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Synthesis and Characterization of Star-like Liquid Crystals Centered by Silicon

Jian Qiang LIU[1,2]*, Qi Zhen ZHANG[3], Jing Zhi ZHANG[3]

[1] Key Laboratory of Education Ministry on Colloid & Interface Chemistry, Ji'nan 250100
[2] School of Physics and Microelectronics, Shandong University, Ji'nan 250100
[3] School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250100

Abstract: The synthesis and characterization of two new star-like liquid crystals are reported. They are made of a silicon core and four alkoxyazobenzene monomers in the periphery. Their phase behaviors and the structures are determined by infrared absorption spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), elemental analysis (EA), polarizing optical microscope (POM) and differential scanning calorimetry (DSC).

Keywords: Star-like, liquid crystals, synthesis, phase behavior.

There are two hotspots in the study of liquid crystal: one is to find the high capability materials and the other is to realize the liquid crystal's functionality[1-2]. So we carried out the following molecule design: starting with tetrachlorosilane ($SiCl_4$) as the core molecule, the mesogenic monomers (butoxyazobenzene **C** or hexyloxyazobenzene **D**) reacted with $SiCl_4$ directly and got two star-like liquid crystals. Their phase behaviors and the structures are investigated in this paper.

The preparation method of mesogenic monomer **C** is shown in **Scheme 1**[3]. 1-Bromobutane was replaced by 1-bromohexane, the other mesogenic monomer **D** could be obtained[4]. Compounds **C** and **D** were characterized by IR, ^{1}H NMR, POM and DSC. They were nematic liquid crystals and their phase behaviors were K112N124I121N110K and K92N126I124N78K respectively.

Two star-like liquid crystals (**E**, **F**) were synthesized by mesogenic monomers reacting with $SiCl_4$ directly as shown in **Figure 1**. The preparation method of them is as follows[5]: A mixture of 2.0 mL of dried pyridine, 15.0 mL of dried THF and 5.3 g (3.5 mmol) of butoxyazobenzene **C** or hexyloxyazobenzene **D** were put into a 50 mL Wolff bottle after a dry nitrogen inlet. 0.1 mL (0.8 mmol) of $SiCl_4$ (prepared in our laboratory) diluted with 10 mL of dried THF was added in 0.5 h. The reaction solution was refluxed for 24 h. Then it was cooled to room temperature and filtrated. The precipitate was washed with THF and anhydrous ether several times. The yellow residue was recrystallized by THF/anhydrous ethyl alcohol and then chromatographed twice on a column of silica gel using THF/anhydrous ethyl alcohol =3:1 (v/v) as the

* E-mail: jqliu@sdu.edu.cn

eluent. The star-like liquid crystals **E** and **F** were obtained in 78％and 80％, respectively.

Elemental analysis was carried out with a Perkin-Elmer 240 C auto elementary analyser. Elemental anal. of compound **E**: calcd. for $SiO_{12}C_{88}H_{116}N_8$: C, 68.07, H, 7.53, N, 7.22 (％); found: C, 67.94, H, 7.42, N, 7.11 (％); Infrared spectra were recorded on a Fourier transform infrared photoacounstic spectral system (KBr/cm^{-1}): 2936, 2872 (-CH_2-), 1602, 1580 (Ph), 1498, 1473 (N=N), 1244.4 (-OCH_2); ^{1}H NMR (90MHz, $CDCl_3$, δ ppm): 0.96 (t, 12H, CH_3), 1.12-1.92 (m, 48H, CH_2), 3.60-4.08 (m, 24H, OCH_2), 6.88, 7.00, 7.64, 7.88 (m, 32H, Ph-H). Elemental anal. of compound **F**: calcd. for $SiO_{12}C_{96}H_{132}N_8$: C, 69.11, H, 7.98, N, 6.72 (％); found: C, 68.93, H, 7.86, N, 6.65 (％); IR (KBr/cm^{-1}): 2935, 2867 (-CH_2-), 1602, 1580 (ph), 1498, 1473 (N=N), 1245 (-OCH_2); ^{1}H NMR (90MHz, $CDCl_3$, δ ppm): 0.88 (t, 12H, CH_3); 1.08-1.92 (m, 64H, CH_2); 3.60-4.08 (m, 24H, OCH_2); 6.88, 6.96, 7.62, 7.82 (m, 32H, ph-H). This showed that the compounds have expectant structures.

Differential scanning calorimetry (DSC) measurement was performed with a Perkin-Elmer 7 series thermal analysis system. The calorimetric data for the compounds are given in **Table 1**. All phase transitions are enantiotropic. The **E** and **F** showed broader liquid crystalline phases between the isotropic liquid and crystalline phase and the two domains were separated by sharp peak in the DSC. Both compounds exhibit the textures characteristic of nematic phase.

