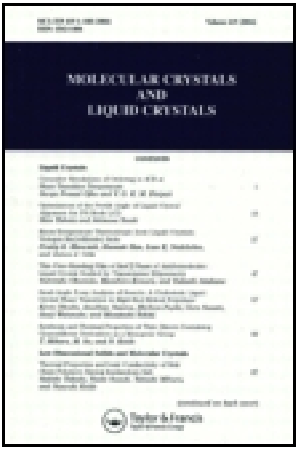

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Synthesis, Characterization of a Chiral Liquid Crystalline Polysiloxane and its Monomer

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Synthesis, Characterization of a Chiral Liquid Crystalline Polysiloxane and its Monomer

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A liquid crystalline polysiloxane and its monomer have been synthesized and characterized by FT-IR and ^{1}H NMR spectra. Their bulk phase liquid crystallinity were studied. The mesomorphic transition behaviors and the mesophases were observed by Differential Scanning Calorimeter (DSC), Polarized Optical Microscopy (POM) and Wide Angle X-ray Diffraction (WAXD) measurements. The monomer showed SmB and SmA phases which are assured by the corresponding broken fan-shaped or mosaic textures and fan-shaped textures by POM observation and WAXD patterns. The polymer had only one mesophase, SmC phase, which showed characteristic of fan-shaped or Schlieren textures by POM and sharp peaks in low angle region and a diffused peak wide angle region from WAXD.

Keywords: Chiral liquid crystal; polysiloxanes; side chain liquid crystal; synthesis

INTRODUCTION

Side chain liquid crystalline polymers (SCLCPs) have been studied extensively because of their potential applications in light-controlling devices [1–6], and nonlinear optical devices [7–9] *etc.*, due to their better mechanical and high stability compared with low molecular weight liquid crystals. The use of polymeric ferroelectric liquid crystals which have chiral end group opens up the possibility to perform such devices in glass (solid)

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state, because of the remaining of the polarization and the pyro-effect in the glassy state at temperatures below the verification point. Among the side-chain polymeric liquid crystals, the glass transition temperature (*Tg*) and mesophase transition temperatures of polysiloxanes are the lowest compared with that of poly(acrylate) [10], poly(methacrylate) [11], *etc.*, because of the low rotational energy of Si—O bond and the thermal stability of the polysiloxanes are very high. Polysiloxanes have lower intermolecular forces upon the shield effect of the organic groups on the backbone than the backbones of hydrocarbon polymers, conformational changes in the backbone may occur more easily to orient the side chain mesogens. Low *Tg* is of benefit to the fast switching of electro-optical in display devices or other related devices.

The SCLCPs remain now an area of strong research activity [12–14]. In this paper we have studied the liquid crystallinity of one kind newly synthesized side-chain polysiloxane (DP = 35) with ester bond as bridge bond and its corresponding monomer. The undecenoyloxy used as flexible spacer, $(CH_2)_{10}$ after side chain grafting to polysiloxane backbone, can better decouple the movements of the backbone and the mesogen units. The undecenoyloxy spacer can influence the nature of the mesophases and thermal transitions, longer spacer is beneficial for the Smectic mesophase. As is true for low-molar-mass LCs, the tendency towards smectic mesomorphism increases with increasing spacer length [6]. The ester bond in the chemical structure of the monomer and the polymer may play an important role affecting the bulk phase behavior, lowering the phase transition temperatures of the mesophases.

EXPERIMENTAL SECTION

Materials

Poly(methylhydrogensiloxanes) (PMHS, DP = 35, Mn = 2160 g/mol), (s)-(−)-2-methylbutanol were obtained from Fluka Inc. and used as received. All of the other chemical reagents were obtained as AR reagent for laboratory use and used as received.

Measurements

IR spectra were measured by Nicolet FT-IR 5DX ($4000\,cm^{-1} \sim 400\,cm^{-1}$ KBr plate or casting films). ^1H NMR measurements were performed by Joel FX 90Q ($CDCl_3$ or CF_3COOH).

