

# Synthesis and mesomorphic properties of novel fishbone-like liquid crystalline polysilsesquioxanes†

## VI. Fishbone-like, ester-based liquid crystalline polysilsesquioxanes

CHUN-QING LIU, LI CUI, YANG LIU, ZHONG-RONG SHEN,  
PING XIE and RONG-BEN ZHANG\*

Polymer Chemistry Laboratory,  
Chinese Academy of Sciences and China Petro-Chemical Corporation,  
Center for Molecular Science, Institute of Chemistry,  
The Chinese Academy of Sciences, Beijing 100080, PR China

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Two novel kinds of fishbone-like, ester-based, liquid crystalline, random copolysilsesquioxanes, LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P, have been synthesized for the first time by stepwise coupling polymerization (SCP) from trichlorosilane monomers (RSiCl<sub>3</sub>) containing mesogenic ester groups, using three main steps including preaminolysis, hydrolysis and polycondensation. Two new monomers 4-(11-trichlorosilylundecyloxy)phenyl 4-methoxybenzoate (**M**<sub>1</sub>) and 4-(3-trichlorosilylpropoxy)phenyl 4-methoxybenzoate (**M**<sub>2</sub>) have been synthesized by hydrosilylation reaction of trichlorosilane and the mesogens 4-*n*-undecenyloxyphenyl 4-methoxybenzoate and 4-allyloxyphenyl 4-methoxybenzoate, respectively, in the presence of dicyclopentadienylplatinum(II) chloride (Cp<sub>2</sub>PtCl<sub>2</sub>) catalyst. The structures and mesomorphic properties of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P were investigated by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>29</sup>Si NMR, gel permeation chromatography, polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. It is proposed from the characterization data that these two polymers not only have an ordered ladder-like, double main chain, but also show thermotropic smectic behaviour with high clearing points and wide mesophase ranges (Δ*T*), which may hold promise for potential applications as highly stable gas chromatographic stationary phases.

### 1. Introduction

Since comb-like liquid crystalline polymers (C-LCPs) with a single main chain were first reported by Platé *et al.* [2], Blumstein *et al.* [3] and Ringsdorf *et al.* [4] more than twenty years ago, they have attracted wide attention. Different from main chain liquid crystalline polymers mainly used as high performance engineering materials with good mechanical properties, side group C-LCPs are potentially functional polymer materials with special electric, optical or magnetic properties, including high separation ability as gas chromatography (GC) stationary phases [5]. However, C-LCPs have not been commercially available so far, partly due to narrow mesophase ranges and poor mechanical properties.

In order to improve the mesomorphic and mechanical properties, we first prepared a series of fishbone-like liquid crystalline polysilsesquioxanes (FBLCPs), including β-diketone-based, imine-based and azo-based

FBLCP, by hydrosilylation reaction of a vinyl-terminated liquid crystalline material with a ladder-like polyhydro-silsesquioxane (HT) or random copolymethylhydro-silsesquioxane (MH-T) [1, 6–9]. Their broad mesophase range and good film-forming ability may be attributed to the high regularity and semi-rigidity of the double chain, ladder-like, macromolecular backbone, different from that in other classical single chain polymers. However, the FBLCPs synthesized by this method occasionally suffer from the drawbacks of instability and readiness to cross-link arising from incomplete substitution of Si–H groups on the starting polymer H-T or MH-T. Therefore, from both academic and practical points of view, it was very important to change the method of synthesis.

In this paper, we report the synthesis and characterization of two new types of fishbone-like, ester-based, liquid crystalline random copolysilsesquioxanes by stepwise coupling polymerization (SCP) directly from trichlorosilane monomers (**M**<sub>1</sub> and **M**<sub>2</sub>) possessing mesogenic ester groups, instead of by hydrosilylation of a

\* Author for correspondence; e-mail: zhangrb@infoc3.icas.ac.cn

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vinyl-terminated mesogen with polymer H-T or MH-T. These two novel liquid crystalline polymers are potentially promising functional polymer materials, especially for highly stable GC stationary phases.

## 2. Experimental

### 2.1. Techniques

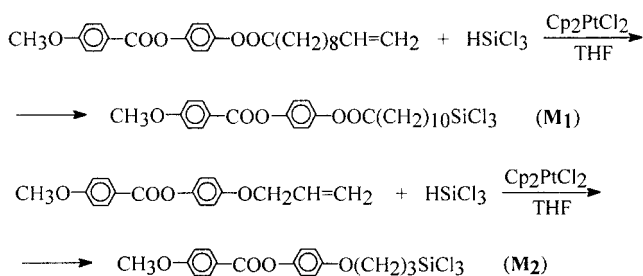
FTIR spectroscopy was carried out using FTIR spectrophotometer PE-80 (USA).  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{29}\text{Si}$  NMR spectra were performed using a JNH-FX100 (JBOX) 300 MHz (USA), with chloroform- $d$  ( $\text{CDCl}_3$ ) as solvent.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are reported relative to the solvent (7.26 and 77.0 ppm, respectively).  $^{29}\text{Si}$  NMR spectra were referenced (0 ppm) to external standards (TMS). Elemental analysis was done using a Heraeus CHN-RAPID, DATEL Systems, Inc (Germany). DSC measurements were made with a Perkin-Elmer DSC-7 (USA). X-ray diffraction (XRD) analysis was carried out using a Rigaku D/MAX 2400 X-ray diffractometer. Molecular masses were measured using a Shimadzu LC-4A chromatograph relative to polystyrene standards in THF solvent and with differential refractive index detection.

### 2.2. Materials

All the solvents were commercially available and of analytical grade. Some solvents were treated before use. Tetrahydrofuran (THF), toluene and diethyl ether were distilled before use, in the case of THF from sodium-benzophenone. Acetone was dried over anhydrous  $\text{Na}_2\text{SO}_4$  before use. 1,4-Phenylenediamine (PDA), trichlorosilane and anhydrous  $\text{Na}_2\text{SO}_4$  were purchased from Beijing Chemical Factory and of analytical grade. Pyridine and triethylamine (TEA) were purchased from Beijing Chemical Factory and dried over  $\text{CaH}_2$ .  $\text{Cp}_2\text{PtCl}_2$  catalyst was prepared by a literature method [5]. 4-(*n*-Undecenoyloxy)phenyl 4-methoxybenzoate and 4(allyloxyphenyl 4-methoxybenzoate were prepared according to the literature [10].

### 2.3. Synthesis

The synthetic routes to  $\mathbf{M}_1$  and  $\mathbf{M}_2$  are shown in scheme 1.



Scheme 1. Synthetic routes to the monomers  $\mathbf{M}_1$  and  $\mathbf{M}_2$ .

