

Effects of the Degree of Substitution on the Properties and Structures of Side Chain Liquid Crystalline Polysiloxanes

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ABSTRACT: Poly[6-(4-cyanobiphenyl-4'-oxy)-hexylmethylsiloxanes] (PCS-n) with various degrees of substitution (DS) were prepared, and the effects of the degree of substitution on the phase transition, structures, and liquid crystallization of PCS-n were investigated. PCS-n showed S_{Ad} in the temperature range from glass transition temperature (T_g) to clearing temperature (T_i) in spite of various DS. T_g and T_i increased linearly with DS, and the temperature range of S_A phase between T_g and T_i expanded with DS. The layer spacing d_L of the S_A structure decreased with increasing DS, since the non-mesogenic flexible backbones were squeezed between smectic layers. d_L of the sample with lower DS highly decreased with increasing temperature, due to entropy relaxation of backbones between the S_A layers. DS remarkably influenced the liquid crystallization of PCS-n. PCS-n with higher DS exhibited faster growth rates of liquid-crystalline textures compared with lower DS.

KEY WORDS Side-Chain Liquid-Crystalline Polymer / Degree of Substitution / Smectic A / Polysiloxane / Liquid Crystallization /

The synthesis and characterization of liquid crystalline polymers have become of interest in recent years, because of potential uses in electrooptical devices.¹⁻⁶ Polysiloxanes have several advantages over other types of polymers due to lower glass transition temperatures and great flexibility of the backbones.⁵

Generally, the phase transition behavior, liquid crystalline textures, and stability of mesophase depend on chemical structures of mesogenic groups, length of flexible spacer group, and mesogenic terminal groups. Many polysiloxanes with different mesogenic side chain units have been synthesized and the influence of molecular weight, nature of mesogenic group, length of spacer group, and composition of copolymers with different mesogens on the liquid crystalline property have been investigated.^{1,2}

The amount of substitution of mesogenic side chain influences the phase transition and liquid crystalline properties.⁷⁻¹² Percec *et al.*^{8,9} investigated the liquid-crystalline properties of poly(methylsiloxane-co-dimethyl-siloxane)s containing 2-[4-(2(*S*)-methyl-1-butoxy)-phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups. The phase transition temperatures of the copolymers increased with composition of mesogenic structural unit.⁹ Diele *et al.*¹¹ explored the dependence of amount of substitution on liquid crystalline structure by means of X-ray diffraction analysis. They suggest that the smectic monolayer thickness remarkably depend on the amount of substitution and a flexible main chain was forced to take part in the layer formation, due to the domaining interaction of the mesogenic groups. Percec *et al.*¹⁰ reported that the thickness of the smectic layer of above copolymer increased with decrease of structural units containing mesogenic units. Thus, the flexible backbone is squeezed between smectic layers in the side-chain liquid-crystalline polysiloxanes.¹³

We investigated the growth of liquid crystal for poly-

siloxane having 6-(4-cyanobiphenyl-4'-oxy)-1-hexene pendant in the isothermal state, and the rates of liquid-crystallization were determined at various liquid-crystallization temperatures.¹⁴ The growth of the liquid crystal during the liquid-crystallization of the polysiloxane is possible to be influenced by the concentration of the mesogenic structural unit. Little is known about the influence of DS on the liquid-crystallization of polysiloxanes. In the present work, we prepared side-chain liquid-crystalline polysiloxanes with various DS of 4-cyano-4'-hydroxybiphenyl mesogenic group and investigated the influence of DS on the phase transition, structures, and liquid-crystallization on the basis of thermal analysis, optical microscope, and X-ray diffraction method.