Differential scanning calorimeter (DSC) measurements were carried out with a Perkin-Elmer DSC-2 instrument. Two separate 20 K/min heating scans were done for each sample with nitrogen as purge gas and Indium calibration, one cooling scan was done just after the first heating. The phase transition temperatures and mesomorphic textures were observed with a Xintian XP-1D Polarized optical microscope (China) and equipped with a hot stage controlled by a thermo-regulator and photographed by DF-300 camera (Seagull, Shanghai, China). The heating and cooling rates were varied from 10 K/min. to 1 K/min. Annealing for hours was found necessary to obtain good results both for POM and DSC for the polymer due to its high viscosity.

Wide angle X-ray diffraction (WAXD) measurements were performed with Rigaku D/max-rB with nickel-filtered Cu Kα radiation and a Rigaku powder diffractometer heating plate controlled by a thermo-regulator. Samples were heated to desired temperatures and annealed for half an hour before the measurements. The optical rotations of the samples were performed with Perkin-Elmer 241MC.

Synthesis

The monomer and the polymer were prepared according to the procedure listed in the Scheme 1, details are described as following [15].

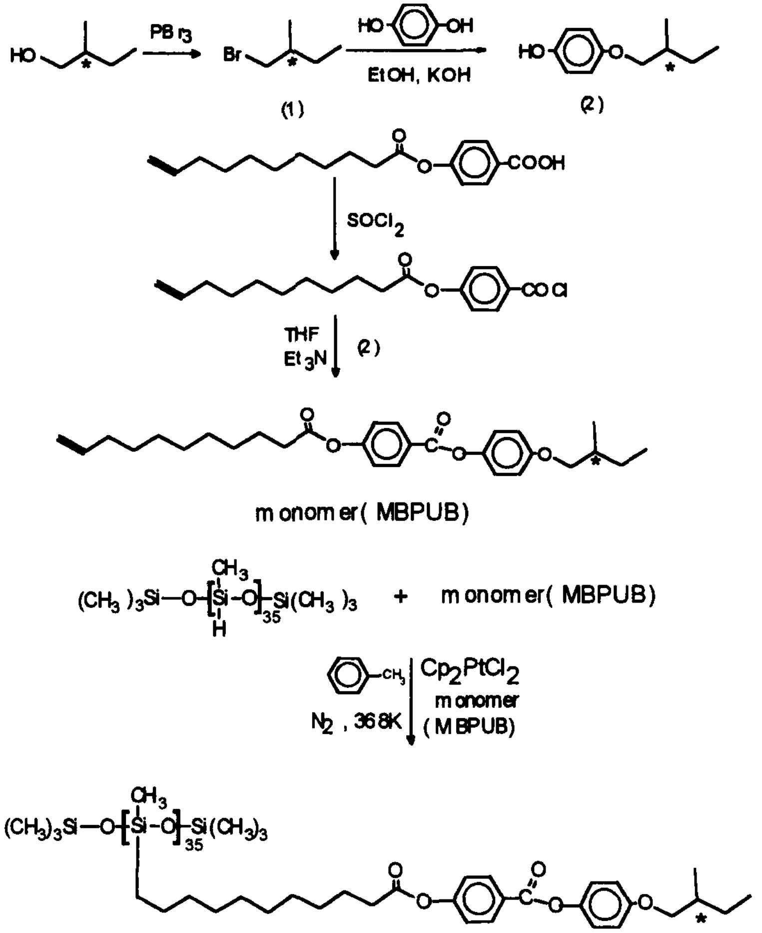
(S)-(+)-1-Bromo-2-methyl butane

Dropwisely added 96 g (0.34 mol) phosphorous bromide to the round flask with (s)-(−)-2-methylbutanol 88 g (1 mol) with ice bath in 2 hrs then stirred for further 6 hrs at 75°C. Washed the mixture with water, conc. sulfuric acid, water, aqueous sodium hydroxide and water, dried on Mg_2SO_4, distilled to obtain colorless liquid of 121°C in yield 70%. $n_D^{25} = 1.4460$, $[\alpha]_D^{25} = +3.86°$ (10 cm, in ethanol) (Ref. + 4.5° in chloroform).

