

An X-ray Investigation of Terminally Carboxyl Oligo (Ethylene Oxide) Monomethyl Ethers-Substituted Side-Chain Liquid Crystalline Polysiloxanes

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SYNOPSIS

4'-[Oligo(ethylene oxide) monomethyl ether carbonyl] biphenyl-4-yl 4-(alkenyloxy) benzoate side-chain liquid crystalline (LC) polysiloxane polymers with various lengths of a terminal group and spacer were prepared. The mesophase structure and transition temperature of those polymers were investigated using methods of X-ray diffraction, polarized optical microscopy, and differential scanning calorimetry, respectively. The mesophases of the polymers were smectic ones. The layer spacing d_1 s and the side-chain distance of d_2 s obtained were around 29–34 Å and 4.4–4.6 Å, respectively. d_1 s were much shorter than twice the lengths of the side chains presumed in the fully extended conformation. Hence, the two-layer end-on packings or the packing with overlapping of tails model seemed not able to interpret the mesophase structure of those polymers studied. The effects of temperature on the mesophase microstructure of 4'-[ethylene oxide monomethyl ether carbonyl] biphenyl-4-yl 4-(pentyloxy)benzoate side-chain LC polysiloxane polymer were also studied using the X-ray diffraction method. It was found that both d_1 and d_2 of the polymer in the mesophase temperature range became shorter with decreasing temperature and the long- and short-range order could remain, to some extent, at temperatures above the isotropic transition temperature and temperatures below the melting temperature. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Side-chain liquid crystalline (LC) polymers have been extensively studied during the last decade.^{1–4} Thermotropic side-chain LC polymers, owing to their particular properties, have been paid attention to as potential advanced materials for speciality applications.^{5–15} Syntheses, structure–property relations, and applications were concisely reviewed by Varshney¹⁶ and Gray et al.¹⁷ Owing to their high viscosity, broad molecular weight distribution, and polycrystalline and amorphous material coexistence, the LC nature of the thermotropic polymer was usually established through a combination of the following methods¹⁸: (a) differential scanning calorimetry (DSC), (b) optical pattern or texture ob-

servations, (c) miscibility studies, (d) X-ray investigations, and (e) the possibility of inducing significant molecular orientations by magnetic or electric fields. Among them, the X-ray diffraction method is powerful for the qualitative determination for the crystalline and LC microstructures.

Gemmell et al.^{19,20} studied the side-chain acrylate and methacrylate LC polymers containing the 4'-alkylbiphenyl-4-yl and 4'-CN-biphenyl-4-yl substituents as a side group by X-ray techniques. They reported that increasing the anisotropy in the biphenyl side chain by suitable terminal substituents greatly increased the propensity for smectic-type ordering of the side chain. Meanwhile, the smectic-like side-chain ordering is affected by the methyl substituent on the main chain and the polarity of the terminal group. Sagane and Lens²¹ reported that poly(vinyl ethers) with side-chain alkoxy–biphenyl and CN–biphenyl groups are LC. They demonstrated that the types of mesophase texture and me-

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sophase microstructure are related to the polarity and lengths of the terminal substituents.

In this study, 4'-[oligo(ethylene oxide) mono-methyl ether carbonyl] biphenyl-4-yl 4-(alkenyl-oxo) benzoate side-chain LC polysiloxane polymers were prepared. The effects of terminal length, spacer length, and methoxy substituted on the mesogenic core on the mesophase texture and thermal properties were studied using the methods of X-ray diffraction, polarized optical microscopy, and DSC.

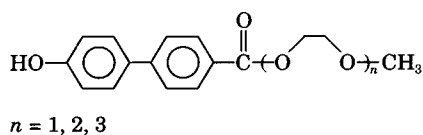
EXPERIMENTAL

Materials

p-Hydroxybenzoic acid, 2-methoxy ethanol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, allyl-bromide, and 5-bromo-1-pentene (from Tokyo Chemical Industry Co.) were used as received. Polysiloxanes (with $\overline{DP} = 35$) and hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) (from E. Merck Co.) were used as received. Toluene, used in the hydrosilation reaction, was first refluxed over sodium and then distilled under a nitrogen stream. 4-(4-Hydroxyphenyl)benzoic acid was prepared according to the four-step procedure of Gray and co-workers.²²