EXPERIMENTAL

Synthesis of Liquid Crystalline Polysiloxanes

The mesogenic compound 6-(4-cyanobiphenyl-4'-oxy)-1-hexene was prepared by the condensation of 4'-hydroxy-4-cyanobiphenyl with 6-bromo-1-hexene. Liquid crystalline polysiloxanes with various DS were prepared by hydrosilylation between poly(methylsiloxane) and 6-(4-cyanobiphenyl-4'-oxy)-1-hexene in the presence of platinum catalyst. Poly(methylsiloxane) having $\bar{M}_n = 3,800$, $\bar{M}_w = 10,500$, $\bar{M}_w/\bar{M}_n = 2.7$ was supplied by Chisso Co. Synthesized polymers, poly[6-(4-cyanobiphenyl-4'-oxy)-hexylmethylsiloxane] (PCS), were purified by repeated precipitation from methylene chloride solution with excess methanol, and then were isolated by the freeze-dry treatment.

Polymers were defined as corresponding polysiloxanes containing the 6(4-cyanobiphenyl-4'-oxy)hexyl group as a side chain mesogenic unit, by IR spectroscopy, ¹H NMR, and ¹³C NMR. The IR spectra exhibited characteristic the C≡N bond stretching at 2220 cm⁻¹, the aromatic C=C bond stretching at 1604 and 1495 cm⁻¹, and C-O-C bond stretching at 1253 and 1020 cm⁻¹. The

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^1H NMR (JEOL EX 270 (270 MHz)) spectrum of the polymer consists of multiplets for the aromatic protons ($\delta=6.8\text{--}7.7$ ppm, 8H), a singlet for the silyl hydride ($\delta=4.75$ ppm), several broad peaks for methylene protons adjacent to ether group ($\delta=3.9$ ppm, 2H), to Si atom ($\delta=0.6$ ppm, 2H) and other methylene protons ($\delta=1.4$ ppm, 6H), and methyl protons ($\delta=0.1$ ppm, 3H), respectively. The most conclusive spectra evidence for the proposed polymer structures was provided by ^{13}C NMR (JEOL EX 270). The calculated chemical shifts are all within 3 ppm of observed values. No duplication peaks was found, clearly indicating formation of the expected polymers.

DS was obtained by the ratio of the integration of silyl hydride of polysiloxane to aromatic protons of the mesogen unit. DS of polymers were 34, 43, 59, 66, 70, and 83%. These polymer samples were coded as PCS-n, where the number n denotes the DS.

Thermal Analysis

Differential scanning calorimetry (DSC) of the samples was performed by DSC 200 (Seiko I & E Ltd.) under an N_2 purge; heating and cooling rates were $20^\circ\text{C min}^{-1}$ and $10^\circ\text{C min}^{-1}$, respectively.

Polarizing Optical Microscopy

Changes in optical textures of the samples during heating and cooling processes were examined using the polarizing optical microscope (POM) equipped with a hot stage (Linkam Co., TH-600RMS) under an N_2 purge. Growth of liquid crystalline textures was observed under POM with a videocassette recorder system.¹⁴

X-Ray Diffraction Measurements

X-Ray diffraction experiments were carried out by a RAD-rA diffractometer (Rigaku Denki Co., Ltd.) equipped with a heating device with temperature accuracy of $\pm 0.2^\circ\text{C}$. Nickel-filtered Cu-K_α radiation was employed. Changes in the X-ray scattering (XRS) traces during heating and cooling processes were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator and $1 \times 1^\circ$ receiving slit. Diffractometry was performed in transmission. XRS traces were obtained by a step-scanning method: step width and fixed time were programmed for steps of 0.05 deg every 4 s. When d -spacings of the reflections were measured, the step and fixed time were programmed for an angle of 0.01 deg and a 10 s step, respectively. The XRS photographs were taken by a flat Laue camera with a 0.5 mm diameter pin-hole collimator.

