디실록실과 폴리메틸렌의 혼성격자를 갖는 주사슬 액정폴리에스테르

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Main – Chain Thermotropic Copolyesters with Mixed Spacers of Disiloxyl and Polymethylene Groups

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Abstrac: A new series of thermotropic random copolyesters were prepared and their thermal and mesomorphic properties were investigated. The copolymers were consisting of triad aromatic ester type mesogens and mixed spacers of disiloxyl and polymethylene groups along the main–chain. The dependence of melting and isotropization transitions on the molecular weight of a copolymer was established using a series of fractionated samples. Differential scanning calorimetry and analysis on a polarizing microscope were the two main research tools employed in this investigation. Optical textures of the polymers did not provide a clear conclusion as to the nature of mesophases formed by the polymers, although they appeared to be poorly organized nematics.

1. INTRODUCTION

One of our earlier reports described the liquid crystalline properties of the polyesters which contained disiloxyl groups in the backbone[1]. The disiloxyl group was found very effective in lowering transition temperatures of the resulting polymers[2~4]. This was ascribed to the very low rotational energy barrier around the Si−O−Si bond. The bulky nature of the dialkylsiloxyl group should also play an important role in reducing transition temperatures.

The so-called flexible spacers existing in the main−chain liquid crystalline polyesters exert various effects in the thermal and mesomorphic properties of the polymers, depending on their structure and length. Reduction of transition temperatures, odd-even effect of polymethylene spacers and change in the nature of mesophase are the three most frequently mentioned important influences observed by incorporation of flexible spacers along the liquid crystalline polyester backbone[5~8].

Recently Aguilera and Ringsdorf[9] reported thermotropic properties of a series of main−chain liquid crystalline polyesters having oligosiloxane spacers and triad aromatic ester type mesogenic units. All of the polymers described by them were in liquid crystalline phases even at room temperature, indicating very low melting or glass−transition temperatures. Thermotropic compositions of side chain polymers consisting of polysiloxane main chains to which various mesogenic groups are attached are also known[3,4].

In the present article we would like to report the synthesis, and thermal and mesomorphic properties of a new series of random copolyesters I of the structure shown below.
Thermal properties of the polymers were studied by differential scanning calorimetry (DSC). The nature of liquid crystal phases was judged by the optical textures observed on a hot−stage attached to a polarizing microscope. The dependence of transition temperatures on the moecular weight of a polymer (x=5) also was examined for a series of samples fractionated through a preparative high−pressure liquid chromatograph.

2. EXPERIMENTAL

2−1. Synthesis of polymers

The polymers were prepared by reacting an equimolar mixture of 1,3-bis (4-chloroformylphenoxy methyl) tetramethyl disiloxane (II) and α, ω-bis (4-chloroformyl-

$$x = 2 - 10 \text{ and } 12$$

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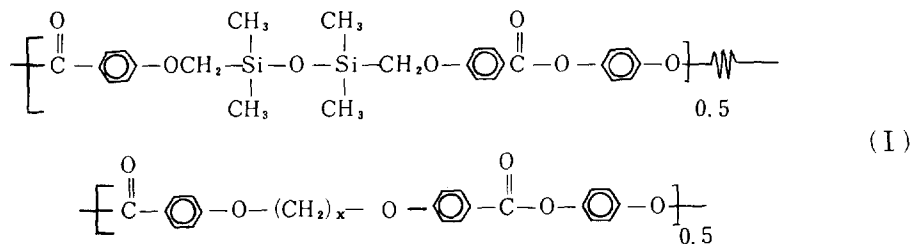
phenoxy) alkane (III) with stoichiometric amount of hydroquinone in 1,1,2,2-tetra-chloroethane (TCE) at room temperature. Pyridine was used as an HCl acceptor.

The compounds II and III were prepared following the literature methods [1,10]. A representative preparative method of the polymers is as follows: An equimolar mixture (0.01 moles respectively) of the compounds II and III dissolved in 75 ml of TCE was added dropwise to a solution of 0.02 moles of hydroquinone dissolved in a mixture of 90 ml of TCE and 10 ml of pyridine. TCE and pyridine were dried by conventional methods before use. The reaction mixture was stirred overnight at room temperature under nitrogen atmosphere. And then the mixture was poured into 500 ml methanol. The precipitates were washed with methanol, water and finally again with methanol. The washed polymers were dried at 50°C under reduced pressure.

