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Synthesis and mesomorphic properties of a novel ladder-like 1,4-phenylene-bridged liquid crystalline polysiloxane containing ester-based mesogenic side groups

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A new ladder-like 1,4-phenylene-bridged liquid crystalline polysiloxane bearing ester-based mesogenic side groups, **LPLCPS**, has been synthesized by hydrosilylation of a SiH-terminated ester-based mesogen compound (**1**) with a ladder-like 1,4-phenylene-bridged polyvinylsiloxane (**LPPVS**) containing vinyl-terminated side groups in the presence of dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) catalyst. Compound **1** was synthesized by hydrosilylation of 1,1,3,3-tetramethyldisiloxane (HMM) with the vinyl-terminated ester-based mesogenic compounds. Various characterization methods including FTIR, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction were used and the results combined to demonstrate that **LPLCPS** shows thermotropic smectic mesomorphic behaviour with a high clearing point and a wide mesophase range.

1. Introduction

Side group liquid crystalline polymers (SGLCPs) which are potentially functional polymer materials for various applications have attracted wide attention from numerous scientific researchers and engineers [1–5]. However, the SGLCPs have not been widely commercially available so far, partly due to their narrow mesophase ranges and poor mechanical properties.

In previous papers, we have reported a series of fish-bone-like liquid crystalline polysilsesquioxanes (FBLCPs) obtained by hydrosilylation of a vinyl-terminated liquid crystalline compound with a ladder-like polyhydrosilsesquioxane (H-T) or a random copolymethylhydrosilsesquioxane (MH-T) containing Si-H-terminated side groups [6–10]. Their broad mesophase range and good film-forming ability are mainly attributed to the semi-rigidity of the double-chain ladder-like macromolecular backbone, different from other classical single chain polymers. However, since the starting polymers H-T and MH-T are very sensitive to oxygen and water, the FBLCPs synthesized by previous methods occasionally suffer from the drawbacks of instability and ease of cross-linking arising from incomplete substitution of Si–H groups on the starting polymer H-T or MH-T. Moreover, the starting polymers H-T and MH-T with a bridge involving siloxane linkages possess relatively poor compatibility with commercial organic polymers and have poor mechanical and electrochemical properties.

In order to improve the stability, mechanical properties and compatibility with commercial organic polymers, etc., of the FBLCPs, it is of great importance to prepare new ladder-like liquid crystalline polysiloxanes containing mesogenic side groups using new starting ladder-like polymers and an alternative synthetic method different from that reported previously [6–10]. In this paper, a novel ladder-like organo-bridged polysiloxane, i.e. a ladder-like 1,4-phenylene-bridged polyvinylsiloxane bearing vinyl-terminated instead of Si–H-terminated side groups (**LPPVS**) is described. It was synthesized by stepwise coupling polymerization in three stages including pre-coupling by Grignard reaction, controlled hydrolysis and polycondensation. This was used as the starting

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polymer, and a new kind of ladder-like 1,4-phenylene-bridged side group liquid crystalline polysiloxane containing ester-based mesogenic side groups (**LPLCPS**) was synthesized for the first time by hydrosilylation of SiH-terminated ester-based mesogenic compounds with **LPPVS**.

2. Experimental

2.1. *Materials*

All solvents were commercially available and of analytically pure grade. Tetrahydrofuran (THF) was distilled from sodium–benzophenone. Toluene and hexane were dried over $CaCl_2$ and then with sodium. Acetone was dried over anhydrous Na_2SO_4 before use. Vinyltrimethoxysilane, trimethylchlorosilane, 1,4-phenylenediamine (PDA) and anhydrous Na_2SO_4 were purchased from the Beijing Chemical Factory and were of analytical grade. Pyridine and triethylamine (TEA) were purchased from the same source and dried over CaH_2 prior to use. 1,4-Dibromobenzene and HMM were purchased from the Acros Organics Company and were of analytically pure grade. Cp_2PtCl_2 catalyst was prepared according to the literature [4], as was 4-allyloxyphenyl 4-methoxybenzoate [11].

2.2. *Characterization*

IR spectra were recorded using a Perkin-Elmer 80 spectrometer. ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra were obtained with a JNH-FX100 (JBOX) NMR (300 MHz) spectrometer using $CDCl_3$ as solvent. ^{29}Si NMR spectra were references (0 ppm) to external standards (TMS). Mass spectrometry was carried out with an AEI mass spectrometer MS-50 using the electron ionization method (EI). DSC measurements were made with a Perkin-Elmer DSC-7 differential scanning calorimeter. X-ray diffraction analysis was carried out using a Rigaku D/MAX 2400 X-ray diffractomer. Number average (M_n) molecular masses were determined using a Knauer vapour pressure osmometer.