Monomer Synthesis

The monomers listed in Table I were synthesized from 4-(alkenyl-oxo)benzoyl chloride by esterification with the appropriate substituted biphenylcarboxylate ester:



An example of ME2S3 is presented as follows: 0.021 mol 4-allyloxybenzoic acid was refluxed with an excess of thionyl chloride containing a drop of dimethylformamide (DMF) in a 50 cc round flask equipped with a HCl absorber until the solution became clear (ca. 3 h). The excess thionyl chloride in it was removed by a vacuum rotary evaporator to obtain yellow viscous 4-allyloxybenzoyl chloride. The acid chloride was dissolved in 5 mL CH_2Cl_2 and slowly added to a solution of 0.019 mol biphenyl carboxylate diethylene glycol monomethyl ether containing an excess mol ratio dry triethylamine in 50 mL of CH_2Cl_2 in an ice-water bath to control the

reaction rate. The reaction was allowed to proceed for 4 h at low temperature and then raised to 45°C for 0.5 h. CH_2Cl_2 and triethylamine in the reaction solution were removed by the rotary evaporator under reduced pressure. The residue material was dissolved in 100 mL CH_2Cl_2 . It was washed with 100 mL of saturated sodium bicarbonate solution twice, then washed with 6N HCl solution and with water twice, and then dried over $MgSO_4$. The $MgSO_4$ was filtered off, and the filtrate was concentrated on a rotary evaporator. The crude product was purified through a silica gel-packed column. The mobile phase was composed of CH_2Cl_2 , *n*-hexane, and methanol solvent. The product was further recrystallized with methanol to obtain a pure product 6.88 g (yield 76%), mp 91°C. The composition of the solution used was dependent on the monomers to be purified—ME1S3: CH_2Cl_2/n -hexane/methanol = 35/15/1 (v/v/v); ME2S3: 35/15/2; ME3S3: 35/15/3; ME1S5 35/15/1; ME1S5L1 35/15/1. The yield and melting point of the other monomers are summarized as follows:

ME1S3 73%, 107°C; ME3S3 65%, 73°C;

ME1S5 67%, 91°C; ME1S5L1 72%, 102°C

Polymer Synthesis

One gram ME2S3 and 0.136 g polymethylhydrosiloxane were dissolved in 10 mL of sodium-dried toluene. Twenty microliters of $5.0 \times 10^{-3} M H_2PtCl_6$ isopropanol solution was added to the above solution using a glass capillary tube. The temperature was kept at 80°C under a nitrogen stream. The reaction was continued until the IR absorption peak of Si—H at 2165 cm^{-1} disappeared.

The product was subsequently purified through methanol precipitation and CH_2Cl_2 redissolution several times. Then, it was dried *in vacuo* at room temperature.

Thermal Transitions and Mesophase Textures in Monomers and Polymers

The thermal transitions of monomers and polymers were studied by a DuPont 910 differential scanning calorimetry (DSC). The transition temperatures and thermal parameters were obtained using a DuPont 9900 computer system. The mesophase textures were observed by using an Olympus BH-2 polarized optical microscopy with a LINKAM THMS 600 hot stage and a TMS 91 central processor.

TABLE I Thermal Transition Temperatures (°C) and Thermodynamic Parameters (J/g) for Monomers

Monomer	<i>m</i>	<i>R</i> ₁	<i>R</i> ₂	Heating	Cooling
ME1S3	1	H	(C ₂ H ₄ O)CH ₃	K107S _A 151(1.62)N 180(0.63)i	i 173(0.56)N 144(1.53)S _A 79 K
ME2S3	1	H	(C ₂ H ₄ O) ₂ CH ₃	K91S _A 146(2.57)N 157(0.51)i	i 155(0.51)N 143(2.33)S _A 65 K
ME3S3	1	H	(C ₂ H ₄ O) ₃ CH ₃	K73S _A 125(7.80)N 128(—)i ^a	i 124(—)N 119(6.72)S _A 48 K
ME1S5	3	H	(C ₂ H ₄ O)CH ₃	K91S _B 171(4.37)N 181(0.73)i	i 177(0.64)N 167(4.29)S _B 64 K
ME1S5L1	3	OCH ₃	(C ₂ H ₄ O)CH ₃	K102i	i 75 K

K, crystalline; S_A, smectic A; S_B, smectic B; N, nematic.

