

# 데카메틸렌 및 올리고실록산 격자를 함께 갖고 있는 주사슬 액정 공중합체

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## Main Chain Liquid Crystalline Copolymers with Mixed Spacers of Decamethylene and Oligosiloxane Groups

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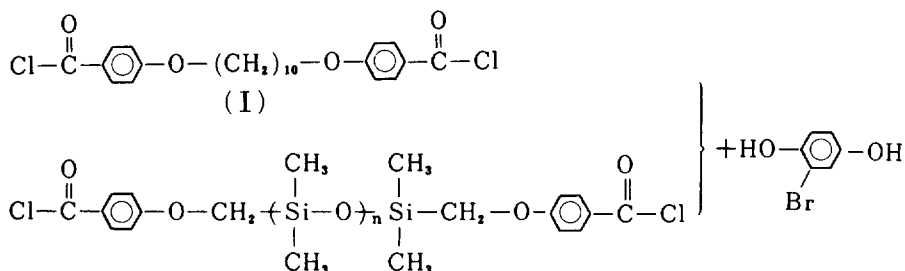
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### INTRODUCTION

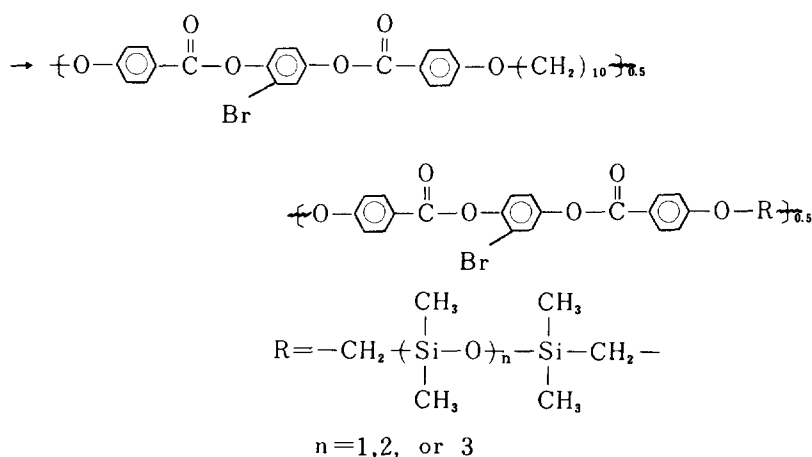
Recently we<sup>1</sup> reported the liquid crystalline and thermal properties of a series of copolymers consisting of a triad aromatic ester type mesogenic unit and equimolar mixed spacers of polymethylene and disiloxyl groups. They were found to be nematic and their thermal transition temperatures, especially of melting, strongly depended on the number of methylene unit in the polymethylene spacer. From this<sup>1</sup> and other studies<sup>2,3</sup> it was also observed that disiloxyl and oligosiloxyl groups lower the transition temperatures of the polymers very effectively. Ther-

motropic, side chain polymers consisting of polysiloxane backbones to which various mesogenic groups are attached are also well known<sup>4</sup>.

In the present investigation we prepared the following equimolar and random copolymers with varying length of siloxyl unit and, their liquid crystalline and thermal properties were studied. The copolymer with  $n=1$ , reported earlier by us, was reprepared in this investigation for comparison and others with  $n=2$  and 3 are new compositions. The thermal transitions of and the nature of mesophases formed by the polymers were studied by differential scanning calorimetry (DSC) and on a polarizing microscope equipped with a hot stage.



(II)  $n=1, 2 \text{ or } 3$



## RESULTS AND DISCUSSION

The synthetic results and the general properties of the polymers are summarized in Table 1. The relatively low yields of polymers seem to have been resulted from the partial solubility of polymers in acetone which was employed in washing.

The equimolar compositions of the two structural units in the copolymers were confirmed by their elemental analyses (Table 2). The IR spectra of the polymers were consistent with those of the expected structures.