2-1. Characterization of polymers

The structure of polymers were confirmed by their IR (Shimadzu IR-440 spectrophotometer) spectra and elemental analyses (Shimadzu CHN corder). One of the samples, x=10, was subjected to ^{13}C-NMR analysis in the solid state on a 300 MHz, NMR spectrometer (Brucker, FT-NMR, S-Y300). The solution viscosity of the poly-

mers was measured using a Cannon-Ubbelhode type viscometer. Elemental analysis of the polymers were conducted on a CHN analyzer (Shimadzu Co., Japan).

Thermal properties of the polymers were examined under a nitrogen atmosphere by DSC (Mettler TA 3000) with the heating rate of 10°C/min. The optical textures and thermal transitions of the polymers were observed on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

2-2. Fractionation

In order to examine the dependence of transition temperatures on molecular weight, one of the polymers, x=5, was fractionated using a preparative liquid chromatograph (Waters Associate, Prep LC 500) equipped with a styragel column (10^3-10^4Å). TCE was employed as an eluent. The polymers in each fraction was precipitated into methanol and the recovered polymers were washed and dried.

3. RESULTS AND DISCUSSION

3-1. General properties of polymers

The yields, solution viscosities and the results of elemental anaysis of the polymers are recorded in Table 1. Both the yields for the recovered polymers and the solution
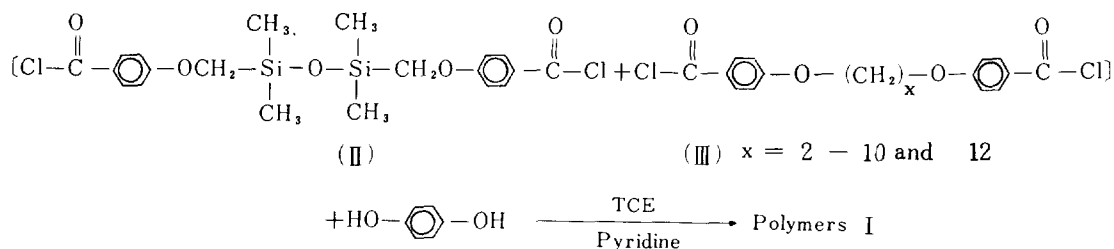
viscosity numbers are reasonably high. The results of elemental analysis are in good agreement with theoretical values.

The IR spectra of the polymers showed the absorption peaks as expected. For example, Fig. 1 shows strong absorption bands at about 1,725 (C=O stretching), 1,600 (aro-

matic C=C stretching), and 1,170cm⁻¹ (C—O stretching). The symmetric—CH₃ deformation of Si—CH₃ shows a sharp absorption band at 1,250cm⁻¹. And the —CH₃

**Table 1.** The Yields, Solution Viscosities and the Results of Elemental Analysis of Polymers Ⅰ

Poly- mers, x	Yield, wt.%	η_{inh}^a	Elemental Analysis, wt.%^{b}	
			C	H
2	85	0.62	65.26 (65.16)	4.98 (4.98)
3	75	0.34	65.29 (65.47)	5.15 (5.12)
4	70	0.60	65.59 (65.79)	5.28 (5.26)
5	99	0.74	66.05 (66.09)	5.43 (5.40)
6	95	0.68	66.20 (66.28)	5.58 (5.53)
7	81	0.42	66.68 (66.67)	5.70 (5.66)
8	92	0.58	66.89 (66.94)	5.70 (5.79)
9	92	0.77	67.12 (67.21)	5.93 (5.91)
10	97	0.70	67.35 (67.47)	6.09 (6.02)
12	93	0.65	67.83 (67.97)	6.30 (6.25)

^{a} The solution viscosities were measured on a 0.5g/100ml solution of the sample in TCE at 30℃.

