is smectic from 98.9°C to 200.2°C, and PM_2 is smectic from 122.3°C to 213.5°C. On the cooling scanning, M_1 is smectic from 195.4° to 102.3°C, M_2 is smectic from 189.5°C to 155.4°, PM_1 is smectic from 198.5° to 85.6°C, and PM_2 is smectic from 204.5° to 118.5°.

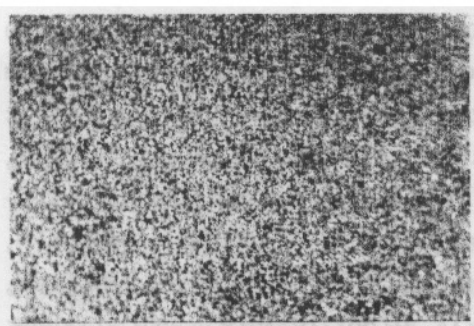


Fig.1 Texture of M_1 at 155°C
(magnification: 200 x)

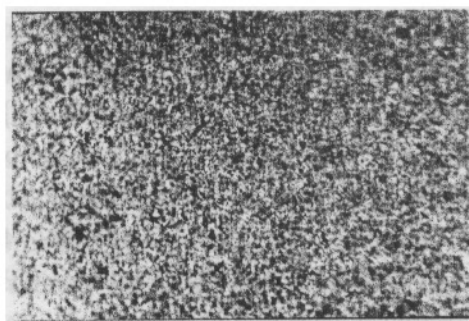


Fig.2 Texture of M_2 at 175°C
(magnification: 200 x)

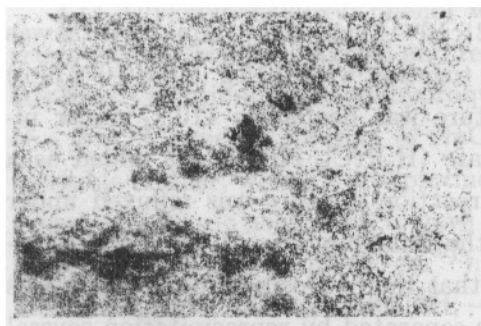


Fig.3 Texture of M_1 at 165°C
(magnification: 200 x)

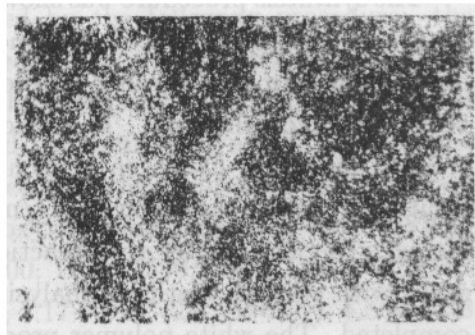


Fig.4 Texture of M_2 at 185°C
(magnification: 200 x)

The phase transitions of polymers were affected by the number of Si—H bonds

reacted with monomers. If the Si—H bonds were all consumed, the glassy transition of synthesized polymers were above 300°C. So in the synthesized polymers, only a part of Si—H bonds reacted with monomers, and other Si—H bonds were reacted with ethylene. PM₁ was obtained as 15.6% of Si—H bonds reacted with M₁, and PM₂ was obtained by 13.8% of Si—H bonds reacted with M₂. The texture of liquid crystals was shown in Fig.1 to Fig.4.

Table 1 The phase transition temperature of liquid crystals

Compound	Phase transitions (°C)*	
	Heating	Cooling
M ₁	k113.5s198.4i	k102.3s195.4i
M ₂	k166.0s194.5i	k155.4s189.5i
PM ₁	g98.9s200.2i	g85.6s198.5i
PM ₂	g122.3s213.5i	g118.5s204.5i

* The phase transition temperature was measured using optical polarization microscopy.

CONCLUSION

The monomeric liquid crystals and polymeric liquid crystals containing crown ether and benzyl ether showed smectic phases.

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