

*Mol. Cryst. Liq. Cryst.*, 1990, Vol. 185, pp. 75-87  
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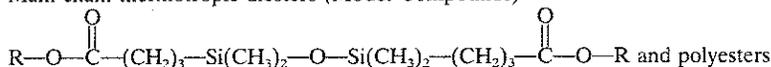
## Mesomorphic Properties of Main Chain Thermotropic PLCs and Model Compounds Containing a Tetramethyldisiloxane Moiety in the Spacer

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(Received November 3, 1989)

Main-chain thermotropic diesters (Model Compounds)



$[\text{O}-\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\overset{\text{O}}{\parallel}{\text{C}}]_n$  containing a tetramethyl disiloxane moiety in the flexible spacer were synthesized and studied in order to investigate the influence of a short sequence of siloxane bonds on the mesomorphic properties of main-chain liquid crystalline compounds. It was

found that the introduction of the  $-\overset{|}{\text{Si}}-\text{O}-\overset{|}{\text{Si}}-$  moiety into the flexible spacer substantially lowers the transition temperatures of both polymers and twin model compounds. In addition, a strong decrease of the order parameter of the siloxane containing twin-model compound was found. Interestingly, while most of the model compounds display monotropic nematic mesophases the corresponding polymers are either non-mesomorphic or smectic.

### INTRODUCTION

It is well known that rigid main chain PLCs display high transition temperatures making the processing of such systems in their liquid crystalline state difficult. The introduction of kinks, side groups and flexible moieties into the chain lowers the transition temperature. In most cases, however, the realm of liquid crystallinity (where flow and chain orientation occur simultaneously) is still well above room

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temperature. This is particularly inconvenient in the case of PLCs containing temperature sensitive moieties such as for example diacetylenic and other thermally fragile structural units. Several years ago Aiguileira *et al.*<sup>1</sup> prepared main chain PLCs with polysiloxane units in the flexible spacer and demonstrated a drastic lowering of the  $T_g$  accompanied by lowering of the liquid crystalline transition temperature. In addition and most interestingly, smectic phases were observed for such polymers while their carbon chain analogs also displayed nematic mesophases. Such behavior could well originate with a microphase separation of the siloxane containing spacer since the number of Si-units in the polymers described in Reference 1 was rather substantial and comprised between 3 and 14 units.

A few studies have been reported in the literature dealing with the synthesis and properties of main-chain liquid crystalline polymers<sup>2,3</sup> and twin-diacetylenic compounds<sup>4</sup> with a short disiloxane spacer such as  $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$ . Such compounds were reported to display nematic and monotropic nematic mesophases. The characterization of these mesophases was based on microscopic observation of optical textures which in the case of polymers is known to be very difficult. The omission of X-ray diffraction as a necessary characterization tool makes such characterization incomplete. It was therefore interesting to explore more extensively the liquid crystalline behavior of polymers and dimeric model compounds with a very short dimethyl siloxane sequence in a spacer predominantly composed of  $-\text{CH}_2-$  units. In particular it is interesting to observe whether the existence of only two siloxane bonds allows for a substantial lowering of  $T_g$ , a substantial decoupling of mesogenic moieties and preservation of nematicity in the polymer and dimeric model compounds.

## EXPERIMENTAL

The structure of the synthesized polymers and model compounds are given in Table I together with the results of elemental analysis. Structures are as shown in Tables II and IV.

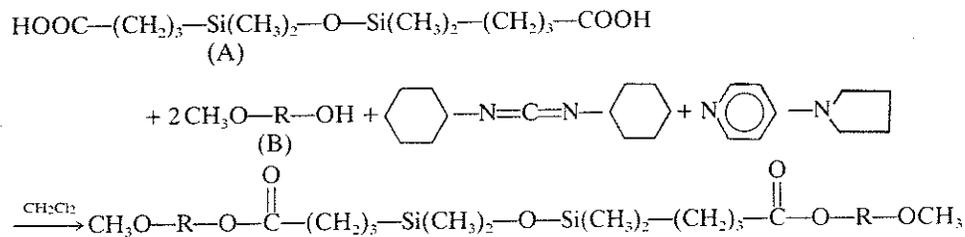
### Synthesis

4,4'-Dihydroxydiphenyl (Aldrich Chemical Company) and bis-carboxypropyltetramethyldisiloxane (Farchan Labs.) were purchased and recrystallized from ethanol-water mixtures. 4,4'-Dihydroxyazoxybenzene, 4,4'-dihydroxy-2,2'-dimethylazoxybenzene,<sup>5,6</sup> 4,4'-dihydroxyphenylbenzoate,<sup>7</sup> trans-1,4-cyclohexylene-di-*p*-hydroxycarbonyloxybenzoate,<sup>8</sup> 4-hydroxy-4'-methoxydiphenyl,<sup>9</sup> 4-hydroxy-4'-methoxyazoxybenzene, 4-hydroxy-4'-methoxy-2,2'-dimethylazoxybenzene, 4-hydroxy-4'-methoxyazoxybenzene,<sup>5,6</sup> and 4-hydroxy-4'-methoxyphenylbenzoate<sup>7</sup> were prepared according to the literature given in the references above. The polymers and diesters were prepared by room-temperature esterification<sup>10</sup> according to the scheme shown below.