^1H NMR ($CDCl_3$, ppm) δ 0.8 – 1.2 (m, 8H, CH_2, CH_3); 1.60 – 2.2 (m, 1H, —CH—); 3.4 (d, 2H, Br—CH_2—).

p-[2-methylbutyloxy] phenol (MBP)

Hydroquinone 11 g (0.1 mol) and (s)-(+)1-bromo-2-methyl butane 7.5 g (0.05 mol) in 40 ml ethanol was refluxed while 2.8 g (0.05 mol) of KOH in 15 ml 95% hot ethanol was added, then stirred and refluxed for 12 hr. The solvent was removed and the residual was acidified with 50% sulfuric acid.



SCHEME 1 Representative procedure for the preparation of the monomer and polysiloxanes.

The organic layer was washed thoroughly with water of 50°C, extracted with 10% NaOH (aq.) for several times. The extract was finally acidified with 50% sulfuric acid to obtain oil, recrystallized the oil from petroleum ether of 60–90°C to yield 2.25 g (25%) of white crystals. m.p. 40–41°C.

IR (KBr, cm^{-1}) 3407 (—OH); 2927, 2876 (CH_2, CH_3); 1510.5, 1406. 5 (—C_6H_4—).

^1H NMIR ($CDCl_3$, ppm) δ0.8–1.2 (m, 6H, CH_3); δ3.68–3.88 (d, 2H, OCH_2); δ6.8–8.0 (m, 4H, —Ar—).

4-[(s)-(+)-2-methylbutoxy] phenyl 4′-(10-Undecen-1-oyloxy) benzoate ester (MBPUB)

Added 9 g (0.03 mol) of *p*-Undecenoyloxy benzoyl chloride [15, 16] to the solution of *p*-[2-methylbutoxy] phenol 5.4 g (0.03 mol) in 20 ml of THF (dried on $LiAlH_4$) with 3 ml of anhydrous pyridine and refluxed for 6 hr, filtered off the precipitation and removed the solvent, recrystallized from ethanol to obtain 6.8 g white solid in yield 51%.

IR (KBr casting, cm^{-1}) 3074.7 (C = C); 2968, 2980 (CH_2, CH_3); 1739.0 (— COO —); 1601.9, 1503.7 ($—C_6H_4—$).

^1H NMR ($CDCl_3$, ppm) 0.8–1.2 (m, 6H, CH_3); 1.12–1.60 (m, 10H, $(CH_2)_5$); 1.62–2.20 (m, 7H, $=C—CH_2—$, $CH_2C—CO$, $OCH(CH_3)CH_2$); 2.48–2.72 (t, 2H, CH_2CO); 3.68–3.88 (d, 2H, OCH_2); 4.84–5.12 (m, 2H, $CH_2=$); 5.60–6.08 (m, 1H, $=CH$); 6.8–8.0 (m, 8H, —Ar—).

Hydrosilylation

The monomer (10% excess) reacted with poly(methylhydrogensiloxane) (DP = 35) by the hydrosilylation reaction of Si—H with carbon–carbon double bond in toluene (sodium dried) at 95°C using $Cp_2 \bullet PtCl_2$ as catalyst [15–17] under N_2 gas atmosphere for 150 hr until the disappearance of Si—H (2160 cm^{-1}) peak by IR and ^1H NMR. After evaporation of large portion of toluene the residual solution was poured into large amount of ethanol to precipitate. Pure polymer was obtained by recrystallization from chloroform into ethanol, yielding the product 90%. The ^1H NMR and IR results assured its structure and purity, there's no monomer left in polymer because there's no detectable $CH_2 = CH$ peaks found in ^1H NMR spectra.