^{b} The values in the parentheses are those calculated for chemical formulas.
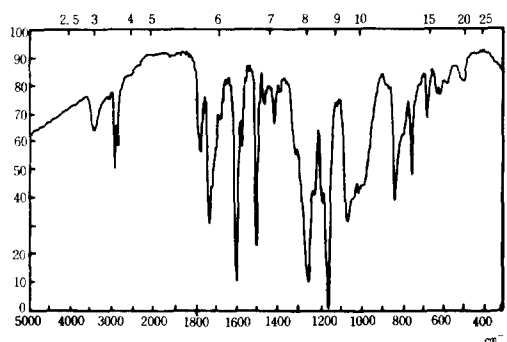
Fig. 1. IR spectrum of the polymer with x=10.
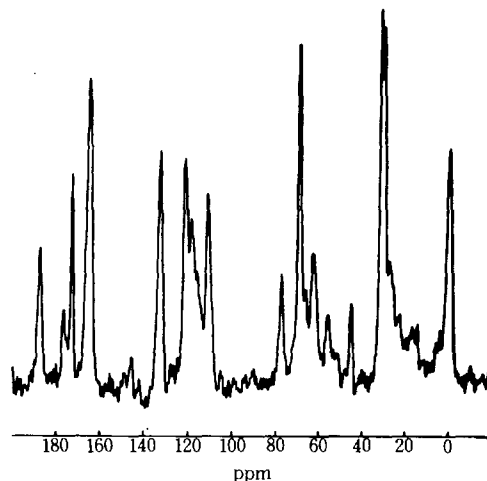
Fig. 2. ¹³C−NMR spectrum of the polymer with x=10.

Table 2. Assignment of Characteristic ¹³C-NMR Peaks for the Polymer with x=10

Chemical Shift, ppm	Functional Group
172.3	$-\bigcirc-\overset{O}{\underset{}{C}}-O-$
164.5	$-O-\bigcirc-\overset{O}{\underset{}{C}}-$
132.2	$-O-\bigcirc-\overset{O}{\underset{}{C}}-$
121.2	$-O-\bigcirc-O-$
118.3	$-O-\bigcirc-O-$
110.8	$-O-\bigcirc-\overset{O}{\underset{}{C}}-$
68.8	$-O-\underline{C}H_2CH_2-$
30.9	$-O-CH_2\underline{C}H_2CH_2-$
29.5	$-O-CH_2CH_2\underline{C}H_2CH_2-$
−0.90	$\underset{\underline{C}H_3}{\overset{CH_3}{\underset{|}{Si}}-O-}$

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rocking and the Si—C stretching vibration band at about 825 cm⁻¹. The asymmetric Si—O—Si stretching band appeared at around 1,070 cm⁻¹ and the corresponding symmetric mode at 500 cm⁻¹

Fig. 2 shows a representative proton-decoupled, ^{13}C-NMR spectrum obtained from a solid sample of the polymer with x =10. The spectrometer frequency was 70.460 MHz. The number of scans and the sweep width were 1,421 and 31,250 Hz, respectively. An assignment of the characteristic ^{13}C chemical shifts for more intense peaks is summarized in Table 2. Certainly the spectrum is consistent with the structure of the polymer.

3-2. Thermal properties of polymers

Thermal behavior of the polymers were studied by DSC and also on a cross-polarizing microscope equipped with a hot-stage. Transition temperatures for melting (Tm) and isotropization(Ti) are known to depend on

the molecular weight of a polymer[11]. We could observe a similar phenomenon for the polymer with x=5 (Table 3). Various fractions of the polymer with different molecular weight were collected using a preparative high pressure liquid chromatograph. Unfortunately the absolute molecular weights of each fractions could not be determined from the chromatogram due to unexpected damages to the column material by the TCE eluent. Instead, the solution viscosities of each fraction were determined. However, it is believed that each fraction is of fairly narrow molecular weight distributions.

Fig. 3 shows how the transition temperatures of the polymer with x=5 depend on the molecular weight. According to this figure especially Ti steeply increases with molecular weight up to η_{inh}=0.70. And then the increase becomes much less pronounced. Another important finding is the significant

Table 3. Dependence of Transition Temperatures on the Molecular Weight of the Polymers with x=5[a]

η_{inh}[b]	Tm, ℃	Ti, ℃	△T, ℃
0.14	65	152	87
0.38	72	205	133
0.61	78.5	250	171.5
0.73	81	270	189
1.02	82.5	272	189.5
1.24	83	273	190

[a] The Tm's shown in this table are the initial birefringent temperatures observed on the polarizing microscope, while Ti's the positions of peak maxima of DSC thermograms.
[b] The solution viscosities were measured on a 0.5g/100 ml solution of a sample in TCE at 30℃.

Fig. 3. Dependence of transition temperatures on the molecular weight of the polymer with x=5.

degree of increase in the mesophase temperature range, i.e., $\triangle T$, with molecular weight of the polymer. This is due to the fact that the enhancement in Ti by molecular weight increment is much greater than that in Tm.