All of the three copolymers exhibited reversible thermal transitions, crystal-mesophase and mesophase-isotropic phase, on DSC analysis (Fig. 1), implying that they are semicrystalline and enantiotropically thermotropic.

All of the polymers revealed a transition peak before melting and annealing did not change its appearance. At present, the peak is believed to correspond to crystal-to-crystal transition.

<sup>b</sup>This copolymer was reported earlier by us<sup>2</sup>. The data recorded in this table were obtained for a newly prepared sample. The data are in excellent accord with those reported earlier.

Observation of polymers on the hot-stage of a polarizing microscope also supported this supposition. Such transitions are very often observed for other polyesters<sup>5,6</sup>.

According to the data in Table 1, melting ( $T_m$ )

**Table 1.** Properties of Liquid Crystalline Copolymers

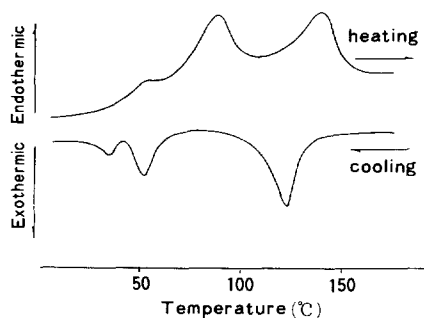
Polymer, n	Yield, wt. %	$\eta_{inh}^a$	$T_m$ , °C	$T_i$ , °C	$\Delta T$ , °C
1 <sup>b</sup>	72.5	0.54	104	178	74
2	69.5	0.50	87	142	55
3	65.5	0.48	76	105	29

<sup>a</sup>Measured at 40°C on a 0.5g/dl solution of the polymers in a 60: 40(w/w) phenol-TCE mixture.

**Table 2.** The Results of Elemental Analyses of the Polymers

Polymer, n	Elemental Analyses, wt. % <sup>a</sup>			
	C	H	Si	Br
1	58.2(58.2)	5.2(5.2)	4.9(4.9)	14.0(13.8)
2	56.5(56.7)	5.3(5.2)	7.0(6.8)	12.9(13.0)
3	55.2(55.3)	5.5(5.4)	8.6(8.6)	12.4(12.3)

<sup>a</sup> The values in the parentheses are the calculated ones.



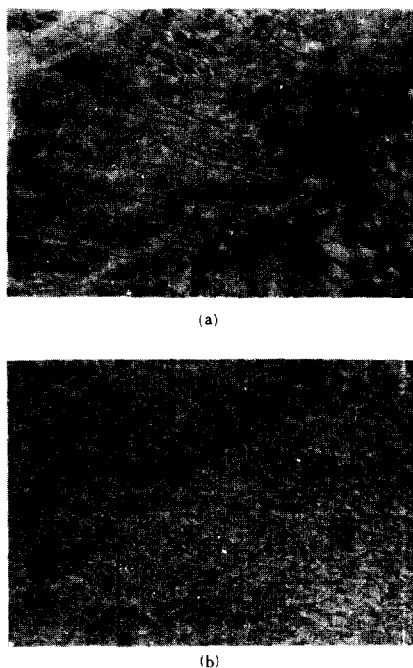
**Fig. 1.** DSC thermograms for the polymer with  $n=2$ .

as well as isotropization temperature ( $T_i$ ) of the polymers decreased with the number,  $n$ , of siloxyl unit in the spacer. The mesophase temperature range,  $\Delta T$ , also decreased with  $n$ . Certainly, lengthening the siloxyl spacer decreases the thermal stability of mesophase to a much higher degree than the reduction in  $T_m$ , resulting in narrower  $\Delta T$ .

The polymer melts were all turbid between  $T_m$  and  $T_i$  and revealed strong stir-opalescence in the same temperature range. They became clear above  $T_i$ . When viewed through the cross-polarizing microscope, the melts showed birefringence. Typical optical textures observed are shown in Fig. 2 and they are the ones typical to nematics. Threaded Schlieren textures can be clearly seen in the photomicrographs.