IR (KBr casting, cm^{-1}) 2962.2, 2980.3 (CH_2, CH_3); 1740.9, 1719.2 (—C = O); 1602.2, 1506.0 ($—C_6H_4—$); 1503.7, 1066.2 (Si —O —Si); 1266.4 ($Si—CH_3$); 1206.2, 1162.1 (CO —O —C); 800.67, 764.06 ($Si—CH_2$).

^1H NMR ($CDCl_3$, ppm) 0–0.2 (s, 3H, $Si—CH_3$); 0.36–0.68 (t, 2H, $Si—CH_2$); 0.8–1.2 (m, 6H, CH_3); 1.20–1.24 (m, 14H, $(CH_2)_7$); 1.62–2.20 (m, 5H, CH_2CCO, $OCH(CH_3)CH_2$); 2.48–2.72 (t, 2H, CH_2CO); 3.68–3.88 (d, 2H, OCH_2); 6.8–8.0 (m, 8H, Ar).

RESULTS

Synthesis and Characterization

Polymerization was considered to be complete because there're no Si—H peaks detected by FT-IR and ^1H NMR results. More than five times of reprecipitations of the product from chloroform to ethanol were performed but the yield for polymer is above 90%.

The chiral end group was linked to the mesogenic unit to form chiral liquid crystals. From the $[\alpha]_D^{25}$ values listed in Table I, it was deduced that the preparation procedure has avoided the racemization, the resulting title products were synthesized from above scheme.

DSC

Representative DSC curves of the monomer and the polymer are shown in Figure 1 and Figure 2, respectively.

For the monomer three peaks were observed at the first heating, indicating that there existed two mesophases. The melting point of the monomer (Tm) and the clear point (Ti) were 50.5°C and 61°C, respectively.

TABLE I The data of the polymer and the monomer by DSC and POM, $[\alpha]_D^{25}$ (°) (Transition temperature: °C, Entropy: JK^{-1} mol^{-1})

Sample	*DSC* *POM*	*Phase transition temperatures (Entropy JK^{-1} mol^{-1})*	$[\alpha]_D^{25}$(°)
monomer	DSC	cryst 36 (13.6) S_B48 (2.1) S_A 60 (4.4) iso.	+4.00
	POM	cryst 37 S_B 48 S_A 53iso	
polymer	DSC	glass 61 (26.4) S_C 119.6 (14) iso	+ 3.62
	POM	glass 62 S_C 119 iso	

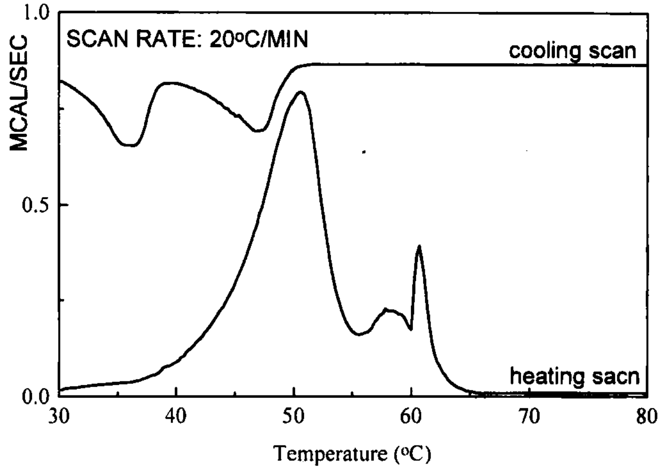


FIGURE 1 The DSC curves of the monomer (scanning rate: 20 K/min.), Bottom: the 1st heating scan; Top: the 1st cooling scan.

