Phase transition behavior of silicone based liquid crystalline polymers

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Abstract: Phase transition behavior of silicone based liquid crystalline (LC) polymers with variable isotropic transition temperatures (T_i), synthesized from poly(methyl hydrosiloxane), 10-undecenoic acid based crosslinking agent and cholesterol based side chain mesogen, was studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements. The chemical structure of the mesogenic monomer and the LC polymers were confirmed by Fourier transform infra-red (FT-IR) spectroscopy and ¹HNMR spectroscopy. DSC studies showed that the glass transition temperatures (T_g) and T_i of the LC polymers decreased with increasing proportion of mesogenic crosslinking agent at its low proportion and at its higher proportion T_i disappeared completely indicating that the polymeric chains had less chance to orient in the network structure. The results were consistent with the XRD and POM studies.

Introduction

Nowadays, liquid crystal (LC) polymers are used in different areas such as fluorescence paint industries, flat-panel displays, gas detector, actuator and sensor, etc due to their excellent optical properties such as selective reflection of light, thermochromism, and circular dichroism [1-6]. After crosslinking, LC polymers may also be useful in some specific optical applications because of their structure being permanently fixed so that the optical properties become temperature independent [7, 8]. Again lightly crosslinked LC polymers may show the basic features of polymeric elastomers with anisotropic physical properties coming from their LC phases with reversible phase transition during heating and subsequent cooling [9-11]. Thus a series of crosslinked LC polymers, prepared by graft copolymerization, and characterized by DSC and POM, show that at low level of crosslinking agent, the phase behavior of the network polymers does not affect largely; however, at high level of crosslinking agent there may be more drastic influences on LC phases by direct coupling through a shorter or stiffer chain formation between the mesogenic side units and the polymer backbone [12]. The effect of ionic crosslinking agent on phase transition behavior of cholesteric liquid crystalline polymer has also been studied [13]. It is found that the ionic mesogens displayed smectic and cholesteric mesophase in the polymers. The increase of ionic groups in the polymers tends to change the glass transition temperatures (T_g) and clear point a little. The effect of

spacer length on LC properties is well reported [14-18]. It is found that with an increase in the number of methylene units in the side chains of the polymers, there is an increase in the layer spacing values for the cholesteric liquid crystalline phases as measured by WAXD. Poly(methylhydrosiloxane) based LC polymers with fluorinated mesogens, show smectic LC phase with very wide temperature ranges during heating and cooling cycles [19]. However, the polymers with high fluorine content exhibit smectic–cholesteric phase transition when they are heated. As the polymers contain more fluorinated mesogens, the segregation of the fluorinated segment to the surface may occur at the mesomorphic temperature. The highly ordered lamellar mesogen–siloxane matrix systems may disturb severely by separation of fluorinated mesogens, suggesting the transition from lamellar smectic to cholesteric phase [19]. Thus there are numerous reports on phase transition behavior of different LC polymers, but there are only a limited number of reports on silicone based liquid crystal polymers [20-26] though these polymers are expected to be more thermally stable after several heating and cooling cycles and thus may have potential industrial applications.

So in our present study, we have prepared 1,4-butanediol diundecylenate based flexible crosslinking agent (M-1) and cholesterol based mesogenic monomer (M-2) and then M-1 and M-2 are introduced simultaneously into the poly(methylhydrosiloxane) chain. The aim of this work is to investigate the effect of crosslinking agent on phase transition behavior and crystallization behavior of the polymers using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements.

Results and Discussion

Spectral analysis by FT-IR and ¹HNMR

Fig.1. shows the FT-IR spectra of the crosslinking agent (M-1), mesogenic monomer (M-2) and one LC polymer (e.g., L-1 at the initial stage (0 h) and after 12 h of reaction). This shows that M-1 has the characteristic peaks corresponding to C–H stretching of vinyl at 3032 cm⁻¹, C–H of methylene at 2921 and 2848 cm⁻¹, alkane ester group (–RCOOR–) at 1710 cm⁻¹ and C=C of vinyl at 1466 cm⁻¹ [10, 27]. The cholesteric monomer (M-2) shows characteristic peaks corresponding to C-H stretching of vinyl at 3018 cm⁻¹, C-H of methylene at 2945 cm⁻¹, C=C of vinyl at 1457 and 1369 cm⁻¹. The spectra for the network polymers (e.g. L-1) formed after 12 h reaction show the complete disappearance of the peaks for the Si–H stretching at 2160 cm⁻¹ and vinyl C=C stretching at about 1466 cm⁻¹ of the monomers [10, 27].