2.3. *Synthesis*

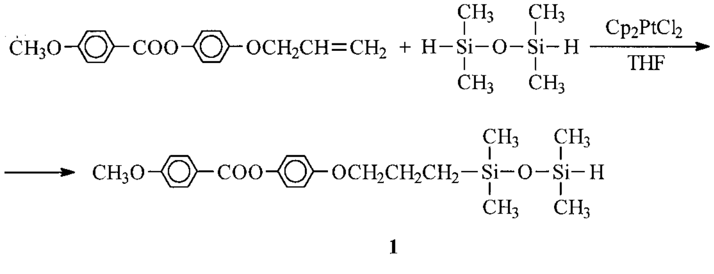
2.3.1. *Synthesis of 4-[3-(1,1,3,3-tetramethyldisiloxane)-propoxy]phenyl 4-methoxybenzoate (1)*

A 100 ml round-bottom flask equipped with a reflux condenser, magnetic stirrer and two-way stop cock was evacuated and charged three times with dry argon. Then the flask was charged with 30 ml of a THF solution containing 2.1 g (7.5 mmol) of 4-allyloxyphenyl 4-methoxybenzoate and 1 ml of a THF solution of Cp_2PtCl_2 ($1\,mg\,ml^{-1}$). The mixture was stirred at room temperature for 30 min, then 5.4 g (40 mmol) of 1,1,3,3-tetramethyldisiloxane (HMM) was added. The resulting mixture was stirred and subsequently warmed to 50°C for 48 h. The solvent and unreacted HMM were removed *in vacuo*. The product **1** was obtained as a clear, colourless, viscous oil. Yield: 94%, $C_{21}H_{30}O_5Si_2$ (M_w 418). IR (KBr): $\nu = 1732$, 1260 (COO), 1609, 1513 (C_6H_4), 2180 (SiH) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) = 8.13, 7.01 (dd, 4H, OC_6H_4CO), 7.08, 6.95 (dd, 4H, OC_6H_4O), 4.66 (m, 1H, SiH), 3.92 (t, 2H, OCH_2), 3.90 (s, 3H, CH_3O), 1.85 (m, 2H, $C\underline{H}_2CH_2Si$), 0.67 (t, 2H, CH_2Si), 0.07–0.21 (m, 12H, $(CH_3)_2SiOSi(CH_3)_2$). Elemental analysis: found C 66.12, H 7.24; calculated for $C_{21}H_{30}O_5Si_2$ C 66.03, H 7.18%.

The synthetic route to compound **1** is shown in scheme 1.

2.3.2. *Synthesis of 1,4-bis(vinyldimethoxysilyl)benzene monomer (M)*

To a mixture of 19.2 g (0.8 mol) of magnesium powder, 400 ml of THF and 222 g (1.5 mol) of vinyltrimethoxysilane a solution of 47.2 g (0.2 mol) of 1,4-dibromobenzene in 200 ml of THF was added dropwise slowly (5 h) and with stirring at reflux temperature. A small amount of iodine was used to initiate the reaction; the reaction mixture was kept at reflux for another 4 h. The solvent in the resulting turbid mixture was removed *in vacuo*. Hexane (500 ml) was added in batches to precipitate magnesium salts from the solution and the clear supernatant liquid was collected. Hexane and the unreacted vinyltrimethoxysilane were distilled out *in vacuo*. The remaining yellow oil was distilled to give a clear colourless oil (b.p. 130–132°C/0.3 mmHg). Yield: 67%, $C_{14}H_{22}O_4Si_2$ (m_w 310). IR: $\nu = 3056$, 1596, 1468, 1404 (C_6H_4, $CH_2{=}CH$), 1082, 1142 (Si–O–C) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) = 7.67 (s, 4H, C_6H_4), 6.23–6.01 (m, 6H, $CH_2{-}CH$), 3.60 (s, 12H, CH_3O). ^{13}C NMR ($CDCl_3$): δ (ppm) = 137.6, 133.8 (C_6H_4), 134.4, 130.8 ($CH_2{=}CH$), 50.8 (CH_3O). ^{29}Si NMR ($CDCl_3$): δ



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Scheme 1. Synthetic route to compound **1**.

(ppm) = − 27.8. MS (EI): 310, 283. Elemental analysis: found C 54.27, H 7.26; calculated for $C_{14}H_{22}O_4Si_2$ C 54.19, H 7.10%.

The synthetic route to monomer **M** is shown in scheme 2.