### 2.3.1. Synthesis of monomer 4-(11-trichlorosilylundecoyloxy)phenyl 4-methoxybenzoate ( $\mathbf{M}_1$ )

A round-bottomed flask equipped with reflux condenser, magnetic stirrer and two-way stopcock was evacuated and charged with dry argon (three times). Then the flask was charged with 4.1 g (0.01 mol) of 4-*n*-undecenoyloxyphenyl 4-methoxybenzoate, 3 ml of a THF solution of  $\text{Cp}_2\text{PtCl}_2$  ( $1 \text{ mg ml}^{-1}$ ) and 50 ml of THF. The mixture was stirred at room temperature for 30 min, then 2 ml (0.02 mol) of  $\text{HSiCl}_3$  was added. The resulting mixture was continuously stirred, after warming up to  $40^\circ\text{C}$ , for 36 h. Finally, the volatile components were removed under reduced pressure below  $40^\circ\text{C}$ , and the product  $\mathbf{M}_1$  was obtained as a white solid. Yield: 95%,  $\text{C}_{25}\text{H}_{31}\text{Cl}_3\text{O}_5\text{Si}$  ( $M_w$  545.5). IR (KBr):  $\nu = 1745$ , 1732 (COO), 1608, 1583, 1511 ( $\text{C}_6\text{H}_4$ ), 2924, 14 678, 1381 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.01, 8.14 (dd, 4H,  $\text{OC}_6\text{H}_4\text{CO}$ ), 7.15, 7.21 (dd, 4H,  $\text{OC}_6\text{H}_4\text{O}$ ), 3.91 (s, 3H,  $\text{CH}_3$ ), 2.57 (t, 2H,  $\text{COCH}_2$ ), 1.77 (m, 2H,  $\text{COCH}_2\text{CH}_2$ ), 1.60 (m, 2H,  $\text{COCH}_2\text{CH}_2\text{CH}_2$ ), 1.32–1.44 (m, 14H,  $(\text{CH}_2)_7\text{SiCl}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 172.2 ( $\text{C}_6\text{H}_3\text{OCO}(\text{CH}_2)_{10}\text{SiCl}_3$ ), 163.9 ( $\text{C}_6\text{H}_4\text{COOC}_6\text{H}_4$ ), 113.8, 121.6, 132.3, 164.7 ( $\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_4\text{OCO}$ ), 122.4, 122.5, 148.1, 148.3 ( $\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_4\text{OCO}$ ), 55.5 ( $(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{SiCl}_3$ ), 24.3 ( $(\text{CH}_2\text{CH}_2\text{SiCl}_3)$ ), 22.2 ( $(\text{CH}_2\text{SiCl}_3)$ ).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 13.7. Elemental analysis: found, C 55.02, H 5.65; calc, C 55.00, H 5.68%.

### 2.3.2. Synthesis of monomer 4-(3-trichlorosilylpropoxy)phenyl 4-methoxybenzoate ( $\mathbf{M}_2$ )

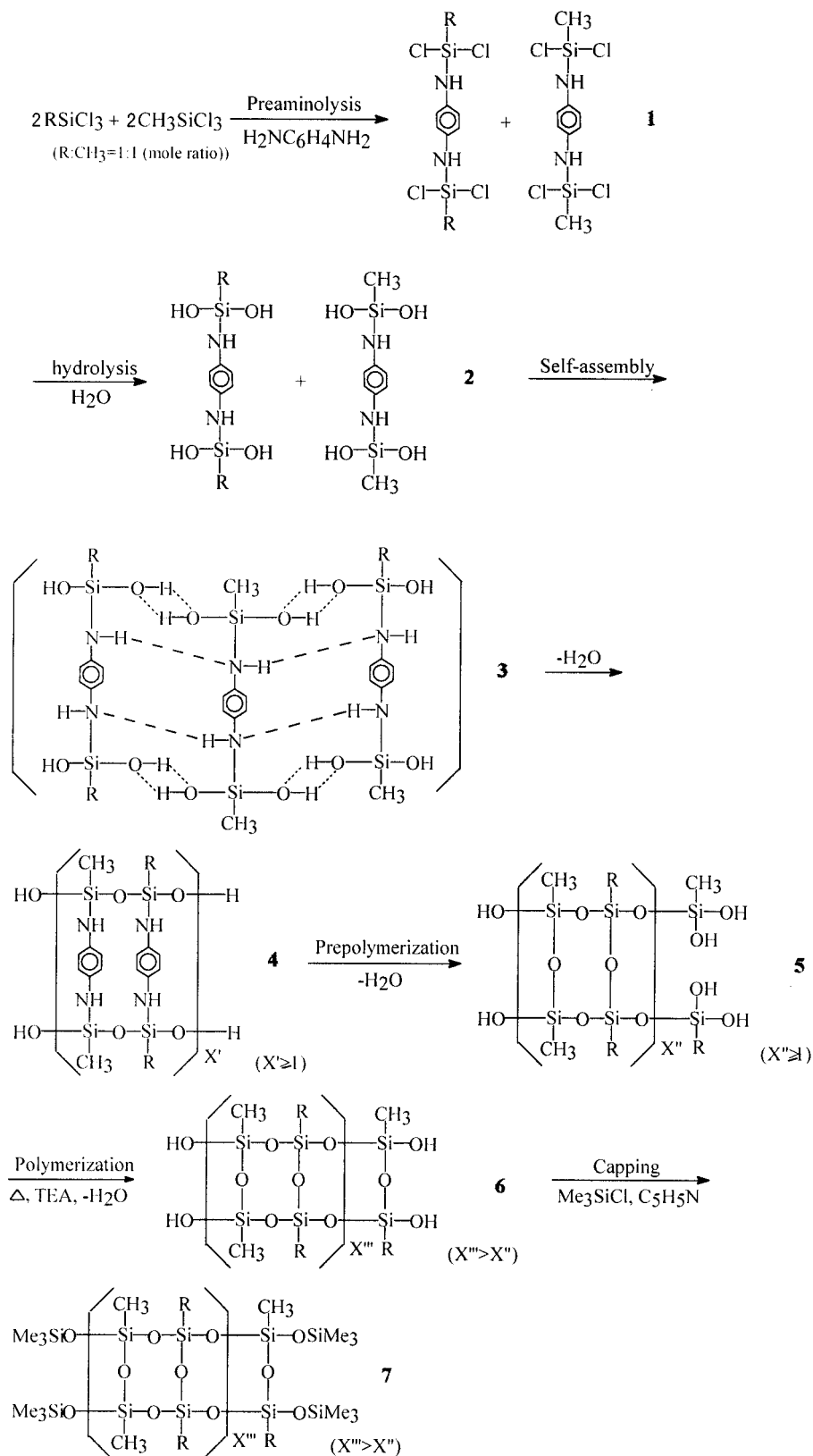
The monomer  $\mathbf{M}_2$  was prepared following the synthetic method for monomer  $\mathbf{M}_1$ . Yield: 97%,  $\text{C}_{17}\text{H}_{17}\text{Cl}_3\text{O}_4\text{Si}$  ( $M_w$  419.5). IR (KBr):  $\nu = 1730$ , 1264 (COO), 1609, 1582, 1513 ( $\text{C}_6\text{H}_4$ ), 2941, 1468 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.21, 8.16 (dd, 4H,  $\text{OC}_6\text{H}_4\text{CO}$ ), 6.93, 7.29 (dd, 4H,  $\text{OC}_6\text{H}_4\text{O}$ ), 4.02 (t, 2H,  $\text{OCH}_2$ ), 3.89 (s, 3H,  $\text{CH}_3$ ), 2.05–2.14 (m, 2H,  $\text{CH}_2\text{CH}_2\text{SiCl}_3$ ), 1.64 (t, 2H,  $\text{CH}_2\text{SiCl}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 163.4 ( $\text{OC}_6\text{H}_4\text{CO}$ ), 114.9, 122.4, 144.5, 156.1 ( $\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_4\text{O}$ ), 113.6, 122.6, 132.1, 163.7 ( $\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_4$ ), 68.3 ( $\text{C}_6\text{H}_4\text{OCH}_2$ ), 55.3 ( $\text{CH}_3\text{OC}_6\text{H}_4$ ), 22.3 ( $\text{CH}_2\text{CH}_2\text{SiCl}_3$ ), 20.8 ( $\text{CH}_2\text{SiCl}_3$ ).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 14.0. Elemental analysis: found, C 48.67, H 4.08; calc, C 48.63, H 4.05%.