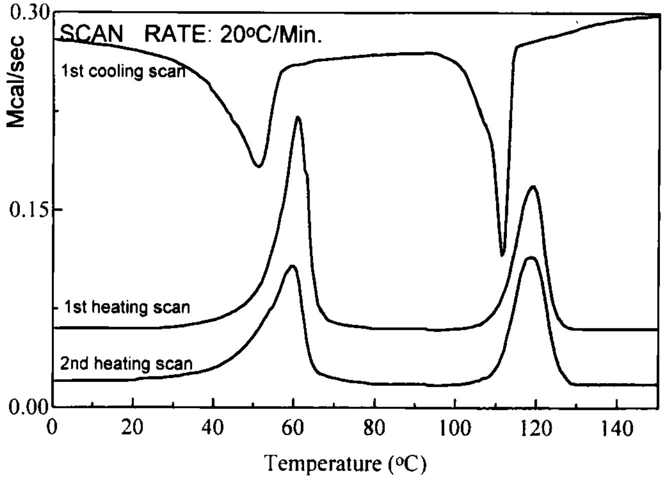


FIGURE 2 The DSC curves of the polysiloxane (scanning rate: 20 K/min.), from top to bottom: (a) the 1st cooling scan; (b) the 1st heating scan; (c) the 2nd heating scan.

Only two peaks were left upon cooling. But there seemed exist a shoulder peak at lower temperature about 44°C, which was seriously overlapped with the peak at 47°C. Different scan rates did not lead to high resolution of the overlapping peaks at cooling scan [18].

Only two peaks which corresponding to the mesophase transition and the clear point can be found for polymer from Figure 2 for both heating (61°C and 119.6°C) and cooling scan, but the peaks of the cooling scan changed little to lower values.

POM

The transition temperatures observed by POM were also listed in Table I. POM can also give strong evidence for the assignment of the mesophase. Apparently, below 37°C the monomer is in crystalline state, which shows typical birefringence of crystal by POM. When cooling the sample from iso.(60°C) to 53°C, anisotropy textures appeared. First it appeared as a point (in Fig. 3(b)), then fused to platelets texture and finally as focal textures (Fig. 3(c)). Further cooling to 50°C, the focal conic textures were fused to form large fan-shaped textures as Figure 3(d). Finally cooled to 38°C, the fan-shaped textures of SmA became increasingly broken in the fan textures and changed to textures with unequidistance homocentric arc and finally the mosaic textures. The mosaic textures could be frozen to room