RESULTS AND DISCUSSION

Influence of the Degree of Substitution on Liquid Crystalline Properties

DSC traces of the liquid crystalline polysiloxanes with different DS are illustrated in Figure 1, which correspond to the 2nd-heating process. Marked glass transition (T_g) and single endothermic peak were observed on the DSC trace of each sample. The endothermic peak of each sample was assigned to be a clearing temperature (T_i), as a dark field appeared above the endothermic peak under POM. After cooling from the isotropic melt,

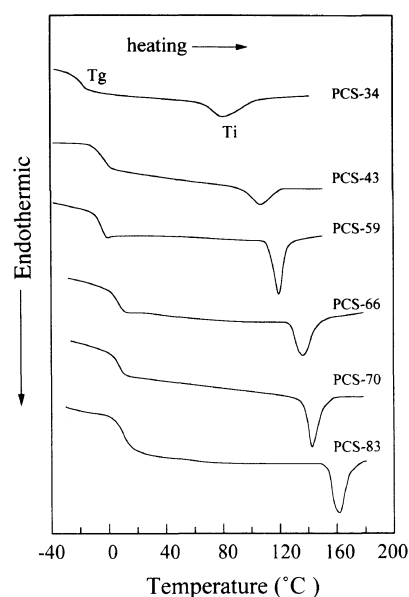


Figure 1. DSC traces of PCS-n during 2nd-heating process.

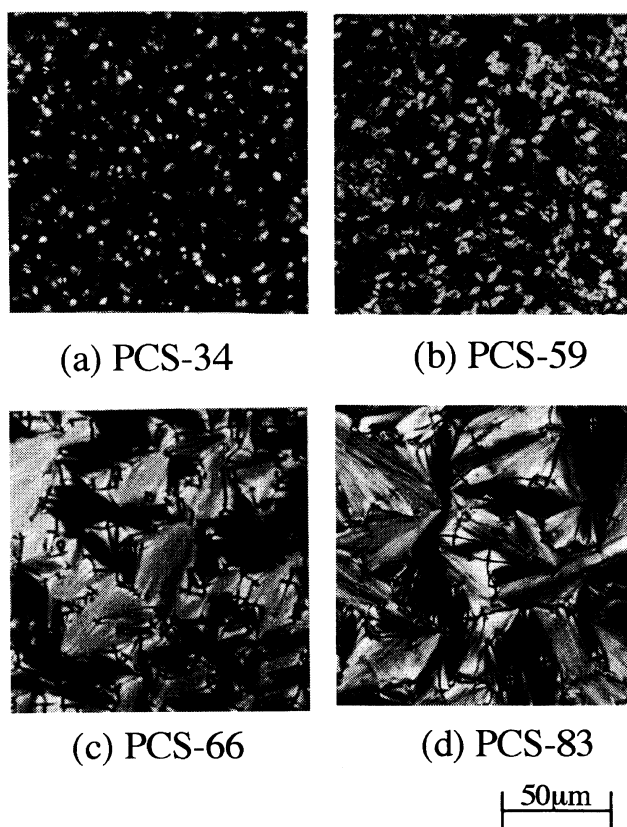
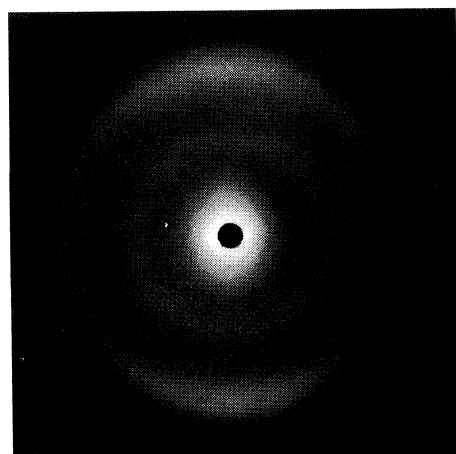