Polarizing optical microscope with a heating stage was used to observe the optical texture of the phases. **Figure 2** shows they are the typical nematic liquid crystalline phase behaviors. According to the data of DSC and the examination of POM[6-8], we can make sure the phase behaviors of the star-like liquid crystals **E** and **F** are K138N147I145N118K and K127N144I142N116K, respectively. The star-like liquid crystal's phase behavior is determined by the mesogenic monomer's phase behavior and they are all nematic phases[9]. The melting point and clearing temperature of **E** and **F** are higher than its mesogenic monomer's due to their bigger molecular weights. The liquid crystal's domain of **E** and **F** are broader than its monomer's, because their espesially star-like structure reduced the interaction of molecules and made them more flexible.

Scheme 1

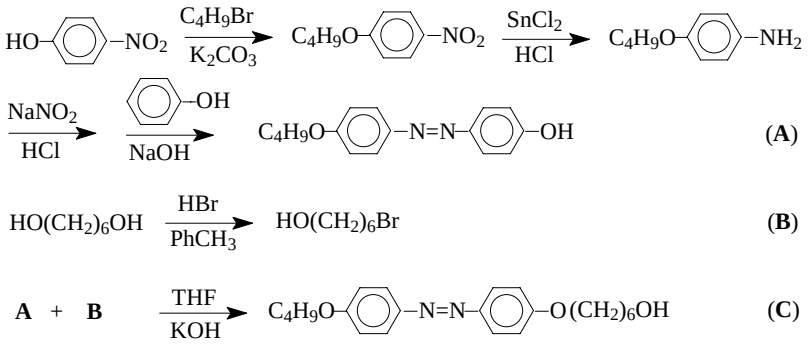


Figure 1 Star-like liquid crystals

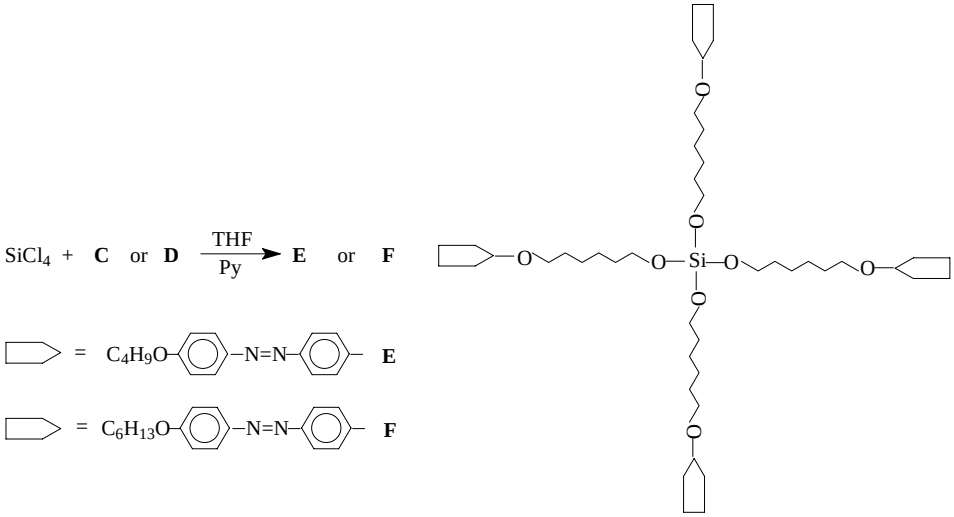
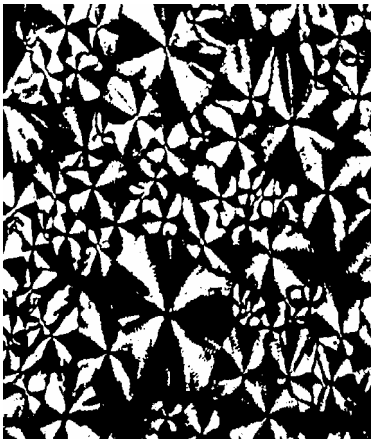


Table 1 DSC datas for **E** and **F**

Compounds	Conditions	T/℃		△H/ J.g^{-1}		△S/ J.g^{-1}.k^{-1}	
E	1st heating	138.26	147.43	68.27	4.244	0.17	0.01
	1st cooling	144.8	118.35	-4.058	-52.97	-0.0097	-0.140
	2nd heating	138.25	147.43	65.17	4.22	0.16	0.01
F	1st heating	126.96	143.96	28.77	2.694	0.072	0.0065
	1st cooling	141.55	115.95	-3.122	-30.27	-0.0075	-0.078

Figure 2 Pictures observed under a POM



(a) **E**, cooling 133℃, Shlieren texture

(b) **F**, cooling 136℃, thread texture

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