2.3.3. *Synthesis of* ***LPPVS***

A mixture of 2 ml of concentrated HCl, 30 ml of THF, and 15 ml of methanol was added dropwise slowly into a flask containing 4.5 g (14 mmol) of **M**, 50 ml of toluene, and 20 ml of THF and held at 0 ~ − 10°C for 6 h. The reaction mixture was then stirred at room temperature for 24 h. For polycondensation, the THF in the reaction mixture was distilled out *in vacuo*. The condensation reaction was then carried out using TEA as catalyst. The solution was stirred at about 50°C for 48 h. The solution after condensation was washed with water until neutral and dried over anhydrous Na_2SO_4. For end-capping the terminal silanol (Si–OH) groups of the polymer, silylation was carried out using trimethylchlorosilane as follows: 39.5 mg (0.5 mmol) of pyridine was added to the solution, and 54.3 mg (0.5 mmol) of trimethylchlorosilane in 20 ml of toluene was added dropwise with stirring at room temperature stirring; a white turbidity gradually developed. The mixture was then stirred at room temperature for a further 24 h, when residual trimethylchlorosilane and pyridine were removed *in vacuo*. The solution was washed with dilute HCl, then with water until neutral, and dried over anhydrous Na_2SO_4. The solution was concentrated to about 20 ml followed by the dropwise addition of 80 ml of methanol, when a precipitate appeared slowly. The precipitate was collected and dried in a vacuum oven for 12 h; the white solid product was obtained in a yield of 81%.

The synthetic route to **LPPVS** is shown in scheme 2 and the results characterizing the product are summarized in table 1.

2.3.4. *Synthesis of* ***LPLCPS***

A 100 ml round-bottom flask equipped with a reflux condenser, a magnetic stirrer and a two-way stop cock was evacuated and charged with dry argon three times. Then the flask was charged with 30 ml of a THF solution containing 0.7 g (6 mmol) of **LPPVS** and 1 ml of a THF solution of Cp_2PtCl_2 (1 mg ml^{-1}). The mixture was stirred at room temperature for 30 min, when 20 ml of a THF solution containing 1.6 g (4 mmol) of **1** was added. The resulting mixture was stirred and subsequently warmed to 50°C for 48 h. The reaction solution was then cooled and the THF removed *in vacuo* to give a solid which was dissolved in toluene and precipitated into methanol five times giving a white solid product. Yield: 72%.

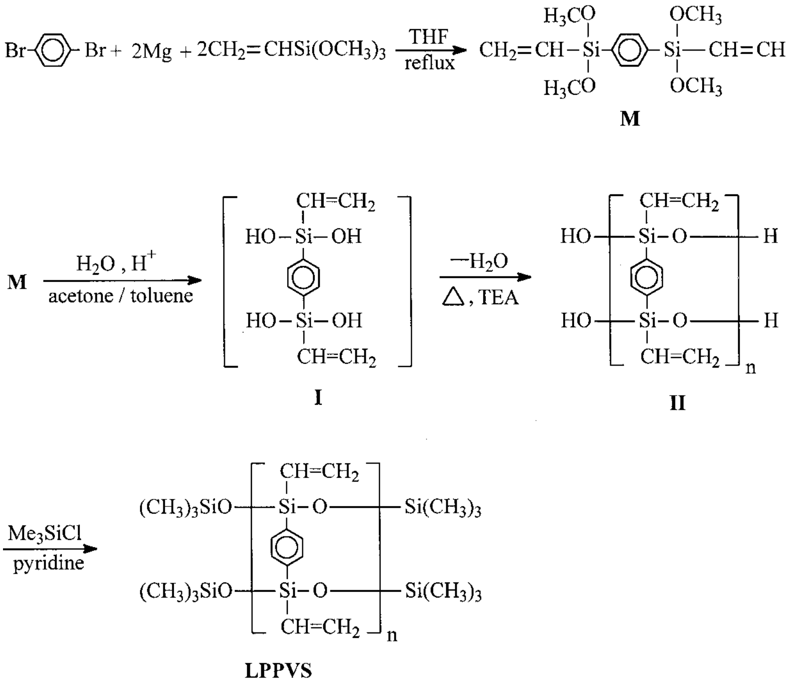
The synthetic route to **LPLCPS** is shown in scheme 3 and the results characterizing the product are shown in table 2.