The structures of the crosslinking agent, mesogenic monomer and LCPs are also confirmed from ¹H-NMR analysis. The chemical shifts as observed; 5.70 (4H, m), 5.71 (2H, m), 4.81 (4H, t), 2.21-1.31(16H, t), 1.98 (4H, m) clearly indicate the formation of crosslinking agent (Fig. 2). Similarly, mesogen has the chemical shift of 3.85 (2H, m), 3.71 (1H, m), 2.25 (2H, t), 0.83 (6H, m), 0.65 (2H, m) and LC polymers have a new shift at 1.60 (2H, m) which is due to the methyl hydrogen coming from Si-CH₂ bond formation (Fig. 2). Thus it is evident that the crosslinking agent (M-1) and mesogenic monomer (M-2) have been successfully incorporated into the poly(methylhydrosiloxane) chain. Moreover, as the yield is more than 95 % in all cases, then almost all M-1 and M-2 molecules have reacted with PMHS.

Fig. 1. FT-IR spectra of crosslinking agent (M-1), mesogenic monomer (M-2) and liquid crystal polymer (LCP-1) at initial stage (0 h) and after 12 h of reaction.

Fig. 2. ¹H NMR of (a) crosslinking agent, (b) mesogenic monomer and (c) LC polymer (L-2).

Phase behavior by DSC

The different transition temperatures of the LC polymers as obtained from their DSC thermograms are reported in Table 1. The polymers with low content of crosslinking agent (<10.71 mol %) (e.g., L-1~ L-3) reveal a T_g near about 40 °C, LC phase transition at about 141 °C and T_i at about 212 °C (Fig. 3(a)-(c)). However, L-4 and L-5 show only T_g and no T_i (Fig. 3(d), (e)). It is well known that for side-chain LC polymers, T_g is influenced by polymer backbone, mesogenic group, flexible spacer length and crosslinking density. The chemical crosslinking imposes additional constraints on the motion of chain segments, and thus makes T_g increase. On the other hand, the flexible chain of the crosslinking agent similar to the plasticization will

cause T_g to decrease. Due to the long flexible chains in both ends of the crosslinking agent for the synthesized polymers, the plasticization of flexible chains was much more significant than the crosslinking limitation on the motion of chain segments [10].

Tab. 1. DSC results of the polymers.

Sample Code	T_g (°C)	T_m (°C)	T_i (°C)	ΔH (J/g)	ΔT (°C)
L-1	38.6	141.1	212.2	2.37	173.6
L-2	37.2	141.0	209.9	1.78	172.7
L-3	35.5	141.0	208.6	1.50	173.1
L-4	34.5	---	---	---	---
L-5	34.2	---	---	---	---

ΔT = Mesogenic temperature range ($T_i - T_g$)

So, with the increasing concentration of crosslinking agent from 3.57 to 21.43 mol%, T_g decreases from 38.6 °C for L-1 to 34.2 °C for L-5. As the density of crosslinking (M-1) units increased from 3.57 to 10.71 mol%, T_i reduced from 212.2 °C for L-1 to 208.6 °C for L-3, and T_i of L-4 and L-5 disappeared for high crosslinking density. At high crosslink density, the plasticizing effect of the flexible chain of the crosslinking agent on T_i of liquid crystalline elastomers becomes minor. The enthalpy changes (ΔH) decreased from 2.37 Jg⁻¹ for L-1 to 1.50 Jg⁻¹ for L-3. Thus in the LC range, L-1, L-2 and L-3 revealed elasticity and reversible phase transitions on heating and cooling. Whereas, L-4 and L-5 with 17.85 and 21.43 mol % of crosslinking agents, respectively, did not show any texture due to high crosslink density.

Fig. 3. DSC thermograms of different LC polymers (a) L-1, (b) L-2, (c) L-3, (d) L-4 and (e) L-5.

Crystallization behavior by XRD

The crystallization behavior of the polymers was studied by XRD measurements. It is well known that a smectic liquid crystalline phase shows a sharp and strong peak in the small-angle region and a broad peak in the wide-angle region [10]. But the nematic and cholesteric liquid crystalline phases show only a broad peak in the wide angle region [10]. In our case, no peak was found in the small-angle region but there

were two broad peaks associated with the lateral packing at about 10.2° (2θ) and 22.5° (2θ) in wide-angle region (Fig. 4.). Thus the formation of nematic and cholesteric phase structure for L-1 to L-3 is confirmed. Again as the peak intensity decreases with increasing the density of crosslinking units in the polymers, it suggests that the crosslinking agent affects largely on the LC order. For the polymers with high crosslink density, there is no such crystalline peak both at for small-angle and wide-angle regions. The high crosslinking leads to the disappearance of isotropic transition of these polymers which is in good agreement with the DSC studies.