^a Overlapped transition $\Delta H = \Delta H(S_A) + \Delta H(N)$.

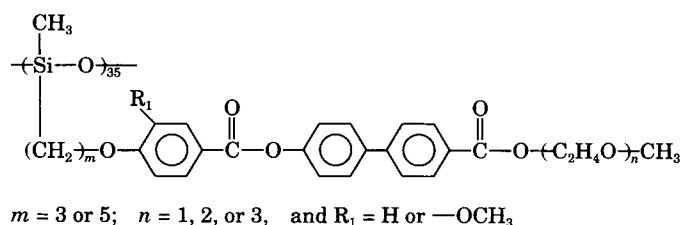
X-ray Diffraction Studies

X-ray studies were performed with a Siemens Diffraktometer D5000 apparatus (40 kV, 30 mA). Nickel-filtered CuK α radiation was used as an incident X-ray beam. The intensity of the scattered X-ray from the sample was measured by a scintillation counter. The diffractometer was scanned over

a range of $2^\circ < 2\theta < 30^\circ$ with a scanning speed of $0.05^\circ/0.1$ s.

RESULTS AND DISCUSSION

The side-chain LC polysiloxane polymers (SLCP) studied are represented as follows:



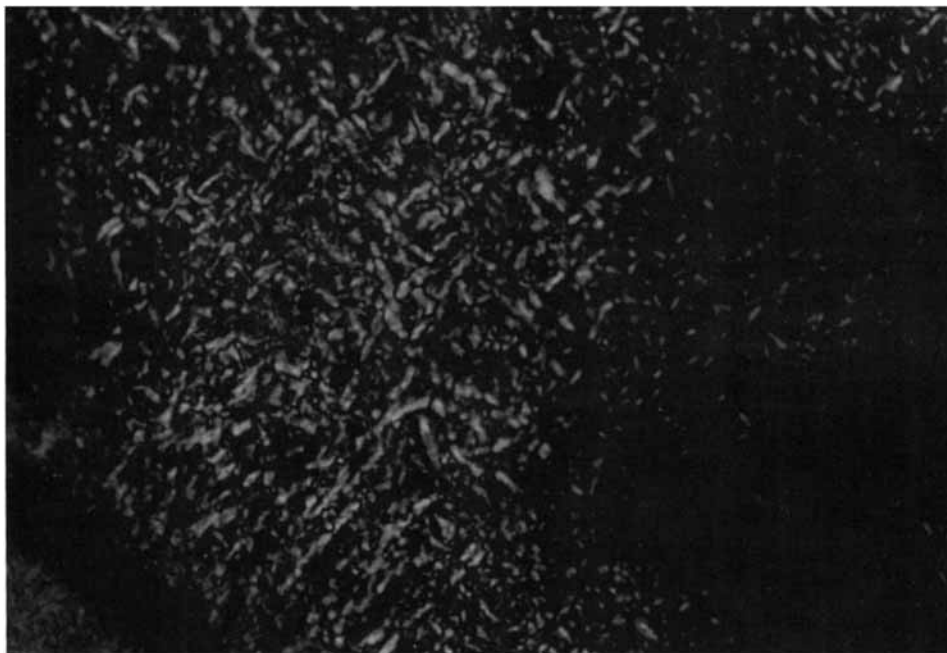
Terminal length, spacer length, and lateral substituent on the mesogenic unit were taken as variables to study the mesomorphic properties of the SLCPs. Tables I and II summarize the mesophase types, mesophase transition temperatures, and thermodynamic parameters for the monomers and the

polymers, respectively. Figures 1 and 2 illustrate the mesophase optical textures and the DSC thermograms for the monomer ME1S5 and the polymer PE1S5. All the monomers, except for ME1S5L1, which has a lateral methoxy substituent on the mesogenic core, showed both smectic and nematic

Table II Thermal Transition Temperatures (°C) and Thermodynamic Parameters (J/g) for Polymers

Polymer	Heating	Cooling
PE1S3	g 29 S 251 (2.29) i	i 248 (1.80) S 24 g
PE2S3	g 22 S 187 (2.21) i	i 184 (2.30) S 21 g
PE3S3	g 12 S 136 (—) i	i 130 (1.65) S 8 g
PE1S5	g 24 K 89 S 258 (2.68) i	i 254 (3.07) S ₁ 126 (0.51) S ₂ 79 K 22 g
PE1S5L1	g 24 K 69 S 170 (1.06) i	i 163 (1.03) S 59 K 21 g

S, S₁, S₂ = smectic phases.