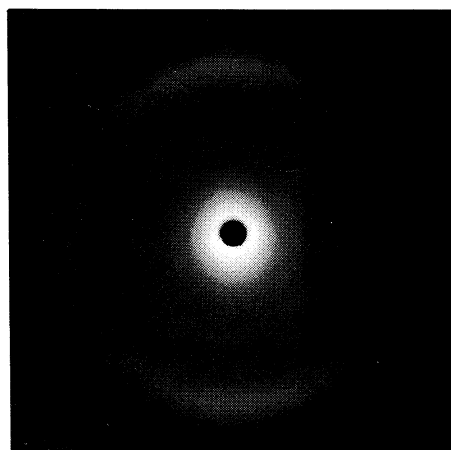
Figure 2. Polarizing Optical micrographs of PCS-34 (a), PCS-59 (b), PCS-66 (c), and PCS-83 (d) taken at room temperature.

well-defined focal-conic fan texture formed in the samples with higher DS, as shown in Figure 2. In samples with lower DS, optical textures were very small; micro-grain liquid-crystalline textures formed.

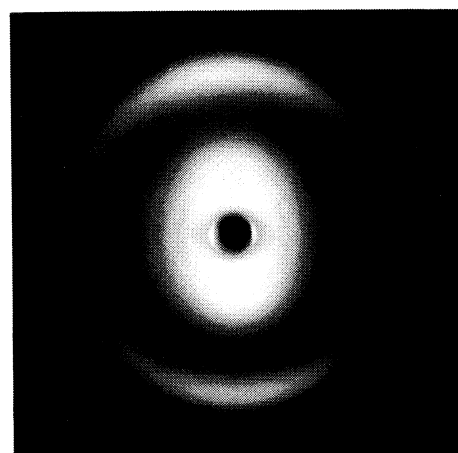
As shown in Figure 3, the XRS patterns of oriented samples for PCS-34, PCS-59, and PCS-83 indicate a diffuse meridional reflection at a wide-angle area, and periodic equatorial arcs at a small-angle area, characteristic of smectic A (S_A) phase. Other samples with different DS showed similar XRS patterns. Thus, the PCS-n exhibited S_A phase below T_i whatever DS was. The values of the layer spacing of S_A determined from the reflection



(a) PCS-34



(b) PCS-59



(c) PCS-83

Figure 3. XRD patterns of oriented samples for PCS-34 (a), PCS-59 (b), and PCS-83 (c) taken at room temperature.

at the small-angle area are approximately 1.6–1.9 times those of the side chain (1.94 nm). This shows the formation of an interdigitated bilayer structure (S_{Ad})¹⁵ because of interactions of strong dipoles induced in the mesogenic groups by CN substituents.^{16,17}

Fiber axis

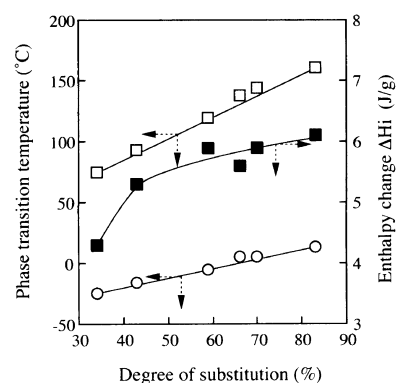


Figure 4. Changes in phase transition temperature (T_g , T_i) and enthalpy change (ΔH_m) of PCS-*n* against degree of substitution. \circ , T_g ; \square , T_i ; \blacksquare , ΔH_i .

The phase transition temperatures of these samples are plotted against DS in Figure 4. Temperatures of T_g and T_i increased linearly with DS. The tendency of phase transition temperature is similar to the results of the copolysiloxanes containing 2-[4-(2(*S*)-methyl-1-butoxy)-phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups.⁹ The slope of the line for T_i was larger than that for T_g . Thus, the temperature range of S_A phase between T_g and T_i expanded with DS; the stability of S_A phase was enhanced by increase in DS. Generally, side groups have profound effect on T_g ; large and bulky side groups cause great stiffening. The increase in T_g comes from steric hindrance by increase in the large and bulky mesogenic side chains. In other words, lowering of T_g with decreasing substitution is due to diluting the mesogenic groups along the backbone with non-mesogenic segments.¹⁸ The enthalpy change (ΔH_i) estimated from the endothermic peak increased with DS, as shown in Figure 4. Thus, S_A phase of PCS-*n* may possibly be thermodynamically stable with increasing DS.