### 2.3.3. Synthesis of liquid crystalline polymers

#### $\text{LC}_1\text{-CH}_3\text{-P}$ and $\text{LC}_2\text{-CH}_3\text{-P}$

The synthetic routes to  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$  are shown in scheme 2.

A solution of 1.08 g (0.01 mol) of PDA in 40 ml of THF was added dropwise during 3 h to a three-necked flask containing 1.50 g (0.01 mol) of  $\text{CH}_3\text{SiCl}_3$ , 5.46 g (0.01 mol) of  $\mathbf{M}_1$ , 4.00 g (0.04 mol) of TEA, and 100 ml



Scheme 2. Synthetic routes to LC<sub>1</sub>-CH<sub>3</sub>-P ( $R = -(\text{CH}_2)_{10}\text{COOC}_6\text{H}_4\text{OOC}_6\text{H}_4\text{OCH}_3$ ) and LC<sub>2</sub>-CH<sub>3</sub>-P ( $R = -(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OOC}_6\text{H}_4\text{OCH}_3$ ).

of toluene at  $-10^{\circ}\text{C}$ . Then the reaction solution was stirred for 30 min at  $-5^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ . After that, 0.72 ml (0.04 mol) of water and 50 ml of THF were added dropwise at  $-5^{\circ}\text{C}$  over 5 h. The final prepolymer solution was washed with water until neutral and dried with anhydrous  $\text{Na}_2\text{SO}_4$  overnight. The polycondensation process was carried out using triethylamine as catalyst. The solution was stirred at about  $50^{\circ}\text{C}$  for 48 h, then the polymer solution was washed with water until neutral and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Then, for capping the end silanol (Si-OH) of  $\text{LC}_1\text{-CH}_3\text{-P}$ , silylation was carried out using trimethylchlorosilane as an end-capper as follows: 39.5 mg (0.5 mmol) of pyridine was added to the above polymer solution, and 54.3 mg (0.5 mmol) of trimethylchlorosilane in 20 ml toluene added dropwise to the reaction mixture at room temperature with stirring; a white turbidity gradually emerged. The mixture was stirred at room temperature for 24 h. The residual trimethylchlorosilane and the pyridine were then removed under vacuum. The solution was washed with dilute HCl and then water until neutral and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Then the solution was concentrated to about 15 ml and 50 ml of methanol added dropwise to the concentrated solution when precipitation gradually occurred. The precipitate was collected and dried in a vacuum oven at room temperature for 24 h; the white solid product  $\text{LC}_1\text{-CH}_3\text{-P}$  was obtained in a yield of 80%.

The synthetic procedure for  $\text{LC}_2\text{-CH}_3\text{-P}$  was similar to that for  $\text{LC}_1\text{-CH}_3\text{-P}$  and the yield of  $\text{LC}_2\text{-CH}_3\text{-P}$  was 78%.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the monomers $\mathbf{M}_1$ and $\mathbf{M}_2$

The new monomers  $\mathbf{M}_1$  and  $\mathbf{M}_2$  were synthesized successfully by a hydrosilylation reaction of trichlorosilane with the mesogen 4-*n*-undecenyloxyphenyl 4-methoxybenzoate or 4-allyloxyphenyl 4-methoxybenzoate, respectively (scheme 1). It is worth mentioning that in order to avoid possible side reactions during the hydrosilylation reaction, the THF solvent must be dried with anhydrous  $\text{Na}_2\text{SO}_4$  and distilled from sodium-benzophenone before use. Also, the reaction system must be protected by dry argon and the monomers obtained stored under dry argon as the Si-Cl bond is easily hydrolyzed and then crosslinked. With careful control of the reaction conditions, yields of the monomers  $\mathbf{M}_1$  and  $\mathbf{M}_2$  can be very high.

#### 3.2. Synthesis of liquid crystalline polymers $\text{LC}_1\text{-CH}_3\text{-P}$ and $\text{LC}_2\text{-CH}_3\text{-P}$

The linear, soluble, ladderlike polyphenylsilsesquioxane (Ph-T), instead of the insoluble random gel, was first synthesized by Brown *et al.* by equilibration polymerization in 1960 [11]. However, this method could

not be used to synthesize reactive ladder-like organosilicon polymers due to its harsh reaction conditions. Moreover, the regularity of Ph-T was comparatively low because of branching and crosslinking. The structurally ordered, reactive, ladder-like polysilsesquioxanes such as polyhydrosilsesquioxane (H-T) and polyvinyl(or allyl)-silsesquioxane (Vi-T or Allyl-T) were first prepared by stepwise coupling polymerization (SCP) in our group [12, 13]. Here, two kinds of fishbone-like, ester-based, liquid crystalline, random copolysilsesquioxanes,  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$ , were synthesized successfully from methyltrichlorosilane and monomer  $\mathbf{M}_1$  and  $\mathbf{M}_2$ , respectively, by SCP in three main steps including the preaminolysis reaction with the  $\alpha,\omega$ -diamine (PDA), controlled hydrolysis, and the polycondensation in the presence of acid or basic catalysts as shown in scheme 2. Based on the difference in activity of the three chlorines in the starting materials, the trichlorosilanes ( $\text{RSiCl}_3$ ), the preaminolysis reaction can be carried out using PDA as the precoupling agent which not only protects the first most active Cl atom in the trichlorosilane from cross-linking, but also acts as a coupling agent to link two chlorosilane molecules. In other words, the precoupled intermediate plays the role of the template to ensure further formation of the ordered ladder-like macromolecules. After controlled hydrolysis and polycondensation of the precoupled twin molecules, the bridged PDA can be eliminated gradually to form the final product **7** with a regular ladder-like structure.