(a)



(b)

Figure 1 Optical polarized micrograph of polymer PE1S5 and monomer ME1S5: (a) smectic texture for polymer PE1S5 at 245°C; (b) smectic B texture for monomer ME1S5 at 145°C.

phases. However, all the SLCPs exhibited only fine-grain smectic textures in the polarized optical microscopy. Taking ME1S3 or PE1S3 as a base for comparison, the mesophase transition temperatures

of the monomers and SLCPs decreased as the terminal length increased; however, they tended to increase as the spacer length increased, whereas the lateral methoxy substituent on the mesogenic core

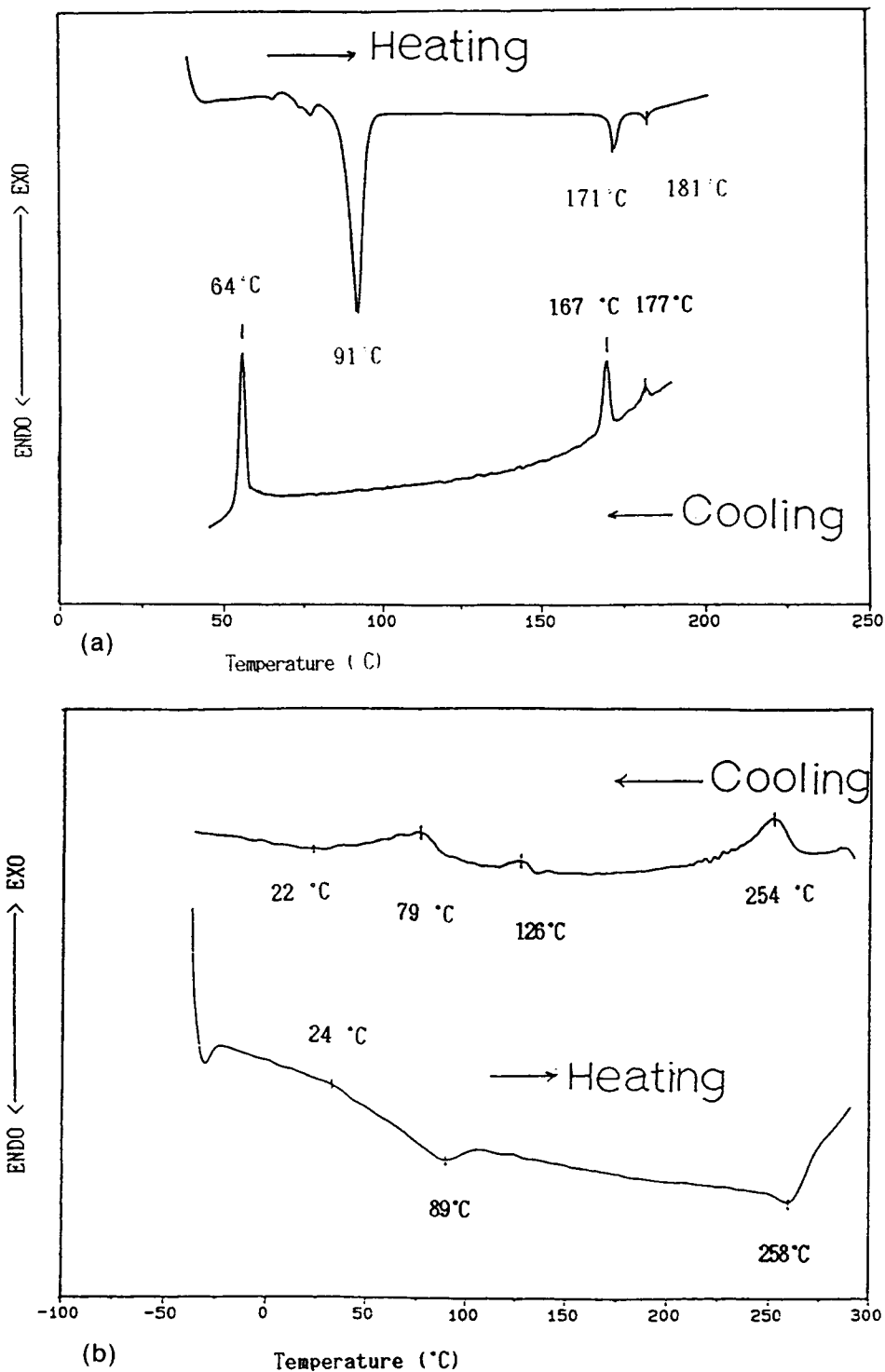


Figure 2 (a) DSC thermograms for monomer ME1S5. (b) DSC thermograms for polymer PE1S5.

lowered the mesophase transition temperature. It was also observed that the increase of spacer length induced crystalline.

Figure 3 shows the X-ray diffraction diagrams of the five polymers. They all showed a sharp reflection