elemental analysis (Table I). Reduced viscosity was obtained for a concentration of 0.5 g/dl of polymer in tetrachloroethane at 30°C.

Diester model compounds were synthesized according to the scheme below:



0.005 moles of bis(carboxypropyl)tetramethyldisiloxane (A), 0.011 moles of the corresponding phenol, 0.011 moles of *N,N'*-dicyclohexylcarbodiimide (B), and 0.001 moles of *N*-pyrrolidinopyridine (C) were mixed in dry dichloromethane and the mixture was stirred at room temperature. The reaction was followed by TLC. The white precipitate of *N,N'*-dicyclohexylurea was filtered. The filtrate was washed with water, 5% acetic acid and again with water successively and dried over anhydrous magnesium sulfate. The solvent was evaporated and the product dried in a vacuum oven. The compound was purified by silica gel column chromatography by using chloroform as eluent. The product was recrystallized from acetone-ethanol mixture.

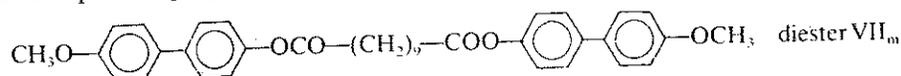
The diesters were characterized by elemental analysis (Table I), IR, <sup>1</sup>H and <sup>13</sup>C NMR.

The polymers and diesters displayed IR absorption bands in the vicinity of 800 cm<sup>-1</sup> (Si-(CH<sub>3</sub>)<sub>2</sub> rocking vibrations) and 1200 cm<sup>-1</sup> (Si-CH<sub>3</sub> deformation vibrations) as well as 1000 cm<sup>-1</sup> corresponding to the Si(CH<sub>3</sub>)<sub>2</sub>-O-Si(CH<sub>3</sub>)<sub>2</sub> absorption region.

<sup>13</sup>C NMR spectra displayed peaks at 36, 18, 17 and 0.2 ppm consistent with the incorporation of a CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si- sequence into the structure. <sup>1</sup>H NMR spectra displayed multiplets at 2.57, 1.79, 0.63 ppm, corresponding to protons located in α, β and γ to the Si atom. A singlet at 0.08 ppm was also observed and is consistent with the presence of methyl protons in this moiety. The transition characteristics and the textures of polymers and model compounds were studied by using a Leitz Ortholux polarizing microscope. Thermal properties were investigated by means of a Perkin Elmer 2C differential scanning calorimeter with a heating rate of 20°C/min.

The phase transition temperature T<sub>IN</sub> and biphasic composition f<sub>N</sub> given in Table III and Figure 3, respectively were obtained from changes in NMR line shapes and line width according to a technique described previously.<sup>11</sup> Order parameters S were deduced from dipolar splittings Δν<sub>0</sub> (KHz) as in Reference 12 using Δν<sub>0</sub> = KS with K = 27.0 KHz for the azoxybenzene mesogen (mesogen 8) the same value as for PAA. X-ray diffractograms were obtained with a Warhus flat plate camera mounted on a Rigaku generator, using Ni-filtered CuK alpha radiation of wavelength 1.54Å with a sample to film distance 5 cm (WAXS) and 17 cm (SAXS).

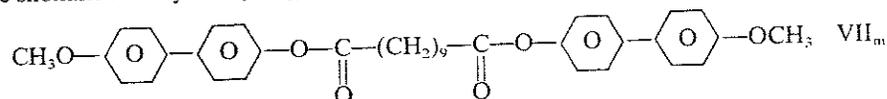
A diester analogue of  $I_m$  with no Si—O bonds in the spacer has also been prepared for comparison purposes:



## RESULTS AND DISCUSSION

The properties of polymers and diester model compounds are given in Tables II, III and IV.