It is obvious that PDA plays two important roles: coupling two Si atoms to form a template between the two Si atoms in intermediates **1** and **2**, and assisting the self-assembly of the silanols **2** by the hydrogen bonding between the N and H atoms to stabilize the intermediate **3**. Through self-assembly, the condensation of the silanols occurs to form intermediate **4**. By hydrolysis, the bridged-PDA can be eliminated gradually as the Si-N bonds are unstable allowing the formation of the final fishbone-like product **7** with a double chain, ladder-like macromolecular backbone.

It is worth mentioning that in order to avoid severe steric hindrance by the comparatively large ester-based mesogenic side group, which would lower the reactivity of the silanol group for polymerization, we did not use pure monomer  $\mathbf{M}_1$  and  $\mathbf{M}_2$  to synthesize homopolymeric FBLCPs. On the contrary, we synthesized two random copolysilsesquioxanes,  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$ , using monomer  $\mathbf{M}_1$  and methyltrichlorosilane (mole ratio = 1:1) or monomer  $\mathbf{M}_2$  and methyltrichlorosilane (mole ratio = 1:1) as the starting materials.

#### 3.3. Structural characterization of the liquid crystalline polymers $\text{LC}_1\text{-CH}_3\text{-P}$ and $\text{LC}_2\text{-CH}_3\text{-P}$

The characterization data for the liquid crystalline polymers  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$  are listed in table 1.

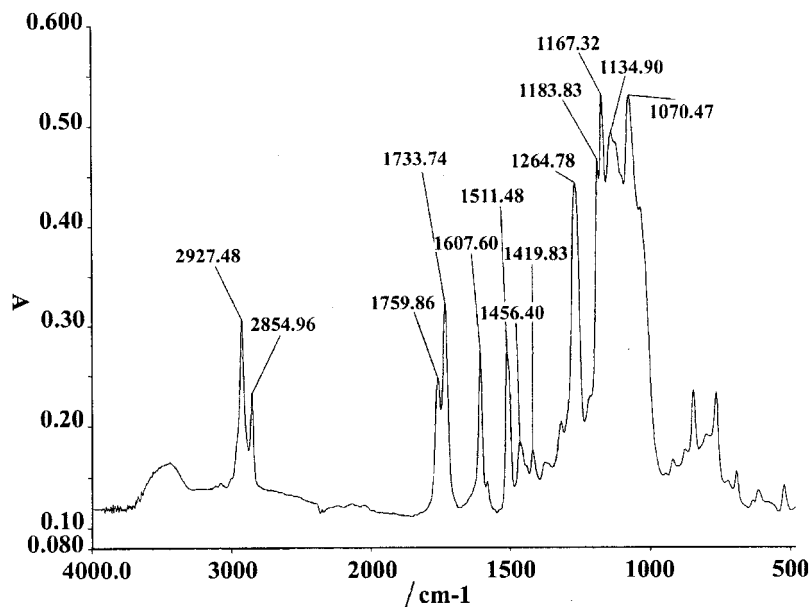
Table 1. Characterization data for LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P.

Item	LC <sub>1</sub> -CH <sub>3</sub> -P	LC <sub>2</sub> -CH <sub>3</sub> -P
Appearance	White solid	White solid
Solubility	Soluble in toluene, THF, chloroform acetone, etc.	Soluble in toluene, THF, chloroform acetone, etc.
FTIR ( $\nu$ in $\text{cm}^{-1}$ )	1734, 1265 (OCO); 1070 ~ 1134 (Si-O-Si); 1607, 1512, 1465 (C <sub>6</sub> H <sub>4</sub> )	1731, 1263 (OCO); 1029 ~ 1106 (Si-O-Si); 1608, 1513, 1470 (C <sub>6</sub> H <sub>4</sub> )
<sup>1</sup> H NMR ( $\delta$ in ppm)	6.98, 8.14 (OC <sub>6</sub> H <sub>4</sub> CO); 7.12, 7.19 (OC <sub>6</sub> H <sub>4</sub> O); 3.89 (CH <sub>3</sub> O); 2.55 (COCH <sub>2</sub> ); 1.88 (COCH <sub>2</sub> CH <sub>2</sub> ); 1.30 (COCH <sub>2</sub> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>7</sub> ); 0.65 (CH <sub>2</sub> Si); 0.13 (CH <sub>3</sub> Si)	6.83, 8.03 (OC <sub>6</sub> H <sub>4</sub> CO); 6.85, 6.97 (OC <sub>6</sub> H <sub>4</sub> O); 3.80 (CH <sub>3</sub> O, OCH <sub>2</sub> ); 1.84 (CH <sub>2</sub> CH <sub>2</sub> Si); 0.74 (CH <sub>2</sub> Si); 0.11 (CH <sub>3</sub> Si)
<sup>13</sup> C NMR ( $\delta$ in ppm)	172.5 (C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> COCH <sub>2</sub> ); 164.3 (C <sub>6</sub> H <sub>4</sub> COOC <sub>6</sub> H <sub>4</sub> ); 114.2, 122.0, 132.6, 165.1 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOC <sub>6</sub> H <sub>4</sub> OCO), 122.8, 122.9, 148.4, 148.6 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOC <sub>6</sub> H <sub>4</sub> OCO), 55.8 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ); 34.7 (C <sub>6</sub> H <sub>4</sub> OCOCH <sub>2</sub> ); 29.6 ~ 30.0 (CH <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> SiCl <sub>3</sub> ; 25.3 (CH <sub>2</sub> SiCl <sub>3</sub> ); 1.4 (CH <sub>3</sub> SiCl <sub>3</sub> )	154.9 (OC <sub>6</sub> H <sub>4</sub> CO); 114.0, 121.8, 144.8, 155.6 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOC <sub>6</sub> H <sub>4</sub> O); 111.7, 122.5, 132.3, 162.7 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COOC <sub>6</sub> H <sub>4</sub> O); 69.0 (C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> ); 54.2 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ); 20.4 ~ 21.9 (CH <sub>2</sub> CH <sub>2</sub> SiCl <sub>3</sub> ); 7.6 (CH <sub>3</sub> SiCl <sub>3</sub> )
<i>M</i> <sub>w</sub> (Dalton by GPC)	6.7 × 10 <sup>4</sup>	6.8 × 10 <sup>3</sup>
<sup>29</sup> Si NMR ( $\delta$ in ppm)	D <sup>1</sup> = - 49, D <sup>2</sup> = - 64	D <sup>1</sup> = - 56, D <sup>2</sup> = - 65