3. Results and discussion

3.1. *Synthesis*

3.1.1. *Si-H-terminated ester-based mesogenic compound* ***1***

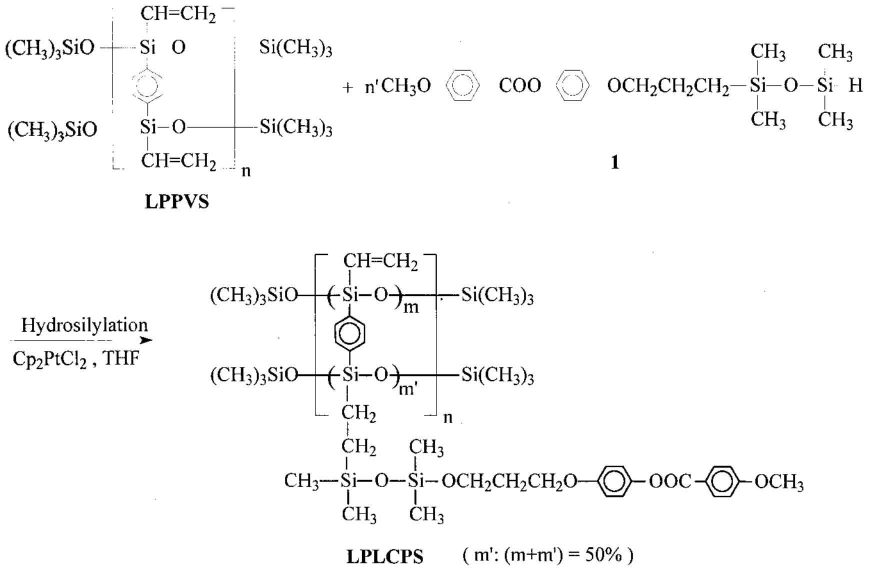
Compound **1** was synthesized by hydrosilylation of the vinyl-terminated ester-based mesogenic compound



Scheme 2. Synthetic routes to monomer **M** and polymer **LPPVS**.

Table 1. Results characterizing **LPPVS**.

Parameter	Results
Appearance	White solid
Solubility	Soluble in toluene, THF, chloroform, acetone, etc.
IR (ν in cm^{-1})	3013, 1596, 1407 (C_6H_4, CH_2=CH); 1009 ~ 1085 (Si–O–Si); 1145 (Si–C_6H_4–Si)
^{1}H NMR (δ in ppm)	7.6 (C_6H_4); 5.8–6.2 (CH_2=CH)
^{13}C NMR (δ in ppm)	136.2, 133.2, 131.3 (C_6H_4, CH_2=CH)
^{29}Si NMR (δ in ppm)	β: − 37.7 (CH_2=CH(C_6H_4)SiO) and α: − 35.2 (CH_2=CH(C_6H_4)SiOH)
Regularity $A_\beta/(A_\beta + A_\alpha)$ by ^{29}Si NMR	90%
DSC	Almost a horizontal trace without T_g
T_d (by TGA) (°C)	536.2
Distance [d (Å)/2θ (°)] by XRD	d_1: 11.24/7.86; d_2: 4.10/21.64
M_n (Dalton by VPO)	6500



Scheme 3. Synthetic route to **LPLCPS**.

Table 2. Results characterizing **LPLCPS**.

Parameter	Results
Appearance	White solid
Solubility	Soluble in toluene, THF, chloroform, acetone, etc.
IR (ν in cm^{-1})	3055, 1606, 1510, 1407 (C_6H_4, CH_2=CH); 1010 ~ 1073 (Si–O–Si); 1144 (Si–C_6H_4–Si); 1732, 1260 (COO)
^{1}H NMR (δ in ppm)	8.13, 7.12 (OC_6H_4CO); 7.18, 6.96 (OC_6H_4O); 7.2–7.8 (Si–C_6H_4–Si); 5.5–6.4 (CH_2=CH); 3.90 (CH_3O, CH_2O); 1.88 ($OCH_2C\underline{H}_2$); 0.70 ($SiC\underline{H}_2C\underline{H}_2Si$, $SiC\underline{H}_2CH_2CH_2O$); 0.15 ($(C\underline{H}_3)_2SiOSi(C\underline{H}_3)_2$)
^{13}C NMR (δ in ppm)	163.7 ($OC_6H_4\underline{C}O$); 115.0, 122.4, 144.2, 156.7 ($O\underline{C}_6H_4O$); 113.7, 122.5, 132.4, 165.2 ($O\underline{C}_6H_4CO$); 136.2, 133.2, 132.1 (Si–$\underline{C}_6H_4$–Si, $\underline{C}H_2$=$\underline{C}H$); 70.8 ($\underline{C}H_2O$); 55.4 ($\underline{C}H_3O$); 23.2 ($OCH_2\underline{C}H_2$); 14.2 ($Si\underline{C}H_2\underline{C}H_2Si$, $Si\underline{C}H_2CH_2CH_2O$); 0.99, 0.30 ($(\underline{C}H_3)_2SiOSi(\underline{C}H_3)_2$)
T_d (by TGA) (°C)	482.6
M_n (Dalton by VPO)	17500

using the Si–H group on one side of HMM as shown in scheme 1. It is worthwhile noting that in order to avoid the reaction leading to incorporation of the vinyl-terminated ester-based mesogenic compound on both sides of HMM, the amount of HMM used in the hydrosilylation reaction was much more than that of the vinyl-terminated compound (mol ratio = 5.3 : 1). With careful control of the reaction conditions, the yield of compound **1** can be very high.