Figure 1 gives DSC thermogram traces for the five diester model compounds after first temperature cycling. It is at once apparent from these results that all model compounds with the exception of  $\text{III}_m$  give nematic mesophases of predominantly monotropic nature. The introduction of the —Si—O—Si— moiety into the spacer substantially reduces the transition temperatures. This can be best seen by comparing the model compound  $I_m$  with its (all carbon atom) analogue in which the siloxane moiety —Si(CH<sub>3</sub>)<sub>2</sub>—O—Si(CH<sub>3</sub>)<sub>2</sub>— was replaced with 3—CH<sub>2</sub>— groups:



This diester was synthesized by us and found to have the following transition temperatures: C168I159N145C.

One can see from Table II that the introduction of the dimethylsiloxane moiety into  $\text{VII}_m$  produces a 63°C lowering of the melting point and an 88° lowering of the (monotropic) I→N transition temperature. This is accompanied by an expansion of the nematic interval.

All the diesters in Table II with the exception of  $\text{III}_m$  displayed nematic monotropism regardless of the nature of the mesogen. Even smectogenic mesogens such as bi-phenyl or azobenzene displayed nematic monotropic mesomorphism. The typical "Schlieren" pattern observed under polarizing microscope is shown in Figure 2a. The compound  $\text{III}_m$  did not give any transition peaks on cooling but displayed considerable cold crystallization on heating. This absence of mesophase and a very easy supercooling could well be due to the presence of substitutions in the 2,2' position, which as a rule, decreases the stability of nematic mesophases generated by such substituted mesogens. Annealing at 70°C for 4 hours induces crystallization of this diester in the form of spherulites. All siloxane twins have shown easy supercooling and extensive cold crystallization during heating and on annealing.

In order to assess the influence of the siloxane bond in the spacer on the order within the nematic mesophase a number of "twin" model compounds containing the same azoxybenzene mesogen (mesogen 8) and various spacers have been synthesized and their order parameter measured by wide-line H-NMR according to a technique described previously.<sup>11,12</sup> Figure 3 shows the variation of the order parameter  $S_{zz}$  as a function of temperature. Directly beneath is plotted for the same

TABLE II  
 Mesomorphic Properties of Diester Model Compounds

$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}$		$\Delta H_{in}$ cal/g	Transition Temp. °C <sup>a</sup>
Twin	R		
I <sub>m</sub>		0.47	C105I I71N53C
II <sub>m</sub>		0.34	C96I I90N7C
III <sub>m</sub>		—	C92I no transition on cooling (isotropic glass)
IV <sub>m</sub>		0.30	C105I I57N32C
VI <sub>m</sub>		0.39	C97I I75N49C

<sup>a</sup>Second heating and cooling.

 TABLE III  
 Order Parameters at the IN Transition for Twin Model Compounds Based on  
 Azoxybenzene Mesogen and Various Spacers

$\text{CH}_3-\text{O}-\text{C}_6\text{H}_4-\text{N}(\text{O})=\text{N}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{N}(\text{O})=\text{N}-\text{C}_6\text{H}_4-\text{OCH}_3$		$T_{IN}(\text{°C})$	$S_{zz}$
	R'		
II <sub>m</sub>	$-(\text{CH}_2)_3-\text{Si}-\text{O}-\text{Si}-(\text{CH}_2)_3-$	87	.280
VIII <sub>m</sub>	$-(\text{CH}_2)_9-$	212.5	.350
IX <sub>m</sub>	$-(\text{CH}_2)_{10}-$	208	.505
X <sub>m</sub>	$-(\text{CH}_2)_8-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-$ <sup>*</sup>	153.5	.485
PAA		136	.350

<sup>\*</sup>For the synthesis of this spacer see Reference 20.

scale of temperatures the corresponding weight fraction of the nematic mesophase  $f_N$ .

Table III gives the IN transition temperature (defined as the temperature for which  $f_N \rightarrow 10$ ) and the order parameter  $S_{zz}$  (at the point of collapse of the nematic mesophase).

