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Preliminary communication

A new route for the preparation of liquid crystalline polyorganosiloxanes containing laterally linked mesogenic units on the main chains

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A new route for the preparation of liquid crystalline polyorganosiloxanes containing laterally linked mesogenic units on the main chains (LLM-POS) is described. First, a novel polyorganosiloxane containing hydroquinone units on the main chains (HQ-POS) was synthesized by hydrosilylation polymerization. To avoid the oxygen silylation side reaction of phenolic groups, tetrahydropyranyl (THP) protective groups were used on the phenols taking part in the hydrosilylation reaction, the results indicating that THP groups are very stable and effective in hydrosilylation reactions. Then HQ-POS was further modified by a grafting reaction with 4-*n*-octyloxybenzoyl chloride, giving the desired LLM-POS, which has an increased molecular mass in comparison with similar polymers prepared by commonly used approaches. The titled LLM-POS was characterized by DSC, POM and XRD and shown to give smectic textures.

Liquid crystalline polymers (LCPs) containing laterally linked mesogenic moieties on the main chains (LLM-LCPs) are a relatively new class of LCP [1–6]. Their structures are different from those of both the traditional main chain liquid crystalline polymers (MCLCPs) and side group liquid crystalline polymers (SGLCPs). It can be seen from figure 1 that the mesogenic units in traditional MCLCPs are longitudinally fixed onto the main chains, and in SGLCPs they are attached to the main chains through flexible spacers (sometimes without spacers); on the other hand, in the titled LLM-LCPs, mesogenic units are laterally fixed onto the main chains through their molecular centres of gravity, with the mesogenic units perpendicular to the main chains. This novel structure gives LLM-LCPs many new properties and potential applications.

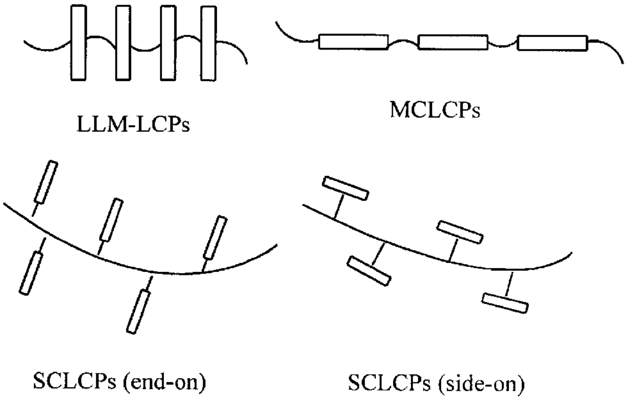

Figure 1. Conceptual diagram of MCLCPs, SCLCPs and LLM-LCPs.

According to Li *et al.* [1], the orientation of the mesogenic groups in LLM-LCPs can be carried out without translocation of the molecular centres of gravity and motions of the main chain segments. Therefore LLM-LCPs have more potential to be used in display devices than traditional MCLCPs. Interestingly, He *et al.* prepared negative Poisson ratio materials by introducing some rod-like mesogenic units laterally fixed onto the main chains [2]. As is known, most polymer materials when stretched will become thinner. However, such a polymer will expand laterally, because the laterally linked mesogenic groups, when stretched, will translocate from a position roughly parallel to the tensile axis to a

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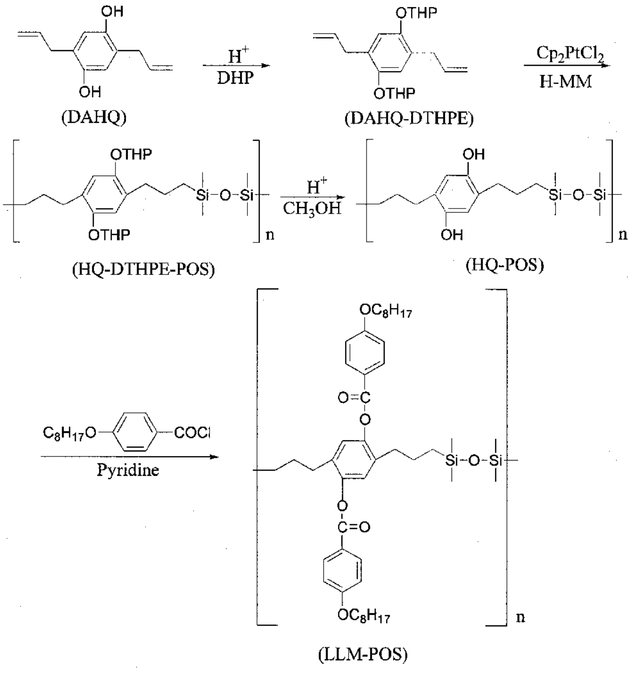
position normal to it, resulting in an increase in the interchain packing distance. Recently, Zhao *et al.* introduced some rod-like units laterally fixed onto rigid chain liquid crystalline polymers [3]. The rigidity and liquid crystallinity of the polymers ensure parallel packing of the polymer chains, whereas the laterally attached rods push the neighbouring polymer main chains apart, resulting in large voids in the polymer bulks. In this way, they obtained low dielectric constant materials. LLM-LCPs were typically prepared by copolymerization from monomers that contain liquid crystalline moieties. However, this approach has the disadvantage that most LLM-LCPs prepared by this method have very low molecular mass (generally only several repeating units) mainly due to the large steric hindrance stemming from the liquid crystalline monomers [4–6]. It is well known that molecular mass has a great influence on the mechanical properties, thermostability, and even the liquid crystalline properties of a polymer. Therefore it is necessary to attempt to find other methods of preparing LLM-LCPs.