3.1.2. *Ladderlike 1,4-phenylene-bridged polyvinylsiloxane **LPPVS***

In our previous work [12–14], a series of ladder-like polysilsesquioxanes with a defined siloxane bridge was synthesized by stepwise coupling polymerization (SCP) in three steps including preaminolysis, controlled hydrolysis and polycondensation. In order to increase the bridge length, the rigidity and the compatability with organic polymers, a Grignard reaction was introduced in the first step of the SCP, and the ladder-like 1,4-phenylene-bridged polyvinylsiloxane **LPPVS** was synthesized. The characterization results are summarized in table 1 where it can be seen that the regularity of **LPPVS** is high, as given by the ratio $A_\beta/A_\beta + A_\alpha = 90\%$ calculated from the ^{29}Si NMR spectrum, where, in term's of Shi's work [15], A_β represents the area of the resonance absorption peak originating from the ordered silicon atoms in $CH_2{=}CH(C_6H_4)SiO$ groups and A_α represents that corresponding to the defective silicon atoms in $CH_2{=}CH(C_6H_4)SiOH$ groups. In the DSC trace for **LPPVS**, there is no noticeable glass transition in the range of 50–250°C, which indicates the high rigidity of the 1,4-phenylene-bridged ladder-like macromolecular backbone. There are two distinct peaks in the XRD spectrum of **LPPVS**. The first halo appearing at 11.24 Å gives the intramolecular chain-to-chain distance in the ladder-like double chain. The second halo, arising from the intermolecular spacings perpendicular to the long axes of the molecules, covers a wide range of diffraction angles giving an average intermolecular spacing of 4.10 Å. The larger value for the first halo emphasises the higher regularity of the ladder-like chain.

The **LPPVS** synthesized is extremely soluble in organic solvents such as toluene, acetone, THF, chloroform, etc., and can form films after the solvent has evaporated.

3.1.3. *Ladder-like 1,4-phenylene-bridged side group liquid crystalline polysiloxane **LPLCPS***

In our previous work, a series of FBLCPs was synthesized by hydrosilylation of a vinyl-terminated mesogenic compound with H-T or MH-T [6–10]. The drawbacks of the previous synthetic method have been mentioned in the introduction, and similar drawbacks are avoided here by using a novel ladder-like organo-bridged polysiloxane **LPPVS** containing vinyl-terminated instead of Si–H-terminated side groups as the starting polymer, and by introduction of the Si–H-terminated ester-based mesogenic compound **1**, which has a flexible siloxane spacer, into **LPPVS** by hydrosilylation, followed by removal of unreacted compound **1** to give the target liquid crystalline polymer **LPLCPS**. The results characterizing **LPLCPS** are summarized in table 2.

The IR spectra of **LPPVS** and **LPLCPS** are shown in figures 1 (*a*) and 1 (*b*), respectively. By comparing these IR spectra it can be seen that the absorption bands corresponding to the stretching vibration of ester groups, which do not appear in the IR spectrum of **LPPVS**, appear at 1732 and 1260 cm^{-1} in the IR spectrum of **LPLCPS**. In addition, compared with the ^{1}H NMR spectrum of **LPPVS**, figure 2 (*a*), new peaks attributed to ester-based mesogenic side groups appear in the ^{1}H NMR spectrum of **LPLCPS** figure 2 (*b*). The IR and ^{1}H NMR results indicate that ester-based mesogenic compound **1** has been introduced at the side groups of **LPPVS**. In addition, it can be calculated from the ^{1}H NMR results that the grafting yield of the ester-based side groups in **LPLCPS** is 50%, compared with the calculated value 67%. The difference is attributed mainly to steric hindrance.

It is worthwhile mentioning that in order to avoid the large steric hindrance resulting from the comparatively bulky ester-based liquid crystalline side groups, which will lower the fluidity of the polymer in the liquid crystalline region, fully grafted homopolymeric **LPLCPS** was not expected or desired. On the contrary, 50% grafted (i.e. the mol ratio of ester-based mesogenic side groups to ungrafted vinyl side chains is 1 : 1) **LPLCPS** was synthesized.

