

SHORT COMMUNICATIONS

**Growth of Liquid Crystal in Poly[[6-(4'-cyanobiphenyl-4-oxy)hexyl]-methylsiloxane]**

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Thermotropic liquid crystalline polymers containing mesogenic side chains show various liquid crystalline textures similar to those of monomeric liquid crystalline materials, as the motions of the main chain and the substituted mesogens are decoupled by flexible spacers.<sup>1-3</sup> In such side chain liquid crystalline polymers (SLCPs), siloxane polymer is often used as a backbone, because of its low glass transition temperature and great flexibility. The polysiloxanes with different mesogenic side-chain units exhibit variety of liquid crystalline textures under the various temperatures and external mechanical and electric fields.<sup>4-6</sup> In the case of the polysiloxane containing cyanobiphenyl mesogenic side group, smectic phase takes place in the temperature range between its glass transition temperature ( $T_g$ ) and clearing temperature ( $T_i$ ). On the cooling process of the polymer from the isotropic melt, batonnet texture was first observed and the batonnets coalesced rapidly into focal-conic fan textures.<sup>7</sup> Such structural changes *via* the phase transitions are frequently observed in other SLCPs. However, little is known about growth of the liquid crystalline texture in the isothermal state.

In this work the growth of liquid crystal for the polysiloxane having 6-(4-cyanobiphenyl-4'-

oxy)-1-hexene pendant in the isothermal state was investigated, and the rates of liquid crystallization were successfully determined in varied liquid crystallization temperatures.

EXPERIMENTAL

Poly[[6-(4'-Cyanobiphenyl-4-oxy)hexyl]-methylsiloxane] (PCS) was prepared by hydrosilylation reaction of poly(methylhydrosiloxane) with 3-(4'-cyanobiphenyl-4-oxy)-1-hexene in the presence of platinum complex as a catalyst. Poly(methylhydrosiloxane) (degree of polymerization  $DP=174$  and  $M_w/M_n=2.7$ ) was offered by Chisso Co., Ltd. The thermal property of the PCS was examined using a differential scanning calorimeter (DSC200: Seiko I & E Ltd.) under an  $N_2$  purge; heating and cooling rates were  $20^\circ C \text{ min}^{-1}$  and  $10^\circ C \text{ min}^{-1}$ , respectively. Structures of the PCS characterized using an X-ray diffraction (XRD) apparatus (Rigaku Denki Co., Ltd.) and a polarizing optical microscope (POM) equipped with a hot stage (TH-600RMS: Linkam Co.). Growth of liquid crystalline textures was observed under the POM with videocassette recorder system.

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## RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of PCS. A glass transition and a comparatively sharp endothermic peak were obtained at 13.4°C and 160.8°C, respectively, on the heating process, and an exothermic peak at 154.0°C on the cooling process indicating temperature hysteresis. The endothermic peak was assigned to be  $T_i$ , as dark field was observed under the POM with crossed polarizers above the temperature of the endothermic peak. After cooling from the isotropic melt, well-defined focal-conic fan texture formed. The XRD pattern of an oriented sample indicated a diffuse meridional reflection at a wide-angle area, and periodic equatorial arcs at a small-angle area, characteristic of smectic A( $S_A$ ) phase. Gemmell *et al.* reported that the polymer with different degree of polymerization ( $DP = 50$ ) indicated  $S_A$  phase between  $T_g$  (13.5°C) and  $T_i$  (165.5°C).<sup>8</sup>

In the cooling process from the isotropic phase of PCS, thin needle-like textures first appeared in high temperature range close to  $T_i$ . On further cooling, the needles developed rapidly to batonnets, and then the batonnets coalesced into the well-defined focal-conic fan texture. On the other hand, when PCS was heated up to the isotropic state (220°C) followed by quenching to 159°C which was close to  $T_i$ , the needle-like texture was kept at this temperature, as shown in Figure 2; that is, no textural change to the focal-conic fan texture was observed. In the isothermal state, the needle-like texture grew preferentially in the direction of the long axis of the needle with increasing time. Little change occurred in their width (1.8–2.5  $\mu\text{m}$ ) throughout the experimental period. Thus, the growth mode is similar to the lineal growth of crystals.

On cooling from above liquid crystallization temperature (159°C), the needle-like texture changed into the batonnets and fan-like textures. Finally, the growth of the needle-like texture is a transient phenomenon during the process of the liquid crystal formation. The

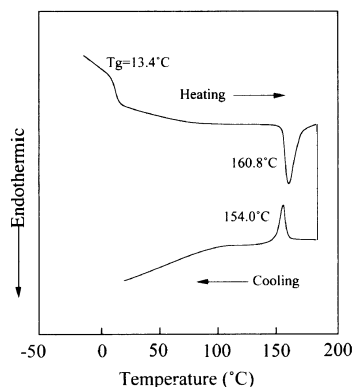


Figure 1. DSC traces of PCS for heating and cooling processes.