Most reported LLM-LCPs have polyester main chains. As is known, siloxane polymers are widely used as backbones in side group liquid crystalline polymers because of their many excellent properties [7–12]. However, liquid crystalline polyorganosiloxanes containing laterally linked mesogenic units on the main chains (LLM-POS) are seldom reported. In this paper, a new route (see the scheme) for the preparation of LLM-POS is described: first, a polyorganosiloxane containing hydroquinone units on the main chains (HQ-POS) is prepared by hydrosilylation polymerization; this may give an increased molecular mass due to the relatively small steric hindrance arising during the polymerization process. Then HQ-POS is grafted by esterification with 4-*n*-octyloxybenzoyl chloride (OBC), giving the desired LLM-POS.



Scheme. Synthetic route to LLM-POS.

The precursor 2,5-diallylhydroquinone (DAHQ) was prepared according to a literature procedure [13].

Because the catalysts for hydrosilylation reactions can also catalyse the silylation of oxygen atoms of phenolic groups [14], these must be protected before hydrosilylation. Many approaches have been used for the protection of phenols. Here tetrahydropyranyl (THP) groups are chosen because they can effectively protect phenols and be readily removed under very mild conditions [15]. The monomer 2,5-diallylhydroquinone di(tetrahydropyranyl) ether (DAHQ-DTHPE) was therefore synthesized from DAHQ and 3,4-dihydropyran (DHP) by the following procedure. A solution of DAHQ (5.7 g, 0.03 mol) and DHP (7.8 ml, 0.09 mol) in dry dichloromethane (200 ml) containing the catalyst pyridinium *p*-toluenesulphonate (1.5 g, 0.006 mol) was stirred for 8 h at 25°C. Then the solution was washed with M sodium hydroxide to remove the catalyst and unprotected phenol. Next, the solution was washed well with water, dried with anhydrous Na_2SO_4 and evaporated to obtain an orange–yellow residue which was recrystallized from methanol, giving 8.13 g of colourless crystals, in a yield of 76%, m.p. 79.3°C. FTIR (KBr): 3076, 1502 (Ph), 1638 (C=C), 1196 (C–O–C). ^{1}H NMR ($CDCl_3$): $\delta = 6.88$ (s, 2H, Ph), 5.90 (m, 2H, $CH_2{=}C\underline{H}-$), 5.30 (m, 2H, THP), 5.03 (t, 4H, $C\underline{H}_2{=}CH-$), 3.57–3.94 (m, 4H, THP), 3.38 (m, 4H, $Ph-C\underline{H}_2-$), 1.58–2.04 (m, 12H, THP). MS (70 eV): $m/z = 358$ (M^+).

4-*n*-Octyloxybenzoic acid (OBA) and 4-*n*-octyloxybenzoyl chloride (OBC) were prepared conventionally. For OBA, 20.7 g (0.15 mol) of 4-hydroxybenzoic acid, 16.8 g (0.30 mol) of potassium hydroxide, a trace of potassium iodide, 55 ml of ethanol and 25 ml of water were mixed. Then 40.4 ml (0.23 mol) of 1-bromooctane was added dropwise to the mixture with stirring at room temperature for 2 h. The mixture was then heated under reflux for 10 h. After solvent had been removed under reduced pressure, 200 ml of water and 50 ml of 36.5% hydrochloric acid were added. Rapidly, a large amount of viscous solid was precipitated. After the liquid was decanted, recrystallization of the viscous residue from 300 ml anhydrous ethanol gave colourless crystals in a yield of 54%. To obtain OBC, a mixture of 1.87 g (7.5 mmol) OBA and 50 ml of thionyl chloride was heated under reflux for 1 h. After the excess of thionyl chloride was removed under reduced pressure, OBC was obtained and used without further purification.