Transition temperatures of the polymers as prepared are given in Table 4. For all of the polymers, melting as well as isotropization endothermic peaks were very weak and broad (Figure 4). The positions of peak maxima on DSC thermograms were taken as transition points. The polymers with odd-number x's exhibited so weak melting endotherms that a fair degree of uncertainty exists in the values of Tm shown in Table 4. Therefore, we tabulated together the temperatures at which initial birefringence was observed for each polymers on the cross-polarizing microscope. We believe that the degree of crystallinity especially of odd members is extremely low. The Tm's shown in Fig. 3 are the initial birefringent temperatures observed on the polarizing micro-
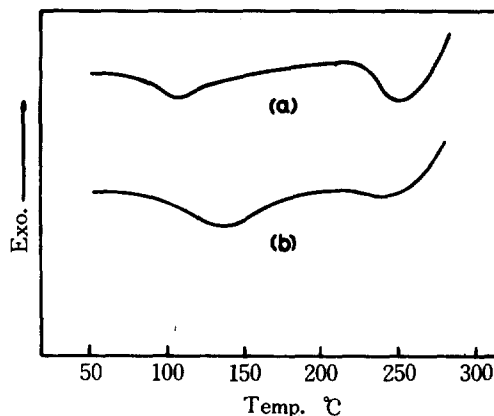

Fig. 4. DSC thermograms of the polymers with (a) x=7 and (b) x=9 obtained on heating runs.

scope. On the other hand all of Ti values reported in this article are those obtained from the positions of peak maxima of DSC thermograms.

Although the molecular weight varies from one polymer to another, as reflected by the values of solution viscosities, the following general trends are borne out: 1) Both Tm and Ti decreased with x, 2) Tm's of the polymers with even numbers of x were much higher than those with odd numbers, 3) the odd-even effect is not so much clear in Ti and 4) the mesophase temperature range ($\triangle T$) of the polymers with odd x's was much broader than that of even members. The depression of the melting points by the odd members of the present polymers appears to be exceptionally great compared with other homologous series.

3-3. Optical textures of mesophase

The optical textures of the polymers in the fluid states did not provide clear information as to the nature of their mesophases (Figure 5). Probably they correspond to the relatively poorly organized ne-

Table 4. Transition Temperatures of the Polymers I

Polymers,x	Tm[a], ℃	Ti, ℃	$\triangle T$, ℃
2	280 (270)	—	—
3	140 (120)	280	140
4	230 (200)	275	45
5	109 (81)	271	162
6	195 (170)	273	78
7	108 (85)	246	138
8	160 (140)	239	79
9	135 (95)	249	114
10	120 (115)	245	125
12	140 (120)	283	143

[a] Those in parentheses indicate the temperatures at which initial biref ringence was observed on the cross-polarizing microscope.
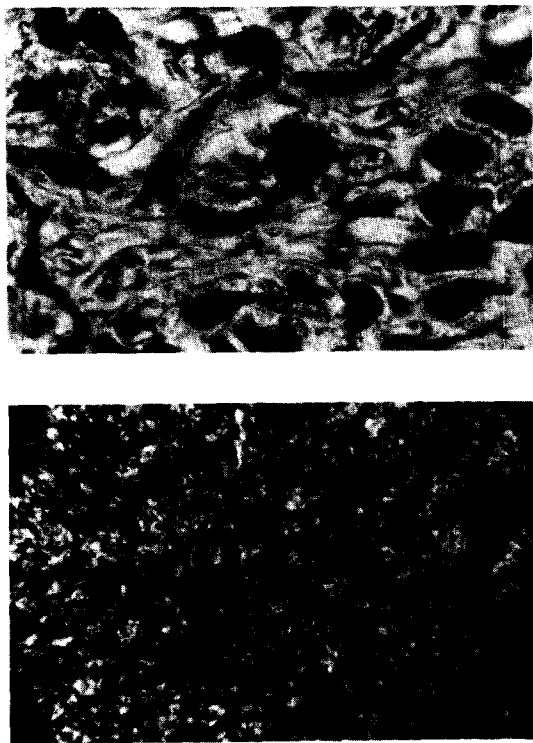
Fig. 5. Photomicrographs of the polymers with (a) x=3 (taken at 226°C ; magnification x 200) and (b) x=12 (taken at 240°C ; magnification x 200).

matic phases. Somehow or other siloxyl group containing polymers seem to show uncommon optical textures which can not be unequivocally related to any known mesophases[9]. Further studies are required to clarify this point. All of the polymers were strongly stir-opalescent and birefringent in the mesophase.

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