Fig. 4. Wide-angle X-ray diffraction of patterns of different liquid crystal polymers, (a) L-1, (b) L-2, (c) L-3, (d) L-4 and (e) L-5..

Phase morphology by POM

The LC polymers with low crosslink density (e.g., L-1 to L-3) show similar type of phase morphology as observed by POM. So for convenience, the phase morphology only for L-3 has been reported here and it is found that L-3 shows a nematic liquid crystal structure (Fig. 5(a)) with different helicoidal forms, characteristic of cholesteric liquid crystalline polymers. So at room temperature it shows both the nematic and cholesteric textures [28].

Fig. 5. POM images of (a) L-3, after 1st heating and subsequent cooling to 25 °C; during second heating for L-3 at different temperatures (b) 142 °C, (c) 206 °C and (d) 208 °C and during 1st heating of L-4 at different temperatures (e) 25 °C, (f) 142 °C, (g) 208 °C and (h) 25 °C, after cooling.

Now again during second heating as the temperature increases, the nematic phase disappears at about 142 °C and only cholesteric phase (Fig. 5(b)) remains in the texture until the temperature reaches to 206 °C (Fig. 5(c)).

Upon further heating up to 208 °C, it changes into an isotropic liquid (Fig. 5(d)). So L-1 to L-3 shows a reversible phase transition on heating and cooling. In case of polymers with high crosslinking agent (e.g., L-4, L-5), the phase transition behavior is surprising. It is clear from the POM that the cross polarized light shows different color reflections from the planes of the liquid crystals (Fig. 5(e)) and the crystals are arranged in a zigzag way. As the temperature rises, the crystals start melting (Fig. 5(f)) at about 142 °C and it continues up to 208 °C (Fig. 5(g)). On cooling no proper crystallization is found (Fig. 5(h)), this is because at high level of crosslinking agent (>10.71 mol %) permanent set of the polymer network has occurred which restricts the chain movement and the crystallization process. Thus, L-4 and L-5 do not show complete reversible phase transition on cooling which is consistent with the DSC studies though there is a small temperature difference between the reading from DSC and POM due to the human error associated with the POM measurement.

Conclusions

The different side chain LC polymers containing with a flexible crosslinking agent and a cholesteric monomer have been synthesized successfully. FT-IR and ¹H-NMR spectroscopes confirm the possible structures of the monomers and the synthesized polymers. DSC studies show that T_i decreases with an increase in crosslinking agent, though the flexible chain of M-1 influences the T_g values to lower down. The LC polymers containing low proportion of crosslinking agents (e.g., L-1 ~ L-3) reveal the elasticity and reversible phase transition on heating and cooling whereas highly crosslinked LC polymers do not show this property, as is quite clear from the POM studies. The XRD studies also confirm that the crosslinking agent at its high proportion affects the LC order appreciably.

Experimental

Materials

Poly(methylhydrosiloxane) (PMHS, $n = 35$); 10-undecenoic acid; allyl bromide; hexachloroplatinic acid (H_2PtCl_6) (8 wt. % in water) and cholesterol were purchased from Sigma-Aldrich, USA. 1, 4-Butanediol was supplied by Junsei Chemicals, Japan. All other chemicals were of LR grade reagents.

Characterization

FT-IR spectroscopic measurements were performed using a Jasco FT-IR 300E with an attenuated total reflectance (ATR) method. ¹H-NMR characterizations were performed using a Bruker Advanced DMX 500 spectrometer. The samples were prepared in $CDCl_3$ at room temperature. DSC experiments were performed in the temperature range of 0 °C to 275 °C on a TA Instruments (Q100) in N_2 atmosphere taking sample of about 10 mg encapsulated in aluminum pan. During 1st heating the heating rate was 10 °C/min but during 1st cooling and 2nd heating, the cooling and heating rate were of 5 °C/min in the both cases. Indium was used as a calibration standard for both the temperature and heat flow scales. The DSC scans for the 1st heating and cooling cycles were discarded. The temperatures corresponding to maxima of the DSC endothermic peaks of the 2nd heating traces were assigned as