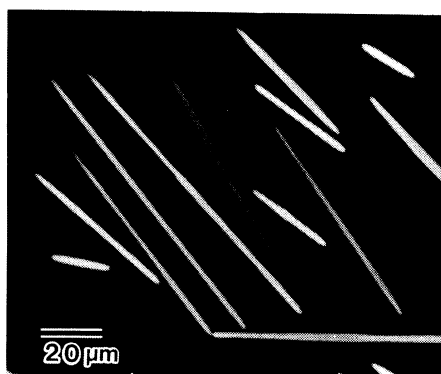
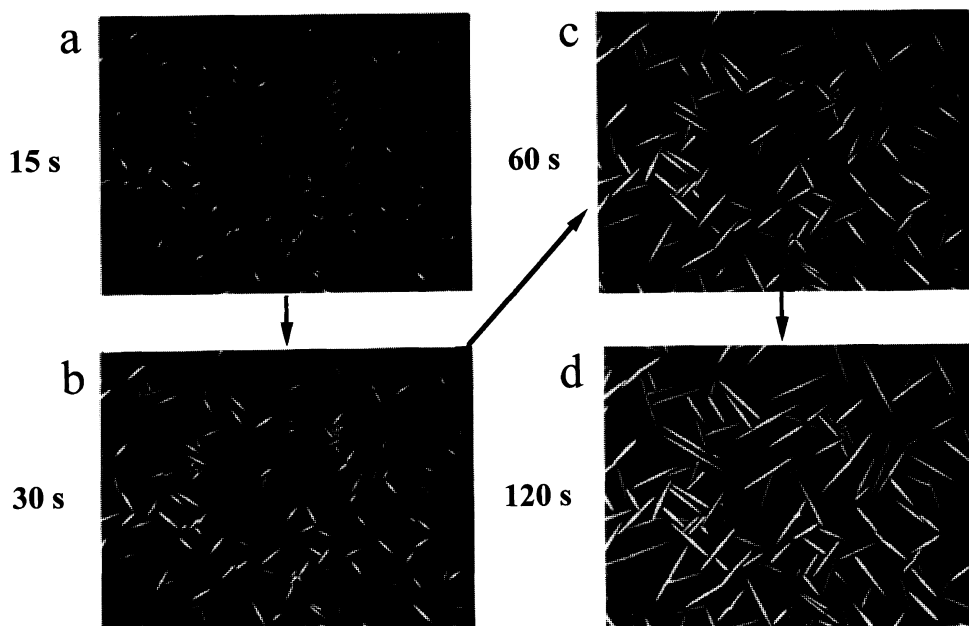


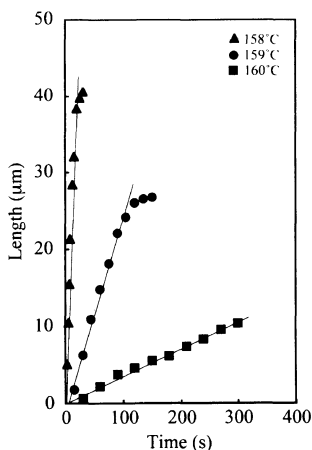
Figure 2. Optical micrograph of PCS taken at 159°C (crossed polarizers).

growth of the liquid crystalline needle-like texture was observed in the isothermal state using the POM equipped with VCR system. Figure 3 shows the growth of the texture at 159°C after heating up to the isotropic melt (220°C); (a) indicates the texture after 15 s; (b) after 30 s; (c) after 60 s; (d) after 120 s. The change in the length of the needle-like textures could be measured in the growth process at 158, 159, and 160°C. It was too fast to observe the growth of the texture at 157°C. Below 156°C, moreover, the needle-like texture changed rapidly into the batonnets or fan-like textures.

The changes in the length of needle-like textures with increasing time was shown in Figure 4, where the half values of the length



**Figure 3.** Polarizing optical micrographs of PCS in the liquid crystallization process observed at 159°C (crossed polarizers).



**Figure 4.** Changes in length of needle-like textures of PCS against time at various temperatures. ▲, 158°C; ●, 159°C; ■, 160°C.

were plotted against time because of the lineal growth. The values increase linearly with increasing time in the initial stage in each case, as shown in Figure 4. Accordingly, the rates of growth in the liquid crystallization process were successfully determined from the slopes of the straight line in the initial stage. The

growth rates were  $163 \times 10^{-2}$ ,  $23.5 \times 10^{-2}$ , and  $3.49 \times 10^{-2} \mu\text{m min}^{-1}$  at 158, 159, and 160°C, respectively. The rates of the liquid crystallization increased extremely with decreasing liquid crystallization temperature. The growth mechanism of the needle-like texture and the packing mode of the cyanobiphenyl mesogens in the texture are now studied in our laboratory and will be reported in near future.

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