## EXPERIMENTAL

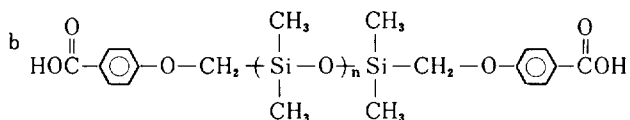
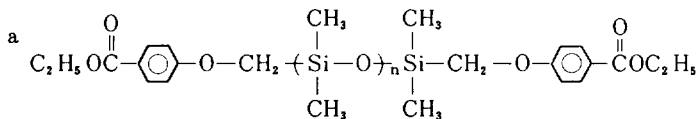
**Monomer Preparation** 1,10-Bis (4-chloroformylphenoxy) decane (I) was prepared following the literature method<sup>5</sup>. 1,3-Bis (4-chloroformylphenoxy)



**Fig. 2.** Microphotographs of the polymers with (a)  $n=2$  and (b) 3 taken at 95°C and 102°C, respectively (magnification  $\times 200$ ).

**Table 3.** Melting Points and Elemental Analyses of the Precursors of Compounds II

Diethyl Esters <sup>a</sup>					Dicarboxylic Acids <sup>b</sup>				
n	M.P., °C	Elemental Analyses, <sup>c</sup> wt. %			n	M.P., °C	Elemental Analyses, <sup>c</sup> wt. %		
		C	H	Si			C	H	Si
1	55	58.8 (58.8)	7.0 (6.9)	11.5 (11.5)	1	156-157	55.0 (55.3)	6.1 (6.0)	13.1 (12.9)
2	46	55.3 (55.3)	7.1 (7.1)	14.8 (14.9)	2	127-128	51.6 (52.0)	6.3 (6.3)	16.6 (16.5)
3	—	52.2 (52.7)	7.2 (7.2)	17.3 (17.6)	3	95-95.5	49.3 (49.5)	6.6 (6.5)	19.2 (19.2)



c

Values in the parentheses are theoretical ones.

xymethyl) tetramethyl disiloxane (II,  $n=1$ ) was prepared by the route reported earlier by us<sup>2</sup>. Other siloxyl group containing monomers (II,  $n=2$  and 3) were also prepared by the same synthetic method. Table 3 shows the melting points and the results of elemental analyses of the precursors, i.e., diethyl esters and corresponding dicarboxylic acids. The compounds with  $n=2$  and 3 are being reported here for the first time.

Their structures could be further confirmed by their IR (Shimadzu IR-440) and NMR (Bruker FT Spectrometer 80 SY) spectra. Bromohydroquinone (Eastman Kodak) was used after purification by sublimation. Elemental analyses were performed by the Microanalytical Laboratory of the University of Massachusetts, U.S.A.

**Polymer Preparation** The monomers of I (0.01 mole) and II (0.01 mole) were dissolved in 75 ml of dry 1,1,2,2-tetrachloroethane (TCE). The solution was then added dropwise to a solution of bromohydroquinone (0.02 mole) in 90 ml of dry TCE and 10 ml of pyridine under a nitrogen atmosphere at room temperature with vigorous stirring. The reaction was allowed to proceed overnight and 300 ml of acetone was added to the mixture. The polymer formed was washed with acetone, distilled water, and finally with acetone again, then dried in a vacuum oven.

**Identification and Characterization of Polymers** The structures of the polymers were verified by

their IR spectra and elemental analyses. Elemental analyses were performed by the Microanalytical Laboratory of the University of Massachusetts, U.S.A.. Thermal properties of polymers were examined on a DSC (Mettler TA 3000) analyzer with a heating rate of 20°C/min. Indium and lead were employed for calibration. The optical textures and thermal transitions were observed on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Orthoplan).

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