phase transition temperatures. The midpoint of the heat capacity stepwise increase was taken as the glass transition temperature. Wide-angle X-ray diffraction studies using monochromatized $\text{CuK}\alpha$ radiation and a nickel filter was carried out in X-ray diffractometer (Bruker AXS). The diffraction was recorded in the range of 5° (2θ) to 30° (2θ) at a scanning speed of $5^\circ/\text{min}$. Polarized optical microscope (Eclipse LV 100 POL) from Nikon Corporation, Tokyo, Japan, equipped with a hot stage (LTS 350) from Linkon Scientific Instruments Ltd, England, UK, was used to observe visual textures and phase transition temperatures for analyzing the mesomorphic properties of the liquid crystalline monomers and polymers. The samples used for POM analysis were sandwiched between two glass cover slips and melted on a hot stage at 250°C , care being taken to avoid cover slip sliding over that would lead to void formation, and subsequently cooled to room temperature. The rate of heating and cooling were selected similar to the DSC studies.

Synthesis of crosslinking Agent (M-1)

About 1 ml concentrated sulfuric acid was added to the mixture of about 22.08 g (0.12 mol) of undecylenic acid and 5.9 g (0.05 mol) of 1, 4-butanediol dissolved in 30 ml benzene. After the mixture was mixed uniformly, it was refluxed at 120°C for 8 h, and the mixture was poured into 200 ml of water. After removing the water layer, the oil layer was neutralized with 2% NaHCO_3 to pH 7, washed several times with distilled water, and dried with anhydrous Na_2SO_4 . Then the distillate of crude product, collected at 175°C under 3 mm Hg pressure gave the transparent liquid as the monomer M-1 (Scheme 1).

Synthesis of mesogenic monomer (M-2):

About 19.3 g (0.05 mol) of cholesterol was dissolved in 80 ml of chloroform, followed by the drop wise addition of 30 ml of an aqueous solution of potassium hydroxide (30 wt %). Then 6.0 g (0.05 mol) of allyl bromide was slowly dropped into the mixture. After the mixture was reacted at room temperature for 2 h and was refluxed at 90°C for 4 h, it was cooled to room temperature and poured into 300 ml of deionized water to get a transparent yellow solution.

Scheme 1. Synthesis route for crosslinking agent, mesogenic monomer and LCPs.

Afterwards, the organic phase was extracted with 50 ml of diethyl ether three times. To the aqueous phase, 80 ml of 30 % hydrochloric acid solution was added, leading to a white precipitation which on further recrystallization from ethanol gave the desired product (Scheme 1).

Synthesis of polymers

The polymers were prepared by a graft reaction, in which the crosslinking agent M-1 and the mesogenic monomer M-2 were simultaneously attached to the highly flexible poly(methylhydrosiloxane) chain via a hydrosilation reaction. For convenience, the synthesis procedure for L-1 polymer was only reported here, however, the other polymers were made, following the same procedure as for L-1, with different proportions of crosslinking agent varying from 3.57 mol % to 21.43 mol % (Table 2). For synthesis of L-1 polymer, the crosslinking monomer M-1 (0.15 g, 0.25 mmol) was taken in 50 ml dry toluene, then mesogenic monomer M-2 (2.45 g, 5.75 mmol), and PMHS (2.450 g, 1.00 mmol) were added to that solution with continuous stirring. The reaction mixture was heated to 65 °C under nitrogen, and then 2 ml of 0.5 wt % H₂PtCl₆/THF catalyst solution was injected.

Tab. 2. Composition of silicone base LC polymers.

Sample Code	PMHS (mmol)	M-1 (mmol)	M-2 (mmol)	M-1 (mol%)	Yield (%)
L-1	1.00	0.25	5.75	3.57	95
L-2	1.00	0.50	5.50	7.14	97
L-3	1.00	0.75	5.25	10.71	97
L-4	1.00	1.25	4.75	17.85	96
L-5	1.00	1.50	4.50	21.43	96

The reaction was kept at 65 °C under nitrogen until the Si–H absorption peak of PMHS at 2160 cm⁻¹ disappeared. It took about 12 h to complete the reaction. Then the elastomers were carefully deswollen with methanol to remove the excessive monomers and the catalyst fragments and then dried under vacuum over night. Deswelling in methanol and subsequent vacuum drying were repeated several times until to get a constant weight of the polymers so that almost all the impurities were eliminated from the polymers.

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