at $2\theta = 3.06^\circ, 3.05^\circ, 4.36^\circ, 2.85^\circ,$ and 2.63° , as well as a broad reflection at $2\theta = 19.21^\circ, 19.52^\circ, 20.26^\circ, 19.51^\circ,$ and 19.13° , respectively. The sharp reflection small angle of 2θ is a characteristic of the smectic phase. It is related to the layer spacing d_1 .²³ Mean-

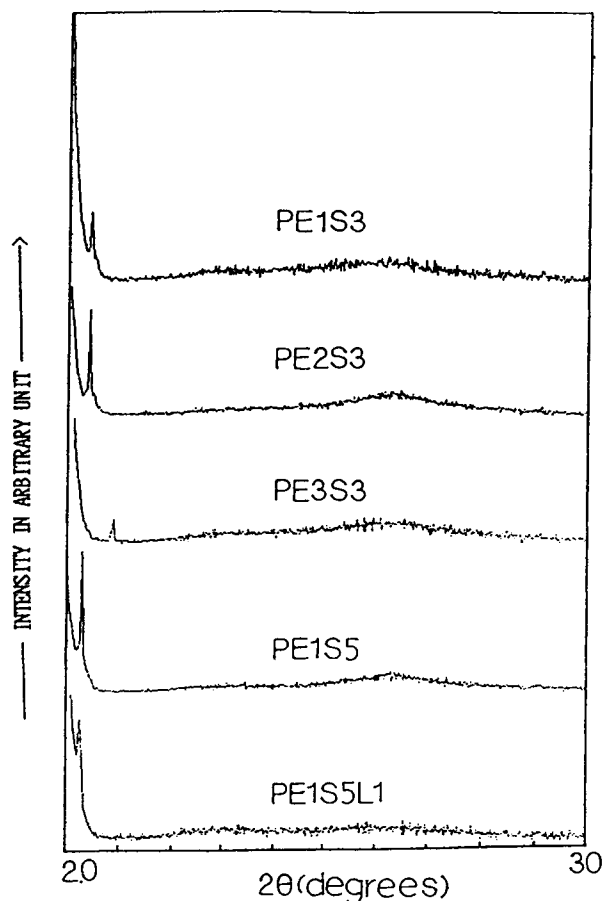


Figure 3 X-ray diffraction patterns for polymers PE1S3, PE2S3, PE3S3, PE1S5, and PE1S5L1.

while, the broad reflection peak at $2\theta = 19^\circ\text{--}20^\circ$ provides the side-chain distance d_2 ²² of the LC polymers. Using the Bragg equation, both d_1 and d_2 were obtained (Table III). The d_2 s obtained were around 4.5 Å. It is interesting to find that the d_2 s values obtained are close to those of side-chain LC polyacrylates and polymethacrylates reported by Gemmell et al.^{19,20} and Frosini et al.²⁴ Noteworthy is that the bond angle ($\theta = 142^\circ$) and bond length