There are two strong absorption bands at 1070 ~ 1134  $\text{cm}^{-1}$  and 1029 ~ 1106  $\text{cm}^{-1}$  in the FTIR spectra of LC<sub>1</sub>-CH<sub>3</sub>-P (figure 1) and LC<sub>2</sub>-CH<sub>3</sub>-P (figure 2), respectively, which do not appear in the FTIR spectra of the monomers **M**<sub>1</sub> and **M**<sub>2</sub>; these are assigned to the ≡Si-O- stretching vibration of the ≡Si-O-Si≡ bond. Moreover, two strong absorption bands indicating absorptions by ester bonds (-OCO-) appear at 1734 and 1265  $\text{cm}^{-1}$  (LC<sub>1</sub>-CH<sub>3</sub>-P) and 1731 and 1263  $\text{cm}^{-1}$  (LC<sub>2</sub>-CH<sub>3</sub>-P).

In the <sup>1</sup>H NMR spectra of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P (figures 3 and 4, respectively), the peaks assigned to ≡Si-CH<sub>2</sub>-, ≡Si-CH<sub>3</sub>-, -CO-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>7</sub>-, -CO-CH<sub>2</sub>-CH<sub>2</sub>-, -CO-CH<sub>2</sub>-, CH<sub>3</sub>O-, -OC<sub>6</sub>H<sub>4</sub>O-

and -OC<sub>6</sub>H<sub>4</sub>CO- of LC<sub>1</sub>-CH<sub>3</sub>-P and the peaks assigned to ≡Si-CH<sub>2</sub>-, ≡Si-CH<sub>3</sub>-, ≡Si-CH<sub>2</sub>-CH<sub>2</sub>-, ≡Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>O-, CH<sub>3</sub>O-, -OC<sub>6</sub>H<sub>4</sub>O- and -OC<sub>6</sub>H<sub>4</sub>CO- of LC<sub>2</sub>-CH<sub>3</sub>-P are all broad compared with the sharp peaks in the <sup>1</sup>H NMR spectra of monomers **M**<sub>1</sub> and **M**<sub>2</sub> indicating formation of a polymer. The broad peaks in the <sup>13</sup>C NMR spectra of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P also indicate the formation of a polymer. By calculating the ratio of the areas of the peaks representing ≡Si-CH<sub>2</sub>- and ≡Si-CH<sub>3</sub> in the <sup>1</sup>H NMR spectra of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P, it can be estimated that the mole ratios of the ester-based, mesogenic side group to methyl side group in polymers LC<sub>1</sub>CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P are 1.0 to 1.6 and 1.0 to 1.2, respectively.

Figure 1. FTIR spectrum of LC<sub>1</sub>-CH<sub>3</sub>-P.

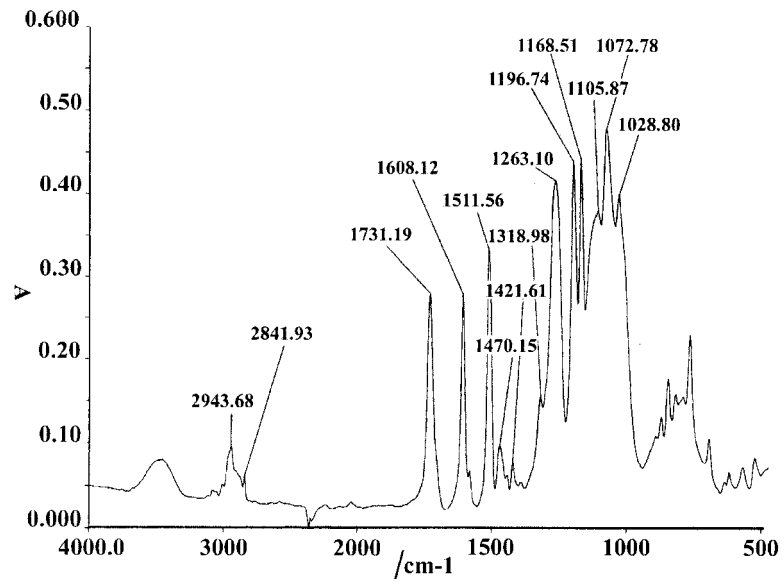


Figure 2. FTIR spectrum of LC<sub>2</sub>-CH<sub>3</sub>-P.

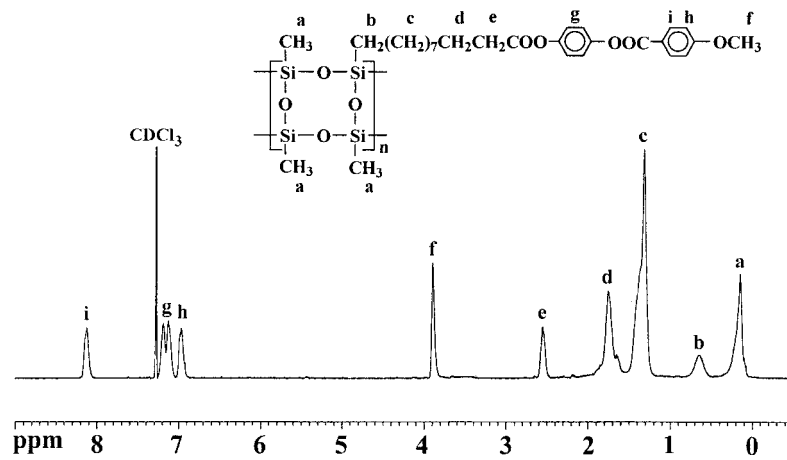


Figure 3. <sup>1</sup>H NMR spectrum of LC<sub>1</sub>-CH<sub>3</sub>-P.