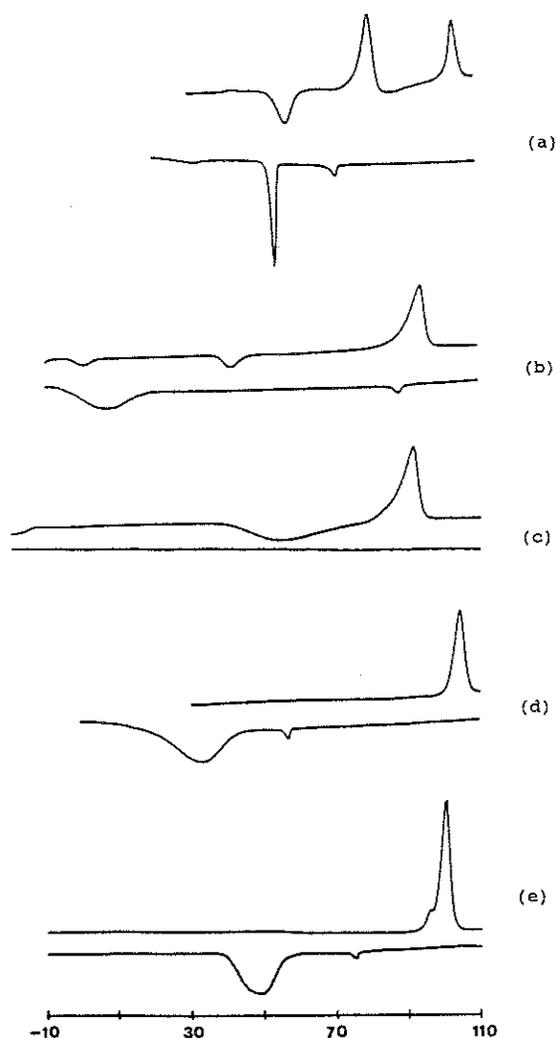
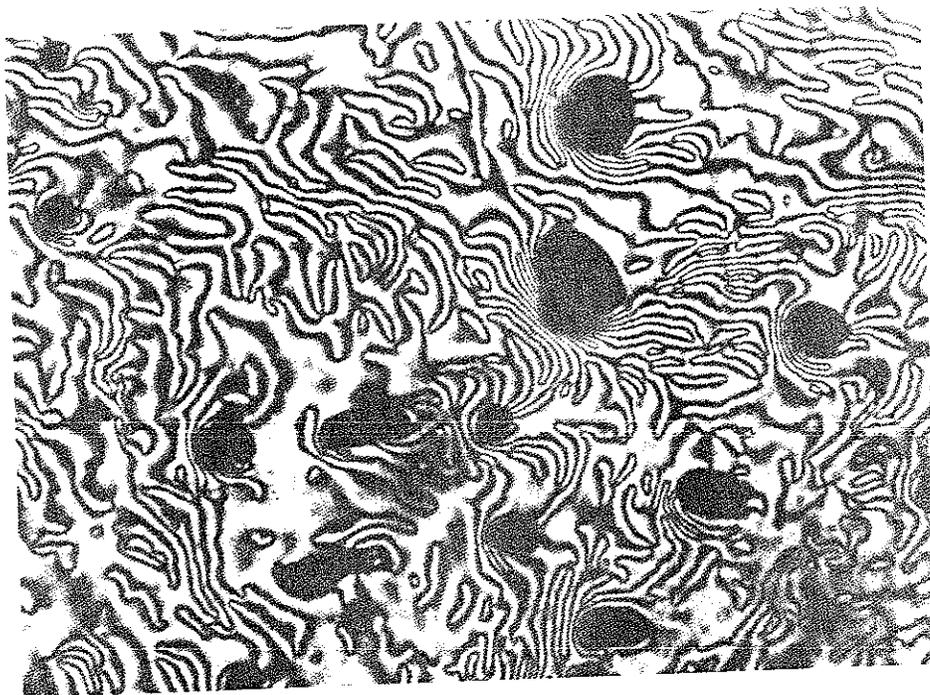
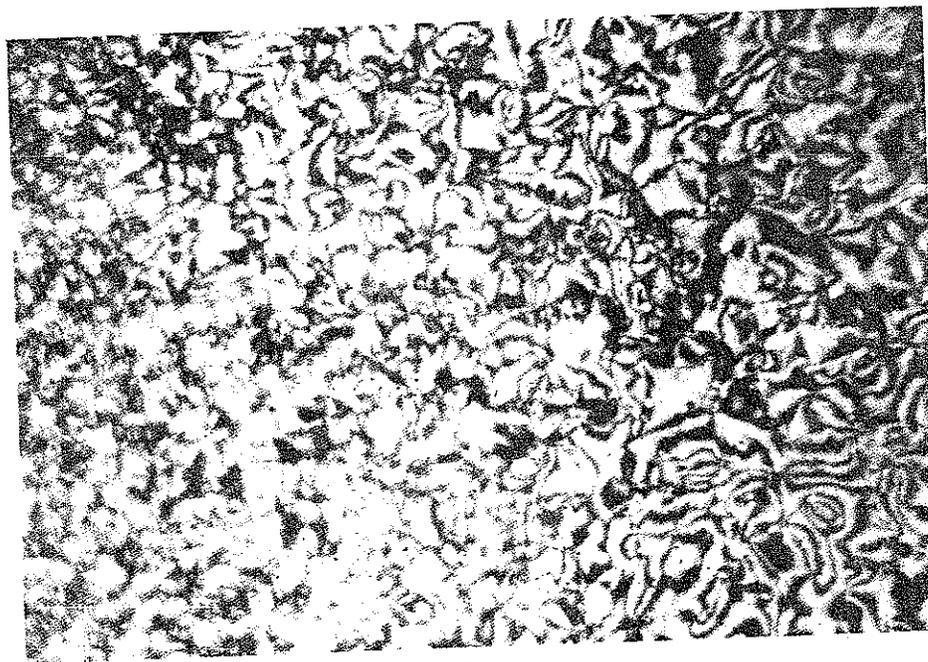