($L = 1.62$ Å) of —Si—O—Si— are larger than those of —C—C—C— in acrylates and methacrylates, which are about $\theta = 109.5^\circ$ and $L = 1.53$ Å. The layer-spacing distances fell in the range of 29–34 Å. Except for PE3S3, the increase of terminal length or spacer length or the introduction of a lateral substituent on the mesogenic core tended to increase d_1 . It was observed that the d_1 s values are not larger than those of acrylic LC polymers, in spite of the lengths of the side chains being much longer than those of the side chains of acrylic LC polymers reported by Gemmell et al.^{19,20} The total length of side chains is estimated (Table III), assuming that they are in the fully extended conformations. It is noteworthy that those layer-spacing distances are much smaller than twice the side-chain length of fully extended conformations. Therefore, the two-layer end-on packings or the two-layer packing with overlapping of tails model²³ seemed not able to ascribe the structure of the side-chain LC polysiloxanes concerned.

In the work, we took PE1S5 to study the effect of temperature on the mesophase structure. Before doing the X-ray diffraction measurement, PE1S5 was preheated to 330°C *in vacuo*. Then, the X-ray diffraction investigations were performed on the preheated sample that was cooled in 50°C steps from 330°C . As shown in Figure 4(a), the wide-angle X-ray reflection patterns of the polymer above 254°C were broad, asymmetric, and of weak intensity. Therefore, the short-range order of the side chain, as expected, was not well developed yet. As the temperature was cooled to 254°C , the X-ray reflection patterns became relatively symmetric, narrow, and strong. They revealed that the LC phase was obtained at the above temperature. From the DSC thermograms [Fig. 2(b)], one knows that there was an isotropic transition temperature (T_{si}) at 254°C , a mesophase transition temperature at 126°C , and a melting point (T_k) at 79°C . The DSC result also confirms the fact that PE1S5 forms LC at 254°C . When the temperature was further cooled below

Table III X-ray Diffraction Data for Polymers

Polymer	Small Angle		Wide Angle		Calculated Length of Anisotropic Unit d (Å)
	2θ (Deg)	d_1 (Å)	2θ (Deg)	d_1 (Å)	
PE1S3	3.06	28.86	19.21	4.62	24.80
PE2S3	3.05	28.97	19.52	4.55	28.72
PE3S3	4.36	20.25	20.26	4.38	31.10
PE1S5	2.85	30.96	19.51	4.55	27.30
PE1S5L1	2.63	33.57	19.13	4.64	27.30

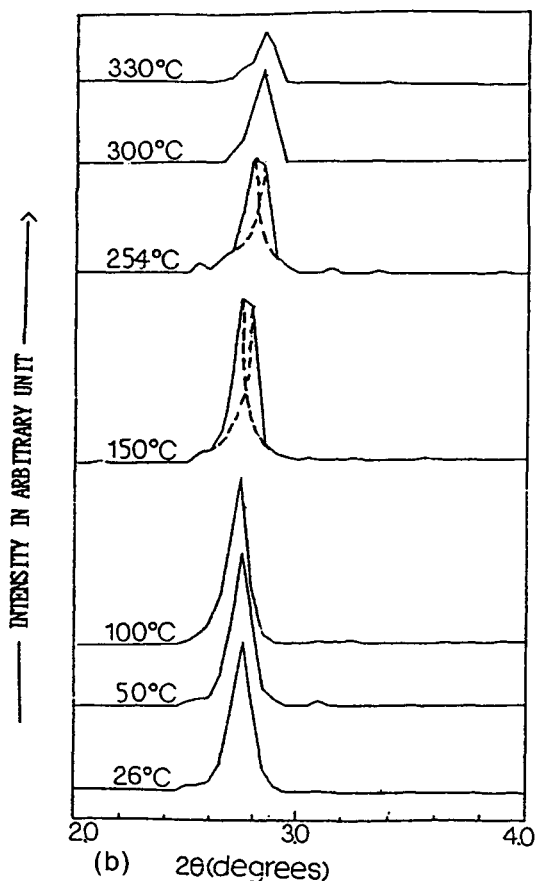
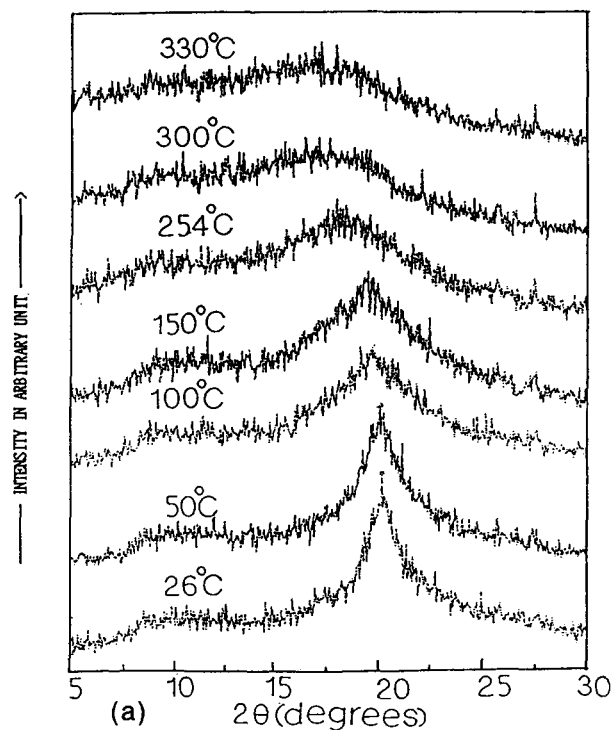