3.2. *Mesomorphic properties of **LPLCPS***

The thermotropic phase behaviour of the resulting **LPLCPS** polymer was investigated by a combination of techniques consisting of DSC, POM and temperature-variable XRD. Figure 3 presents the DSC first heating and first cooling traces for **LPLCPS**. The transition temperatures and the corresponding enthalpy changes are summarized in table 3. As can be seen from figure 3 and table 3, **LPLCPS** is a semi-crystalline polymer without any noticeable glass transition at 50 ~ 250°C, but it exhibits a crystalline melting process at 92°C which gives a liquid crystalline phase undergoing isotropization at 194°C. Optical microscopic observations of this polymer are consistent with this behaviour. A melting point occurs at about 90°C, after which the sample shows bright birefringence. When the temperature is elevated above 190°C, the birefringence disappears. As the temperature returns to below 190°C, the birefringence reappears. Apparently, in the temperature range 90–190°C the **LPLCPS** is in a liquid crystalline state; a mosaic texture was observed by POM as shown in figure 4. However, the transition enthalpy ΔH (*c.* 22.61 J g^{-1}) between the semi-crystalline state and the liquid crystalline state obtained by DSC is not very big, which means

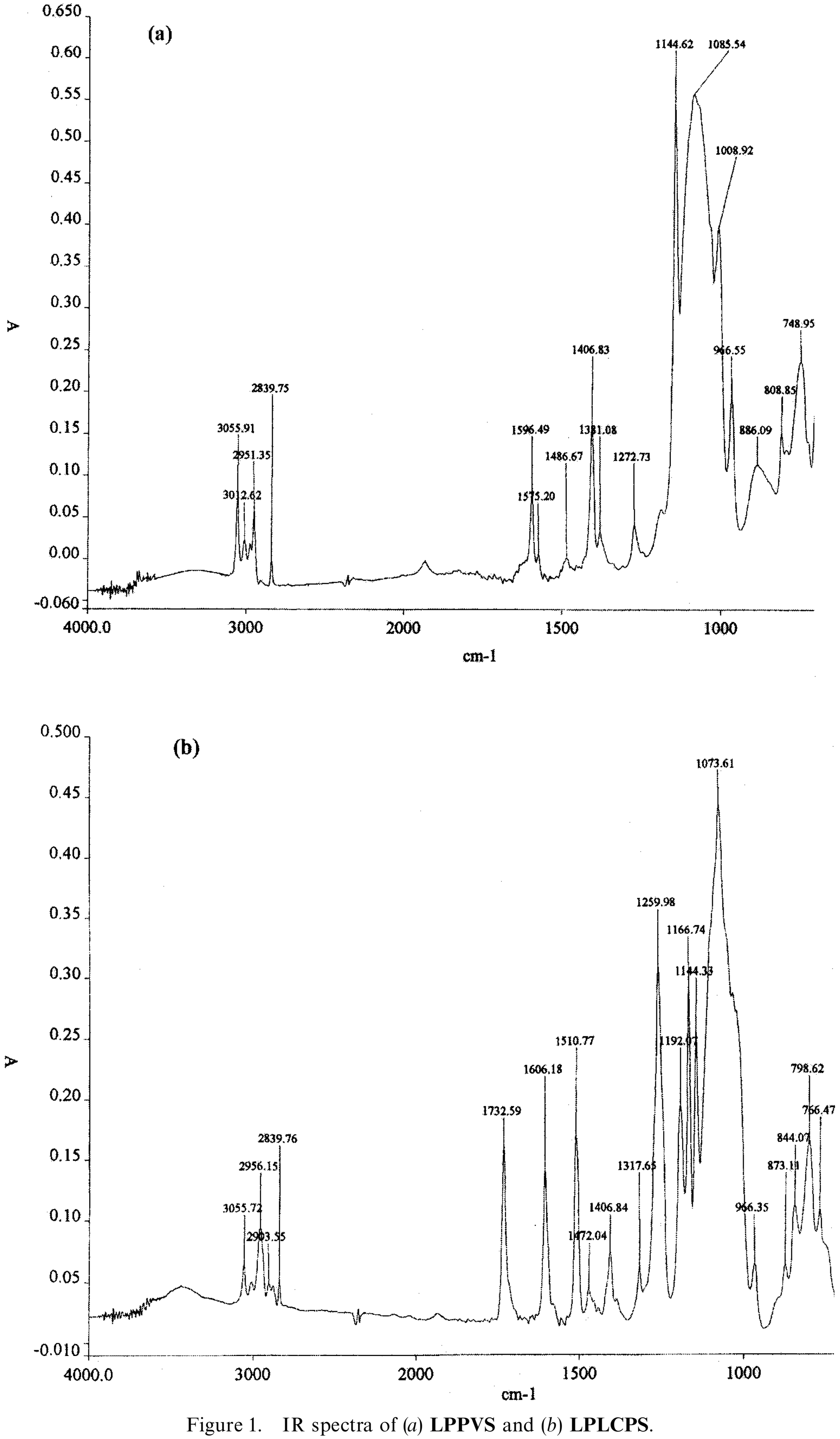


Figure 1. IR spectra of (*a*) **LPPVS** and (*b*) **LPLCPS**.