Smectic Layer Structures of PCS-*n*

XRS intensity curves were measured to investigate the order of the layer structures. XRS traces are illustrated in Figure 5. The periodic reflection associated with layer structure of S_{Ad} was observed in the small angle area in each sample. High order reflections appeared in the samples with higher DS. 2nd and 3rd order reflections could be obtained clearly in the case of PCS-83; d -spacings of these three Bragg maxima (d_1 , d_2 , and d_3) were determined as 3.22 nm, 1.63 nm, and 1.08 nm, respectively. The higher order reflections disappeared in PCS-43 and PCS-34. Accordingly the order of S_A layer structure was governed by DS. These findings show that the thermal stability of S_A phase is enhanced by increase in DS.

The diffuse arc set lied on the meridian with a spacing of approximately 0.44 nm, associated with intermolecular spacing (d_m); that is, the distance between successive mesogenic side groups. d_m almost remained unchanged with increasing DS, as shown in Figure 6. Thus, the interlayer packing mode of S_{Ad} for PCS-*n* is independent of DS. One reason for this is that the S_{Ad} phase is formed by interactions of strong dipoles induced in the mesogenic groups by CN substituents. The layer spacing (d_L) determined from the low angle reflection (d_1) decreased with increasing DS, as shown in Figure 6. The decrease in d_L

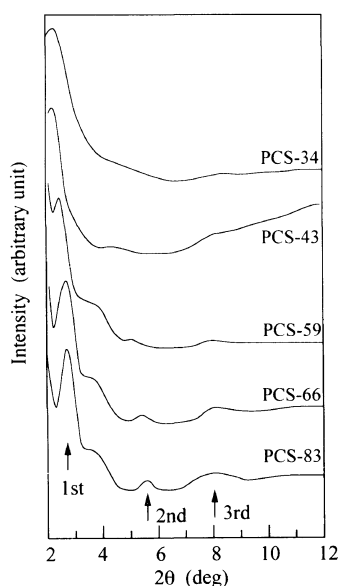


Figure 5. Changes in XRD traces of PCS-n with substitution.

is ascribed to decrease in backbones with non-mesogenic segments between smectic layers. In other words, the non-mesogenic flexible backbone is forced to take part in the layer formation of PCS-n. This is similar to copolysiloxanes containing 2-[4-(2(*S*)-methyl-1-butoxy)-phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups.⁹ Chain packing models were proposed in side-chain liquid-liquid crystalline polysiloxanes based on the results of X-ray diffraction studies^{9,11,13} and other side-chain liquid-crystalline polymers.¹⁹ Thus, it was confirmed that non-mesogenic backbones are confined between smectic layers in the case of PCS-n.

Many non-mesogenic flexible backbones between the smectic layers may influence the order of smectic layer structure and thermodynamical stability. The disappearance of 2nd or 3rd order reflections in the low angle area presumably is due to the flexible backbones confined between the layers.

Temperature Dependence of Layer Spacings

Flexible backbones between the smectic layer may influence the structural change of the smectic layer at elevated temperatures because of large chain mobility. In this section the influence of DS on the smectic layer structure of PCS-n during the heating process was investigated. d_L of PCS-n was measured during the heating process using the XRS method. Changes in d_L of PCS-43, PCS-59, PCS-66, and PCS-83 are plotted as a function of temperature in Figure 7. d_L decreased with temperature, whereas the d_L of PCS-66 and PCS-83 slightly increased with increasing temperature in lower temperature range, and started to decrease at approximately 40 and 55°C respectively. Increase in d_L is considered due to thermal expansion of the smectic layers. The onset of temperature decrease in d_L tends to lower with decreasing DS. In the cases of PCS-43 and PCS-59, increase in d_L is presumably observed at lower temperature range close to T_g 's. d_m of each sample increased monotonously with temperature by thermal expansion, so that little change was observed in the interlayer packing mode at the temperature range. These findings suggest that decrease in d_L with increasing temperature is ascribable to the con-