Figure 4 (a) Variation of the intensity of the wide-angle diffraction with the temperature for the polymer PE1S5. (b) Variation of the intensity of the small-angle diffraction with the temperature for the polymer PE1S5.

254°C, the reflection peak maximums shifted to a higher angle, and the peak became more symmetric, stronger, and narrower with decreasing temperature in the range of 254°C > T > 50°C. It indicated that d_2 was continuing to become smaller in the above temperature range (e.g., the lower the temperature, the closer the side-chain groups). It may have resulted from the effect of the secondary interaction forces imposing on the side chain, because the secondary intermolecular interaction forces increased with decreasing temperature. Whereas the temperature was cooled to 50 and 26°C, the reflection peak maximum did not significantly shift but the intensity and symmetry of the reflection peaks became higher than those of the above smectic phase mentioned. As indicated from the DSC thermograms, the melting point T_k was 79°C. Hence, the side-chain distance remained unchanged as the side-chain LC polysiloxanes existed at or below T_k .

As indicated from the small-angle reflections of Figure 4(b), PE1S5 at the temperature even higher than T_{si} could show a reflection peak of 2θ at about 2.9°. This reveals that the long-range order of the layer spacing could still exist above T_{si} . It is noteworthy that the small-angle reflection above T_{si} tended to be sharper and shifted to a lower angle with decreasing temperature. Meanwhile, in the temperature range 254°C > T > 150°C, the bimode reflection pattern was exhibited. This indicates that two conformers coexisted in this temperature range. As the temperature was further cooled to 100°C, the reflection peak became unimode. Therefore, one of the conformers disappeared below 100°C. Examining the DSC thermogram of Figure 2(b), there appeared two mesophase transition temperatures at 254 and 126°C. However, the DSC results cannot tell if the coexistence of two mesophases is in the temperature range 254°C > T > 150°C. It is noted that as the temperature was continuously cooled down to below T_k , the smectic characteristic X-ray diffraction pattern still kept. This fact reflects that the smectic phase structure was "frozen" below T_k .

CONCLUSION

X-ray diffraction studies show all the 4'-[oligo(ethylene oxide)monomethyl ether carbonyl] biphenyl-4-yl 4-(allyloxy) benzoate side-chain LC polysiloxane polymers investigated were of the smectic phase. The terminal length and the spacer length affect on not only the mesophase transition temperature of the LC but also the layer-spacing d_1 and the side-chain distance d_2 . The long- and short-range orders could remain to some extent above the

isotropic transition temperature and below the melting-point temperature. The bond angle and bond length of the backbone chain of polysiloxanes as well as the chain length of the side chain are larger than those of polyacrylates or poly(methyl acrylates). However, their d_1 and d_2 did not differ much.

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