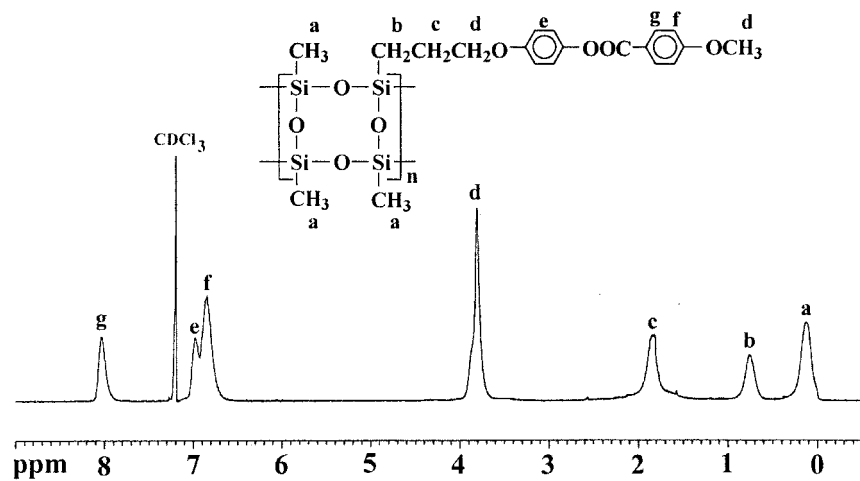


Figure 4. <sup>1</sup>H NMR spectrum of LC<sub>2</sub>-CH<sub>3</sub>-P.

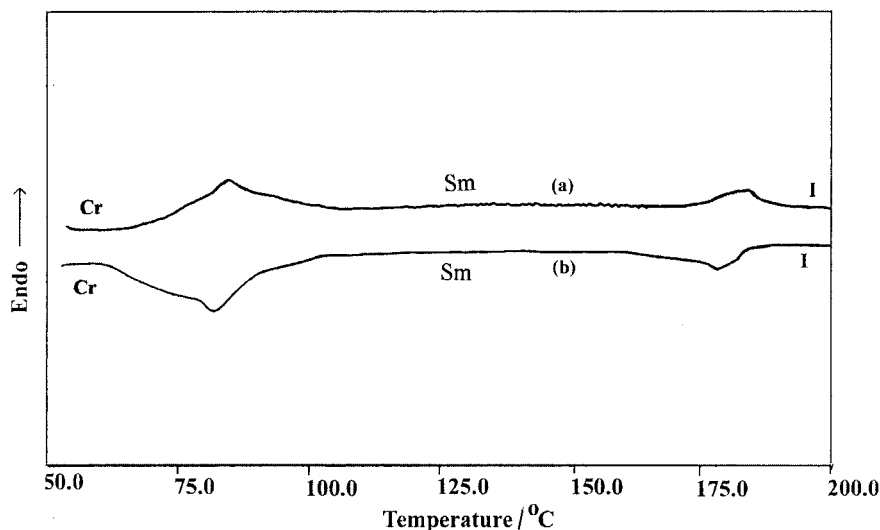


Figure 5. DSC curves of  $LC_1-CH_3-P$  (a) on first heating and (b) on first cooling at a scanning rate of  $10^\circ C \text{ min}^{-1}$ .

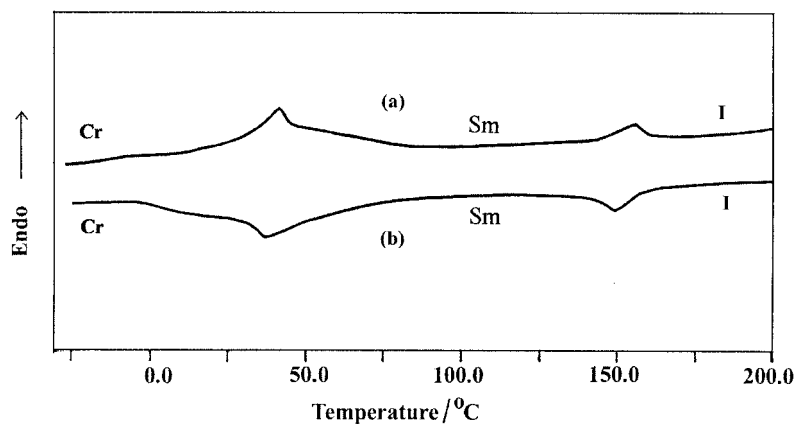


Figure 6. DSC curves of  $LC_2-CH_3-P$  (a) on first heating and (b) on first cooling at a scanning rate of  $10^\circ C \text{ min}^{-1}$ .

It is clear by the FTIR,  $^1H$  NMR, and  $^{13}C$  NMR results that both monomers  $M_1$  and  $M_2$  have been hydrolysed and condensed to form polymers containing  $\equiv Si-O-Si\equiv$  bonds. The results from gel permeation chromatography (GPC) show that the molecular masses of the polymers  $LC_1-CH_3-P$  and  $LC_2-CH_3-P$  are about  $6.7 \times 10^4$  and  $6.8 \times 10^3$ , respectively.

In the DSC curves of polymers  $LC_1-CH_3-P$  and  $LC_2-CH_3-P$  (figures 5 and 6, respectively), there are no noticeable glass transitions in the range  $20 \sim 200^\circ C$  and  $0 \sim 200^\circ C$ , respectively, which indicates the great rigidity of the ladder-like macromolecular backbone.

Generally, there are three groups of distinct peaks ( $D^0$ ,  $D^1$  and  $D^2$  peaks) for silicon atoms with different degrees of condensation in the  $^{29}Si$  NMR spectrum [17, 18]. Among them, the  $D^0$  peak indicates the Si with two hydroxyl substituents,  $(HO)_2-Si-O-$ . The  $D^1$  peak indicates the Si with two siloxane bonds and one hydroxyl substituent,  $-(O)_2-Si-OH$ . The  $D^2$  peak indicates the fully condensed Si with three siloxane bonds,  $-(O)_3-Si-$ . In the  $^{29}Si$  NMR spectra of  $LC_1-CH_3-P$  and

$LC_2-CH_3-P$  (figures 7 and 8, respectively), there are two groups of peaks assigned to  $D^1$  and  $D^2$  peaks. The large peak  $D^2$  appearing at  $-64$  ppm for  $LC_1-CH_3-P$  and  $-65$  ppm for  $LC_2-CH_3-P$  indicates the perfect, fully condensed Si of the  $SiO_{3/2}$  unit in the ladder-like double

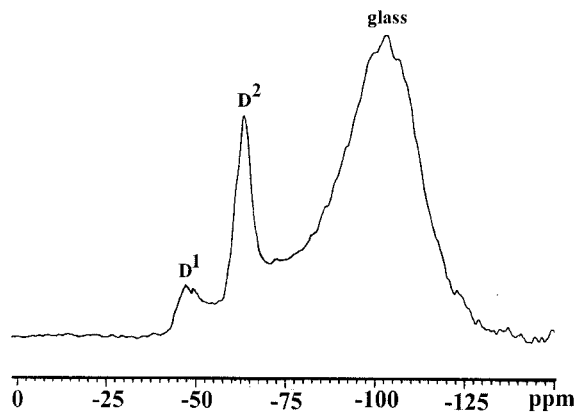


Figure 7.  $^{29}Si$  NMR spectrum of  $LC_1-CH_3-P$ .