Polyorganosiloxane containing hydroquinone ditetrahydropyranyl ether units on the main chains (HQ-DTHPE-POS) was synthesized by hydrosilylation polymerization under an argon atmosphere from DAHQ-DTHPE and 1,1,3,3-tetramethylhydrosiloxane (H-MM) in the presence of dicyclopentadienylplatinum dichloride (Cp_2PtCl_2) as catalyst. Because H-MM has a relatively low boiling point (71°C), its loss by evaporation during polymerization often gives rise to a stoichiometric imbalance and results in the production of low molecular mass oligomeric products. Therefore, in this process, 'the one monomer deficient method' [16] was used. 3.58 g (10.0 mmol) of DAHQ-DTHPE, a trace of Cp_2PtCl_2 and 10 ml of THF were added to a Schlenk flask, and the mixture stirred at room temperature for 30 min. Then 1.70 ml (9.50 mmol) of H-MM was added to start the reaction at the molar ratio of reacting functional groups, $r=0.950$ ($r=[Si-H]/[CH_2=CH-CH_2-]$). After about 8 h, additional H-MM (0.05 ml, 0.3 mmol) was then added to the reaction mixture to increase r to 0.98. This procedure was repeated until r reached 1.01 when unreacted $Si-H$ groups were detected by FTIR. After the solvent was removed under reduced pressure below 40°C, a dark brown, viscous liquid polymer HQ-DTHPE-POS was obtained. This procedure ensures that allyl groups are converted gradually and completely.

HQ-POS was prepared by removing the THP groups from HQ-DTHPE-POS according to a commonly used procedure [15]. A solution of 4.92 g of HQ-DTHPE-POS in 40 ml of acidified ethanol (prepared from 100 ml of ethanol and 5.0 ml 0.1 M hydrochloric acid) was heated to 40°C for 1 h. The HQ-POS obtained was purified by selective precipitation with water from THF solution; some low molecular mass (cyclic/linear) oligomeric products, accounting for 28% of all products, were removed in this process. ^1H NMR (300 MHz, CD_3COCD_3, ppm): $\delta=6.60$ (2H, Ph), 2.50 (4H, $Ph-CH_2-$), 1.60 (4H, $-CH_2-C\underline{H}_2-CH_2-$), 0.62 (4H, $Si-CH_2-$), 0.10 (12H, $Si-CH_3$). FTIR: 2870–2958 cm^{-1} (aliphatic $C-H$), 1508 cm^{-1}, 800 cm^{-1} ($-C_6H_2-$), 1423 cm^{-1}, 1257 cm^{-1} ($Si-CH_3$), 1062 cm^{-1} ($Si-O-Si$) and 3382 cm^{-1} ($-OH$). ^{29}Si NMR (200 MHz, CD_3COCD_3, ppm): $\delta=8.017$ (midchain Si), -2.618 (end Si). The results indicate that the THP groups are very stable during the hydrosilylation polymerization and can be removed completely under very mild conditions.

LLM-POS was synthesized by esterification of HQ-POS and OBC. 20 ml of THF and 1.5 ml of pyridine were added to the OBC obtained above to give a solution, into which 1.97 g of polymer HQ-POS (containing 2.5 mmol of repeat units) dissolved in 30 ml of THF was added dropwise at 0°C. The solution was then stirred at room temperature for about 15 h. In this stage, all the HCl generated during the reaction was immediately absorbed by the pyridine, so that the $Si-O-Si$ main chain was not broken by the HCl. After the salt was filtered, the solvent was removed by rotary evaporation. The crude product was dissolved in 80 ml of diethyl ether, and the solution washed with 3 × 50 ml of 1 M $NaHCO_3$ and 3 × 50 ml of water, respectively, to remove any residual OBC. After solvent was removed under reduced pressure, the LLM-POS was obtained in a yield of 85%. In order to increase the graft ratio, an excess of OBC and an appropriately long reaction time are necessary. The FTIR results indicate that the peak for $-OH$ (3380 cm^{-1}) becomes very weak after the esterification reaction. Meanwhile, two new peaks at 1732 and 1467 cm^{-1} appear in the LLM-POS spectrum, and are assigned to the ester groups newly generated. Therefore most of the $-OH$ groups have been converted to ester groups.