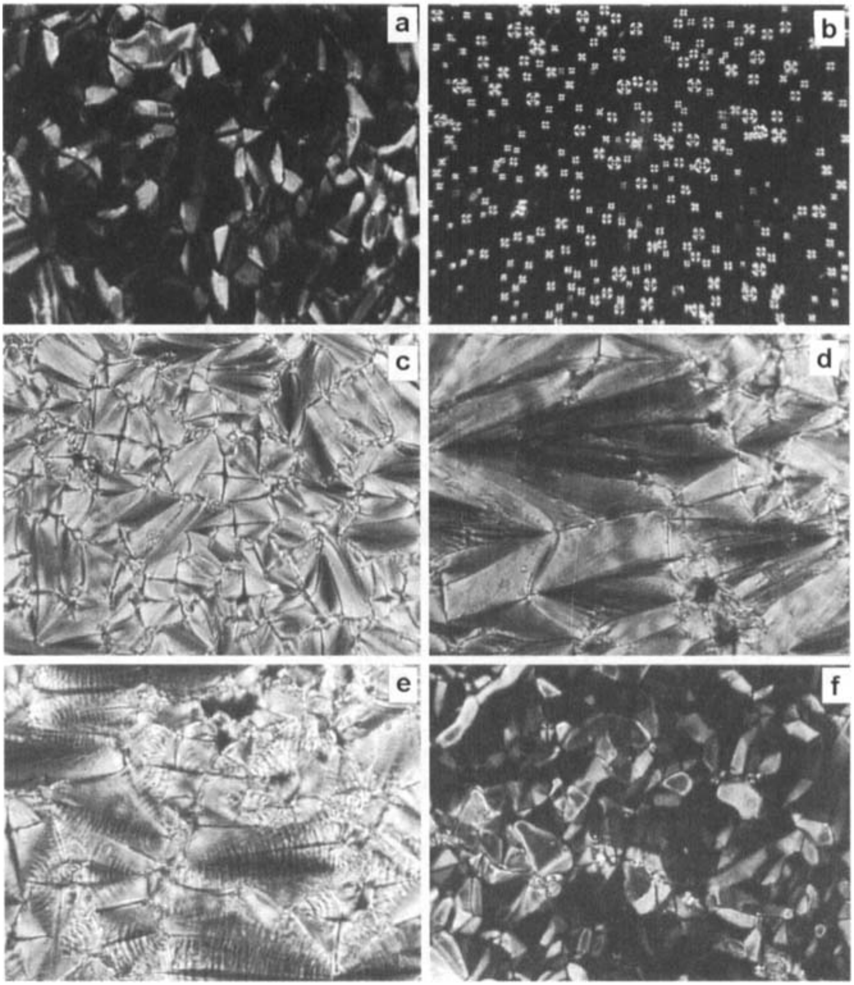


FIGURE 3 Polarized optical microscopy observation of the monomer at different temperatures (magnification: 400x). a. mosaic textures of the original sample annealing at 38°C for half an hour; b. the anisotropy textures appeared first as a point cooling from iso. state (60°C); c. focal-conic texture at 53°C; d. The fan-shaped textures of SmA formed by melting the adjacent focal conic texture to larger ones, at 51°C; e. the unequidistance homocentric arc in the fan further cooling to 40°C; f. the mosaic texture cooling to 35°C or shearing.

temperature and kept for weeks without change. The mosaic textures can also be observed when heating the original sample from room temperature (crystal state) and annealing for hours at 38°C as in Figure 3(a). Annealing is necessary for the formation of SmB phase from SmA phase after shearing at 37°C.

The results of POM observation for the polymer showed that only fine-grained textures can be observed without annealing. Often, textures occurs whose characteristics are somewhat obscure and observable only with difficulty even after annealing for hours at temperature just below the iso [21], the fan-shaped textures and another Schlieren textures have been found in the observation of some "sandwich" samples as in Figure 5.

X-Ray Diffraction

X-ray diffraction results are shown in Figure 4 for monomer and Figure 6 for polymer. Both of the WAXD results for monomer measured at 30°C and

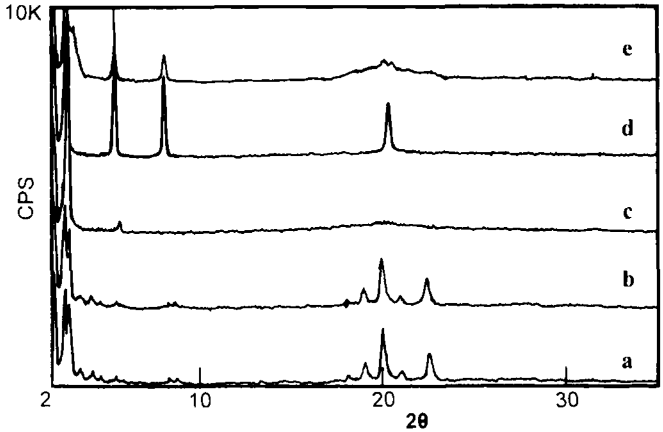


FIGURE 4 WAXD patterns of the monomer at different temperatures: a. Original sample at 25°C; b. heating to 30°C; c. at 50°C followed b; d. Cooling from iso. to 45°C; e. cooling to 25°C.