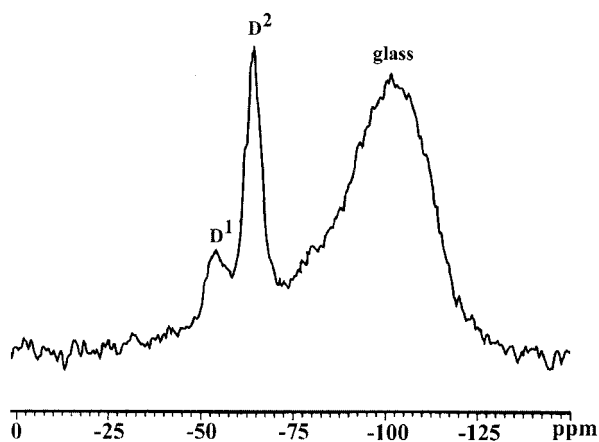


Figure 8.  $^{29}\text{Si}$  NMR spectrum of  $\text{LC}_2\text{-CH}_3\text{-P}$ .

chain, while the small peak  $\text{D}^1$  appearing at  $-49$  ppm for  $\text{LC}_1\text{-CH}_3\text{-P}$  (and  $-56$  ppm for  $\text{LC}_2\text{-CH}_3\text{-P}$ ) indicates the defective Si atoms connected to one hydroxy group.

There are three distinct diffraction halos in each of the X-ray patterns of  $\text{LC}_1\text{-CH}_3\text{-P}$  (figure 9) and  $\text{LC}_2\text{-CH}_3\text{-P}$  (figure 10). The meaning of the first halo will be discussed later. The second halo indicating the intramolecular chain-to-chain distance (i.e. the width of each double chain) in the ladder-like polymers and appearing

at  $d_2$  ( $11.12 \text{ \AA}$  for  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $8.66 \text{ \AA}$  for  $\text{LC}_2\text{-CH}_3\text{-P}$ ) is narrow and sharp which means that both macromolecules  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$  have a fairly rigid skeleton in which movement around the longitudinal axis is limited, and that the conformations are practically invariant. The third diffuse halo, arising from the intermolecular spacings perpendicular to the long axes of the molecules, covers a wide range of diffraction angles giving the average intermolecular spacing ( $4.38 \text{ \AA}$  for  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $4.41 \text{ \AA}$  for  $\text{LC}_2\text{-CH}_3\text{-P}$ ). The above results are in good agreement with previous work [2, 19, 20].

The characterization data from the  $^{29}\text{Si}$  NMR and XRD spectra, as well as the good solubility of the polymers  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$  in a series of solvents such as toluene, THF, chloroform, acetone, etc. indicate that both polymers have ordered ladder-like structures, although some defective branched structures still exist.

#### 3.4. Mesomorphic properties of the liquid crystalline polymers $\text{LC}_1\text{-CH}_3\text{-P}$ and $\text{LC}_2\text{-CH}_3\text{-P}$

The liquid crystalline properties of  $\text{LC}_1\text{-CH}_3\text{-P}$  and  $\text{LC}_2\text{-CH}_3\text{-P}$  were examined by DSC, polarizing optical microscopy (POM) and temperature-variable XRD; the

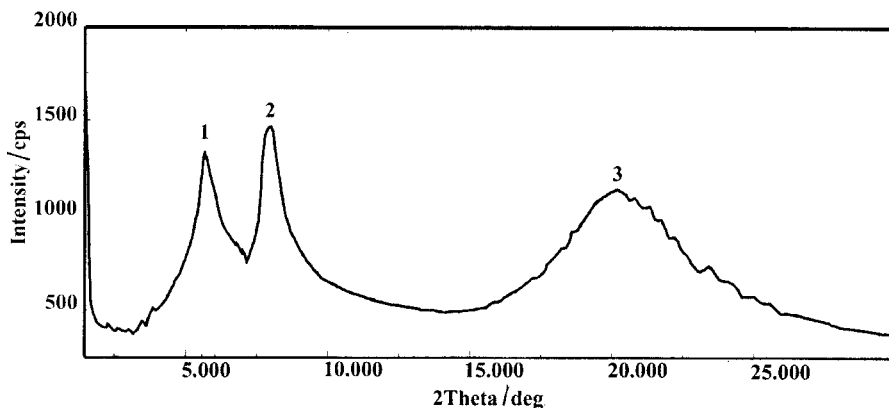


Figure 9. XRD pattern of  $\text{LC}_1\text{-CH}_3\text{-P}$  taken at  $100^\circ\text{C}$ .

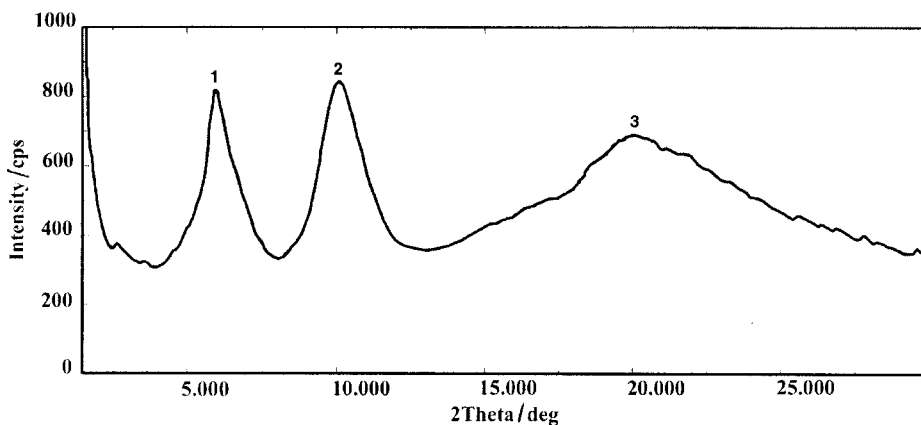


Figure 10. XRD pattern of  $\text{LC}_2\text{-CH}_3\text{-P}$  taken at  $100^\circ\text{C}$ .



results are shown in figures 5, 6, 9, 10, and 11, and table 2. The DSC curves shown in figures 5 and 6 show that both polymers are semi-crystalline polymers without noticeable glass transitions in the ranges 20–200°C and 0–200°C, respectively; but that there are two endothermic peaks at 85°C and 184°C for LC<sub>1</sub>-CH<sub>3</sub>-P, and at 42°C and 157°C for LC<sub>2</sub>-CH<sub>3</sub>-P. From the