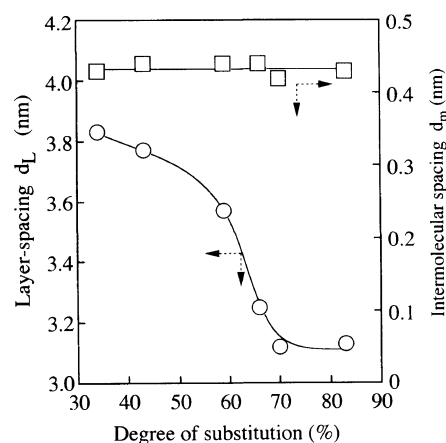


Figure 6. Changes in layer-spacing (d_L) and intermolecular spacing (d_m) of PCS-n against degree of substitution. \circ , d_L ; \square , d_m .

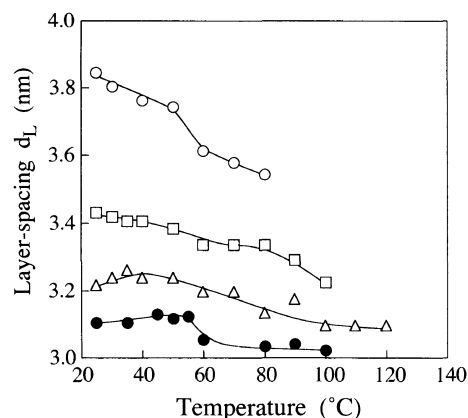


Figure 7. Changes in layer-spacing d_L of PCS against temperature. \circ , PCS-43; \square , PCS-59; \triangle , PCS-66; \bullet , PCS-83.

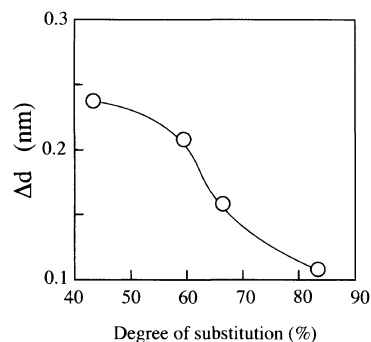


Figure 8. Changes in Δd of PCS against degree of substitution. $\Delta d_m = d_{Lmax} - d_{Lmin}$ in Figure 7.

formational change of the flexible spacers and backbones between the smectic layers. Change in d_L was reversible in repeated heating and cooling.

The difference (Δd_L) between maxima and minima of d_L in Figure 7 is plotted against DS in Figure 8. Δd_L decreased with DS. The variation in the d_L due to the conformational change of the flexible spacer is considered the same in each sample, as the length of flexible spacer is the same in any sample. From this it follows that change in Δd_L with DS is governed by the number of non-mesogenic backbones. This can be understood by the following reason. The backbones might have an internal stress by the formation of S_A , because of the S_A layer packing with overlapping antiparallel side groups with strong dipoles induced by CN substituents. On heating, the internal stress of the backbones is relaxed,

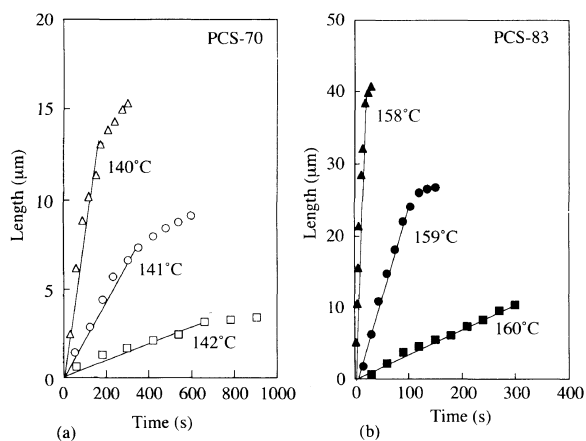


Figure 9. Changes in length of needle-like textures of PCS-70 (a) and PCS-83 (b) against time at various temperatures.