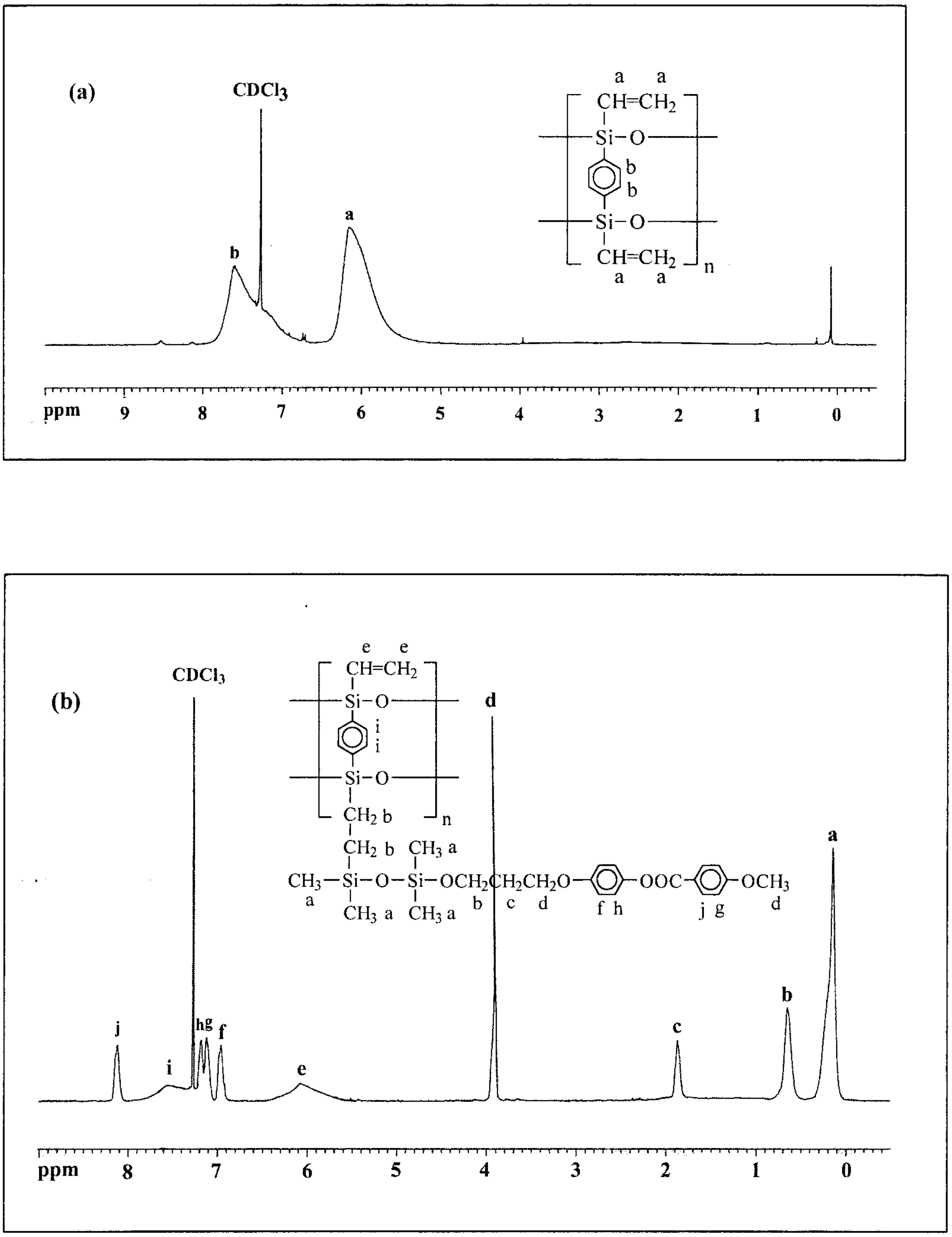


Figure 2. ^{1}H NMR spectra of (*a*) **LPPVS** and (*b*) **LPLCPS**.

that the total change in the ordering between the crystalline phase and the mesophase is not very conspicuous. In the XRD measurements a sharp peak in the small angle region ($2\theta = 3.28°$) corresponding to a smectic layer structure was observed as shown in figure 5. In addition, two peaks corresponding to the ladder-like double-chain structure were observed in the XRD spectrum of **LPLCPS**. It can therefore be concluded from the POM and XRD results that the liquid crystalline state of **LPLCPS** should be assigned as smectic.