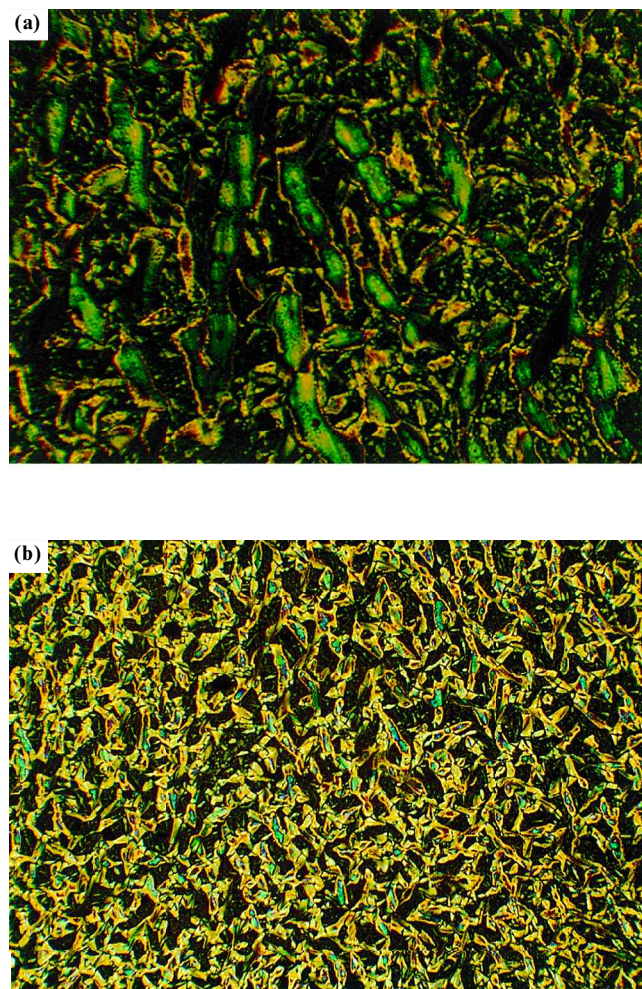


Figure 11. Mesomorphic textures of (a) LC<sub>1</sub>-CH<sub>3</sub>-P (250 times) and (b) LC<sub>2</sub>-CH<sub>3</sub>-P (100 times) as viewed by POM at 100°C.

POM observations, melting points ( $T_m$ ) can be seen at about 82°C for LC<sub>1</sub>-CH<sub>3</sub>-P and 42°C for LC<sub>2</sub>-CH<sub>3</sub>-P. Above the melting points, the samples show bright birefringence. When the temperature is elevated to above 180°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) or 155°C (for LC<sub>2</sub>-CH<sub>3</sub>-P), the birefringence disappears. As the temperature returns to below 180°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) or 155°C (for LC<sub>2</sub>-CH<sub>3</sub>-P), the birefringence reappears. Apparently, the temperatures of 82°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) and 42°C (for LC<sub>2</sub>-CH<sub>3</sub>-P), which correspond to the first endothermic peaks at 85°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) and 42°C (for LC<sub>2</sub>-CH<sub>3</sub>-P) in the DSC heating curves, are the solid-to-liquid crystalline transition temperatures of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P, respectively. The temperatures of 180°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) and 155°C (for LC<sub>2</sub>-CH<sub>3</sub>-P), which correspond to the second endothermic peaks at 184°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) and 157°C (for LC<sub>2</sub>-CH<sub>3</sub>-P) in the DSC heating curves, are the isotropic transition temperatures of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P, respectively. In the temperature ranges 82–180°C (for LC<sub>1</sub>-CH<sub>3</sub>-P) and 42–155°C (for LC<sub>2</sub>-CH<sub>3</sub>-P), the samples are in a liquid crystalline state. However, the transition enthalpy  $\Delta H$  (c. 19.38 J g<sup>-1</sup> for LC<sub>1</sub>-CH<sub>3</sub>-P and 12.11 J g<sup>-1</sup> for LC<sub>2</sub>-CH<sub>3</sub>-P) between the semi-crystalline and liquid crystalline states is not large, which means that the total change in the macromolecular order between the crystalline phase and the mesophase is not very great. It can be seen from the XRD patterns of LC<sub>1</sub>-CH<sub>3</sub>-P (figure 9) and LC<sub>2</sub>-CH<sub>3</sub>-P at 100°C (figure 10) that the first sharp peak at small angle ( $d_1 = 15.90$  Å for LC<sub>1</sub>-CH<sub>3</sub>-P and 14.59 Å for LC<sub>2</sub>-CH<sub>3</sub>-P), corresponding to the layer spacing, indicates the existence of smectic layers; the third diffuse halo appearing at large angle, which corresponds to the average intermolecular spacings, indicates a lack of periodic lateral order. The above results from the XRD patterns indicate that the liquid crystalline states of both polymers should be assigned to a smectic state. The mesophase textures of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P are shown in figure 11. In summary, all these results prove the formation of an ordered smectic texture in the liquid crystalline regions of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P.

Table 2. Mesomorphic properties of LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P examined by DSC, XRD and POM.

Sample	Phase transition by DSC $T/^\circ\text{C}/\Delta H/\text{J g}^{-1}$	Mesophase range $\Delta T/^\circ\text{C}$	$d/\text{Å}$ by XRD <sup>a</sup>	Texture
LC <sub>1</sub> -CH <sub>3</sub> -P	$\begin{array}{c} \text{Cr} \xrightarrow{85/19.38} \text{Sm} \xrightarrow{184/3.57} \text{I} \\ \text{Cr} \xleftarrow{81/-24.12} \text{Sm} \xleftarrow{178/-4.01} \text{I} \end{array}$	99	$d_1 = 15.90$ $d_2 = 11.12$ $d_3 = 4.38$	Smectic
LC <sub>2</sub> -CH <sub>3</sub> -P	$\begin{array}{c} \text{Cr} \xrightarrow{42/12.11} \text{Sm} \xrightarrow{157/1.93} \text{I} \\ \text{Cr} \xleftarrow{39/-13.52} \text{Sm} \xleftarrow{150/-2.17} \text{I} \end{array}$	115	$d_1 = 14.59$ $d_2 = 8.66$ $d_3 = 4.41$	Smectic

<sup>a</sup> The measurements were taken at a temperature of 100°C in the liquid crystalline state.

#### 4. Conclusions

Two novel soluble fishbone-like, ester-based, liquid crystalline, random copolysilsesquioxanes, LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P, were successfully synthesized by SCP from two new monomers M<sub>1</sub> and M<sub>2</sub>, which were synthesized by hydrosilylation reaction between trichlorosilane and two kinds of ester-based mesogens. The characterization data from FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>29</sup>Si NMR, GPC, DSC and XRD indicate that both LC<sub>1</sub>-CH<sub>3</sub>-P and LC<sub>2</sub>-CH<sub>3</sub>-P have ordered ladder-like main double chains, although some structural defects still exist. Furthermore, the characterization data from POM, DSC and XRD indicate that the two ladder-like polymers are thermotropic liquid crystalline polymers with smectic properties in the liquid crystalline ranges.

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