The number average molecular mass (M_n) of both HQ-POS and LLM-POS determined by vapour pressure osmometry (using a VPO, Knaeur, Germany) are listed in the table. It can be seen that the number of repeating units is 19, which is much higher than values reported in the literature [4–6]. Meanwhile, the graft ratio is above 90%, which further indicates that most of the phenolic groups have been used.

The liquid crystalline properties of the LLM-POS were examined by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). The results are shown in figures 2, 3 and 4, respectively.

The DSC curve in figure 2 shows that there are two endothermic peaks at 75.6 and 98.3°C. From the POM

Table. Molecular mass of HQ-POS and LLM-POS determined by VPO.

Polymer	Molecular mass	Number of repeating units	Graft ratio/%
HQ-POS	6300	19	
LLM-POS	13800	19	92

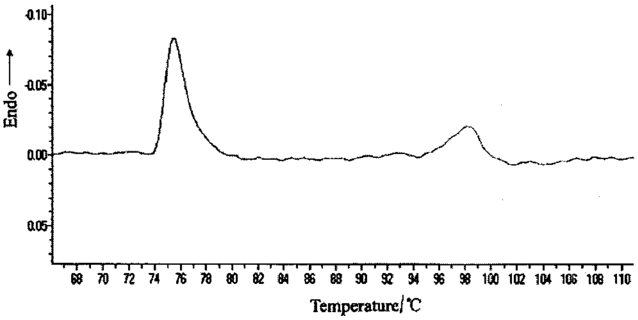


Figure 2. DSC trace for LLM-POS on first-heating at a scanning rate of 5°C min^{-1}.

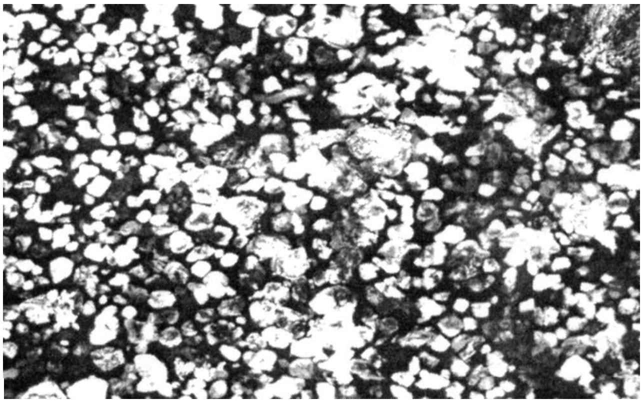


Figure 3. Mesophase texture of LLM-POS obtained by POM at 82°C.

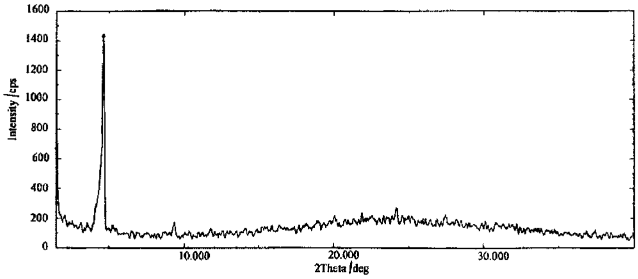


Figure 4. XRD pattern of LLM-POS at room temperature after quenching the sample from 82°C.

observations, the melting point can be observed at 73°C; above this, a smectic phase can be observed with a typical mosaic texture (figure 3). When the temperature is raised to about 101°C, the mosaic texture disappears. Apparently the temperature of 71°C, which corresponds to the first endothermic peak at 75.6°C in the DSC heating curve, is the solid to liquid crystalline transition temperature of the LLM-POS. The temperature of 101°C, which corresponds to the second endothermic peak at 98.3°C in the DSC heating curve, is the isotropization temperature. In the XRD measurements on LLM-POS, a sharp peak in the small angle region ($2\theta = 4.640°$, $d_1 = 1.903$ nm), corresponding to a smectic layer arrangement, was observed as shown in figure 4. This further indicates that LLM-POS is a smectic liquid crystalline polymer.

In conclusion, a well defined organosiloxane polymer HQ-POS was successfully synthesized by hydrosilylation polymerization from DAHQ-DTHPE and H-MM. THP groups as protective groups of phenols are demonstrated to be very stable and effective in the hydrosilylation reaction. Chemical modification of HQ-POS by a grafting reaction with OBC resulted in the desired LLM-POS, which has an increased molecular mass in comparison with similar polymers prepared by commonly used approaches. The LLM-POS obtained was demonstrated by DSC, POM and XRD to possess smectic properties.

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