4. Conclusions

A new soluble ladder-like 1,4-phenylene-bridged side chain liquid crystalline polysiloxane **LPLCPS** was prepared successfully by hydrosilylation reaction. The results from DSC, POM and XRD studies demonstrate

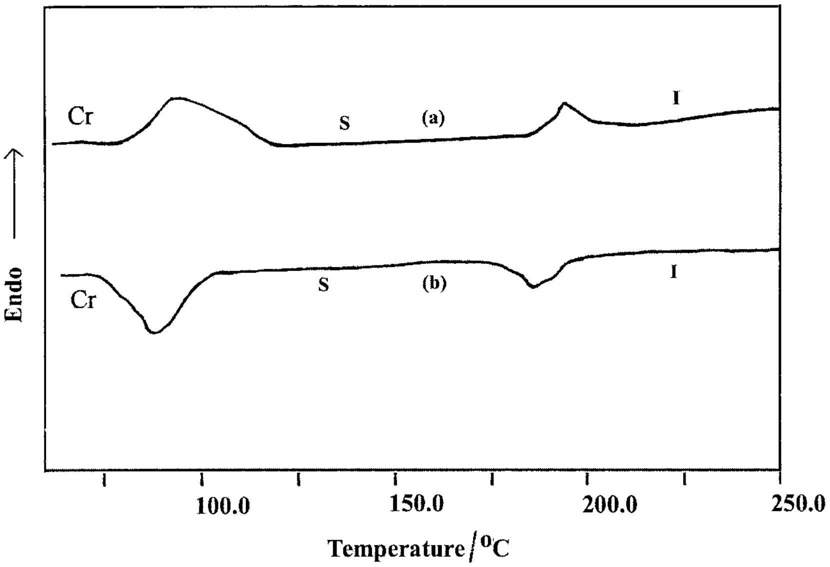


Figure 3. DSC trace for **LPLCPS** (*a*) on first heating and (*b*) on first cooling at a scanning rate of 10°C min^{-1}.

Figure 4. Mesophase texture of **LPLCPS** (250×) obtained by polarizing optical microscopy at 100°C.

Table 3. Mesomorphic properties of **LPLCPS** examined by DSC, XRD and POM.

Parameter	Results
Phase transition by DSC T(°C)/ΔH(J g^{-1})	Cr $\xrightarrow{92/22.61}$ S $\xrightarrow{194/6.79}$ I Cr $\xleftarrow[87/-24.13]{}$ S $\xleftarrow[185/-6.92]{}$ I
Mesophase range ΔT(°C)	102
Distance [d(Å)/2θ(°)] by XRD[a]	d_1: 26.91/3.28 d_2: 16.23/5.44 d_3: 4.39/20.20
Texture	Smectic

[a] The measurements were taken at 100°C for the liquid crystalline state.

that **LPLCPS** is a thermotropic liquid crystalline polymer with a smectic structure in the liquid crystalline region, and with a high clearing point (194°C) and wide mesophase range (102°C). The synthetic method for

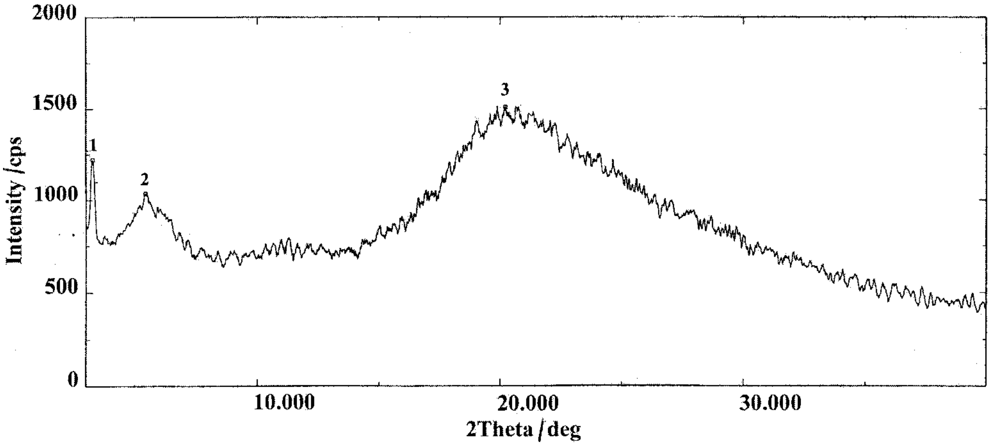


Figure 5. XRD pattern of **LPLCPS** at 100°C.

preparing **LPLCPS** has potential prospects for developing other liquid crystalline polymers with promising applications in many fields.

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