and simultaneously, d_L decrease in comparatively high temperature range. Therefore, the decrease in d_L with increasing temperature results from the entropy relaxation of backbones between the S_A layers. On cooling, d_L increased reversibly by reformation of S_A structure.

Influence of Degree of Substitution on Liquid Crystallization of PCS-n

In the case of PCS, thin needle-like textures with 1.8–2.5 μm width first appeared at high temperature range close to T_i on cooling from the isotropic phase. On further cooling, the needles developed rapidly to batonnets, and then the batonnets coalesced into the well-defined focal-conic fan texture. The needle-like texture grew preferentially in the direction of the long axis of the needle with time in the isothermal state close to T_i . The rates of growth in the liquid crystallization process of PCS-83 sample were determined in the previous paper.¹⁴ The growth rates were 163×10^{-2} , 23.5×10^{-2} , and $3.49 \times 10^{-2} \mu\text{m min}^{-1}$ at 158, 159, and 160°C, respectively.¹⁴

The growth of the liquid crystal is possibly influenced by the concentration of the mesogenic structural unit. The growth of needle-like texture also took place at the temperatures close to T_i (144°C) in PCS-70. In other samples with lower DS, no growth of needle-like texture was observed. Needle-like textures hardly grew in samples with lower DS, when the liquid-crystallization time was prolonged. Thus the layer structures of smectic A in the samples with lower DS exhibited comparatively less order and were thermodynamically unstable because of increased non-mesogenic flexible backbone. The backbones were relaxed at the elevated temperatures as described above.

Figure 9 shows changes in the length of needle-like textures of PCS-70 and PCS-83 with increasing liquid crystallization time. The growth rates for PCS-70 were 6.65×10^{-2} , 2.00×10^{-2} , and $0.38 \times 10^{-2} \mu\text{m min}^{-1}$ at 140, 141, and 142°C, respectively. As the rates of the liquid-crystallization increased with decreasing liquid-crystallization temperature, it was impossible to measure the growth rate at lower temperature. The growth rates of PCS-83 were faster than those of PCS-70. The difference of growth rates between them is due to the concentration of mesogenic side groups, and mobility of

backbones and self-diffusion of segments at each liquid-crystallization temperature. Thus the liquid-crystallization of PCS-n remarkably depends on DS.

CONCLUSION

The influence of the degree of substitution on the phase transition, structures and liquid-crystallization of the side chain liquid crystalline polysiloxane containing 4-cyano-4'-hydroxybiphenyl mesogenic group were investigated, and the following findings were obtained.

PCS-n showed S_{Ad} in the temperature range from T_g to T_i in spite of various DS. T_g and T_i increased linearly with DS, and the temperature range of S_A phase between T_g and T_i expanded with DS. The layer spacing d_L of the S_A structure decreased with increasing DS, since the non-mesogenic flexible backbones were squeezed between the smectic layers. d_L decreased with increasing temperature, and Δd_L increased with DS. The decrease in d_L with increasing temperature may thus be due to entropy relaxation of backbones between S_A layers.

Thin needle-like textures first appeared at high temperature range close to T_i on cooling from the isotropic phase in PCS-70 and PCS-83 with comparatively high DS. They grew preferentially in the direction of the long axis. The growth rates of PCS-83 were faster than those of PCS-70. In other samples with lower DS, no growth of needle-like texture was observed. The liquid-crystallization of PCS-n remarkably depended on DS. This results from the concentration of mesogenic side groups, and mobility of the backbones and self-diffusion of the segments.

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