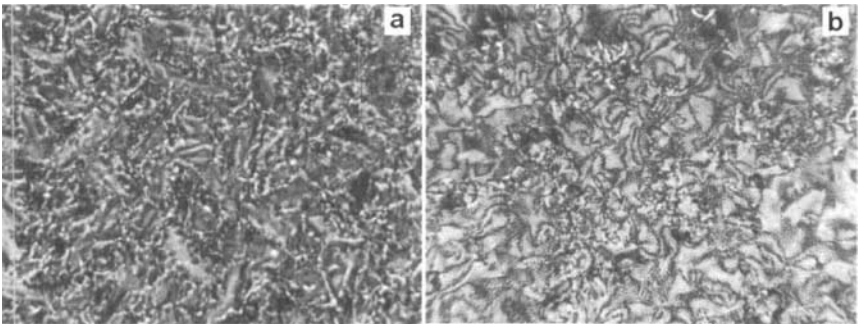


FIGURE 5 The Polarized optical microscopy photography of the polymer (magnification: 400x). a. The fan-shaped texture after annealing the original sample for 24 hr at 109°C then quenched; b. Coating film from chloroform and annealing at 109°C for 0.5 hr, there appears Schlieren textures with well-ordered spots.

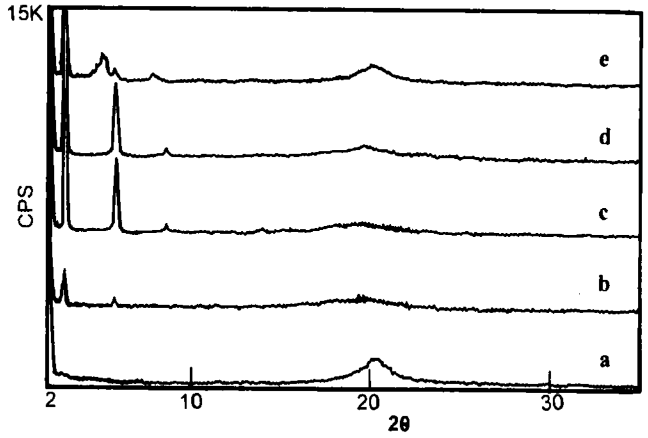


FIGURE 6 The WAXD patterns of the polymer: a. at room temperature; b. Heating to 110°C; c. cooling from Iso. and annealed at 100°C for 1 hr, the characteristic of SmA or SmC phase; d. at 80°C after c; e. further cooled from 80°C to 25°C.

room temperature (25°C) show only sharp peaks at wide angle and low angle regions, the characteristic pattern of crystalline state (in Fig. 4). The sharp peaks became a diffused peak at 50°C and only one sharp peak when cooled the sample from iso. (65°C) to 45°C. The diffraction pattern of monomer for sample cooled from iso. to 25°C is similiar to that of original sample. There are some similarity for all the diffraction patterns of polymer as in Figure 6, they all showed sharp peaks at low angle regions and diffused peak at wide angle region.

DISCUSSIONS

Synthesis and Characterization

Polymerization was successfully performed and avoided the racemization, the resulting title products were synthesized. The percentage conversion can be estimated from the integration of the peaks of Si—CH$_2$ and Si—CH$_3$ in ^{1}H NMR spectra as following:

$$\mathbf{Pc(\%)} = (A_{Si-CH_2}/A_{Si-CH_3})/(70/123)$$

where **Pc(%)** is the conversion percentage, A is referred to the integration of the H-peaks by ^{1}H NMR. 70/123 is the H-atoms ratio of Si—CH$_2$ to Si—CH$_3$ in the polysiloxane backbone when 100% conversion is realized.

The grafting number of the side chain is **Pc(%)** × 35. In this paper, the percentage conversion is about 92%, that is, the grafting degree is 35 × 92% = 32.2 *i.e.*, each polysiloxane backbone has 32.2 side-chains linked to it in average.

Liquid Crystal Phases

The phase transition temperatures measured by DSC and POM and the nature of phases assigned from the results of WAXD and textures observed by POM for the monomer and polymer are summarized in the Table I [19].

Both the polymer and the monomer have shown good liquid crystallinity from the results of DSC and POM. POM results have given strong evidence for the phase transition temperatures and the assignment of mesophase. The reversible and more ordered texture changes can be observed in the cooling scan respect to the heating scan, so it is easier to assign the mesophase by POM in cooling scan than in heating scan.

The dynamics of the phase transition may play a very important role in the measurements, because the phase transition temperatures of both the monomer and the polymer obtained by DSC on the cooling scan are lower than that on the heating scan. It was also found that the melting point and the clearing point of the monomer became higher after polymerization, the liquid crystal range ($\Delta T = T_{\text{iso}} - T_{\text{m.p.}}$) also became larger, so the polymerization was of benefit to the formation and the stabilization of the mesophase. The phase transition temperatures obtained by POM are consistent with DSC results. The glassy temperature for the polymer was not detected over 0°C. It is thought that the longer spacer has increased the tendency of the polymer to crystallize [6].

According to the results of POM and WAXD, the monomer is apparently in crystalline state below 37°C, because of the existence of several diffraction peaks in the WAXD patterns at 25°C and 37°C. The monomer showed typical fan-shaped textures when cooling from isotropic state to 53°C from POM and sharp peaks at small-angle region and a diffused in the wide-angle region peak from WAXD at 50°C, typical characteristic of SmA. The entropy of this transition measured by DSC at 47°C is $14.7\,\text{J}\cdot\text{K}^{-1}\bullet\text{mol}^{-1}$ at cooling, the same order of the entropy as that of Iso–Sm transition [6]. X-ray results at 45°C exhibited a sharp peak in the wide-angle region in addition to the sharp peak in the small-angle region, which showed the typical hexagon structure in Sm layers, attributed to a SmB phase. Accordingly, there's mosaic texture and broken fan-shaped textures from POM at 45°C.

The observation by POM for the polymer is relatively difficult, but fan-shaped textures and Schlieren texture can be observed after annealing for hours. The Schlieren texture [21, 22] often have been observed at homeotropic regions of SmC phase with four brushes originating from them. But there are well-ordered black point in the bright fan for this polymer and it was still a question for us to well explain the appearance of the ordered black point. The WAXD patterns showed sharp peaks in the small-angle area and a diffuse peak in the wide-angle region, attributed to SmA or SmC phase. Only one mesophase should exist in the polymer from DSC, thus we can deduced that the phase is SmC phase, not SmA phase.

In the WAXD patterns, two peaks at 32.939 Å, and 30.441 Å for the original sample and one peak at 31.084 Å at 50°C for first heating scan were found for the monomer. The calculated extended molecular length is 30 Å, the *d*-spacing value is very near to the extended molecule length, the molecules may show a monolayer structure, not interdigited bilayer structure [23, 24]. The polymer shows almost the same *d*-spacing as found in the monomer, the movement of the backbone of polysiloxanes and mesogens have been decoupled. The packing of the molecules is dominated by the mesogenic core with the long molecular axis paralleled to the film normal for the monomer. Taking the presence of the SmC in polymer into account, the mesogens may show a tilted orientation, it is reasonably because the backbone extended the length of the molecules and tend to show a statistical conformation, but it is difficult to obtain the exact tilt angle of the mesogens only by WAXD.

In our previous paper [15, 16], we have synthesized one couple of monomer-polysiloxane materials with similar structure except that the linkage of the chiral end-group to the mesogen is different and the previous ester bond [16] was substituted by ether bond in this paper. The molecule with ester bond can rotate more easily along their axis to change the conformation than ether bond, therefore their bulk phase transition temperatures of the material with ester bond decreased compared with that with ether bond.

CONCLUSIONS

A pair of monomer-polysiloxane liquid crystals with undecanoyloxy as spacer have been synthesized and characterized. This monomer has shown good liquid crystallinity in bulk phases with low transition temperatures and a SmA phase cooling from iso. and changed to SmB state from POM and

WAXD. The comb-like structure of the mesogens give rise to the stability of the bulk mesophase with increased clear point. The molecules oriented to form monolayer smectic structure in mesophase both for the polymer and the monomer.

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