FIGURE 1 DSC Thermograms of Diester Model Compounds. The traces are taken on 2nd heating and cooling with a heating and cooling rate of  $20^{\circ}\text{C}/\text{min}$ . a) Compound  $\text{I}_m$ ; b) Compound  $\text{II}_m$ ; c) Compound  $\text{III}_m$ ; d) Compound  $\text{IV}_m$ ; e) Compound  $\text{V}_m$ .

It is apparent from Table III that the diester containing the siloxane bonded spacer displays the lowest order parameter at the I/N transition, followed closely by the diester with the undecanoic acid spacer ( $n = 9$ ) and PAA. The compounds with spacers of even parity such as  $\text{IX}_m$  or  $\text{X}_m$  display a higher order parameter. It is significant that the decline of  $S(T)$  in the vicinity of  $T_{IN}$  (as given in Figure 3) is most rapid for the siloxane containing twin model compound, similar to the very fast decline of  $S(T)$  for PAA. This suggests a stronger conformational disorder (or mesogene decoupling) in the siloxane containing model compounds than in the conventional analogues with spacers based exclusively on sequences of  $-\text{CH}_2-$  units. It is interesting that the introduction of one  $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$



(a)



(b)

FIGURE 2 Photomicrographs of "schlieren" textures of a) Diester  $II_m$  at  $76^\circ\text{C}$  (100X) b) Polymer  $II_o$  at  $81^\circ\text{C}$  (100X).

TABLE IV  
 Mesomorphic Properties of Polymers

Polymer	R	Viscosity <sup>a</sup> $\eta_{30}$ red.	Transition Temp. °C <sup>b</sup>
I <sub>p</sub>		0.24	C <sub>1</sub> 63C <sub>2</sub> 98I I76(S <sub>c</sub> )63C <sub>1</sub>
II <sub>p</sub>		0.22	C83S <sub>2</sub> 99I I79S <sub>2</sub> 33C
III <sub>p</sub>		0.22	C62I <sup>c</sup> Tg(-4)
IV <sub>p</sub>		0.23	C <sub>1</sub> 47C <sub>2</sub> 64I <sup>d</sup> I44C
V <sub>p</sub>		0.20	C <sub>1</sub> 109C <sub>2</sub> 139I I79C

<sup>a</sup>0.5 g/dl in tetrachloroethane, <sup>b</sup>from DSC, 2nd heating and cooling, <sup>c</sup>1st heating, <sup>d</sup>after annealing, <sup>e</sup>cold crystallization

sequence into a 9 bond containing methylene spacer produces a decrease of  $S_{zz}$  from .350 to .280 and an even more pronounced collapse of  $S$  at the isotropic/nematic transition (Compare II<sub>m</sub> and VIII<sub>m</sub> in Table III and see the respective  $S(T)$  slopes in Figure 3).

The properties of polymers with 5 different mesogenic moieties are given in Table IV. It can be seen that these polymers display a low value of reduced viscosity of about 0.2–0.25 dl/g in sym.tetrachloroethane at 30°C. Since chlorinated solvents such as sym.tetrachloroethane are good solvents for these polyesters (see for example Reference 13), the molecular mass corresponding to such values of viscosity is low and corresponds to degrees of polymerization in the high oligomeric range (DP 8-12). These estimates were confirmed by GPC measurements in chlorinated solvents.

It is interesting to observe that out of the five polymers described in Table IV only one polymer II<sub>p</sub> displays liquid crystallinity. The polymer II<sub>p</sub> gave a complex thermogram on heating while on cooling two distinctive and reproducible peaks were apparent. This can be seen from Figure 4(a).

The X-ray pattern of II<sub>p</sub> unequivocally indicates a mesophase of the type A or C. To distinguish between these two possibilities is difficult for the following reason: if we assume a model in which the smectic layers are composed of completely extended "all trans" repeating units then the measured layer thickness (24.4Å) and the Van der Waals length of the repeating unit 26.1Å differ by approximately 1.5Å and would suggest a maximum tilt of the repeating unit of some 20° (with respect

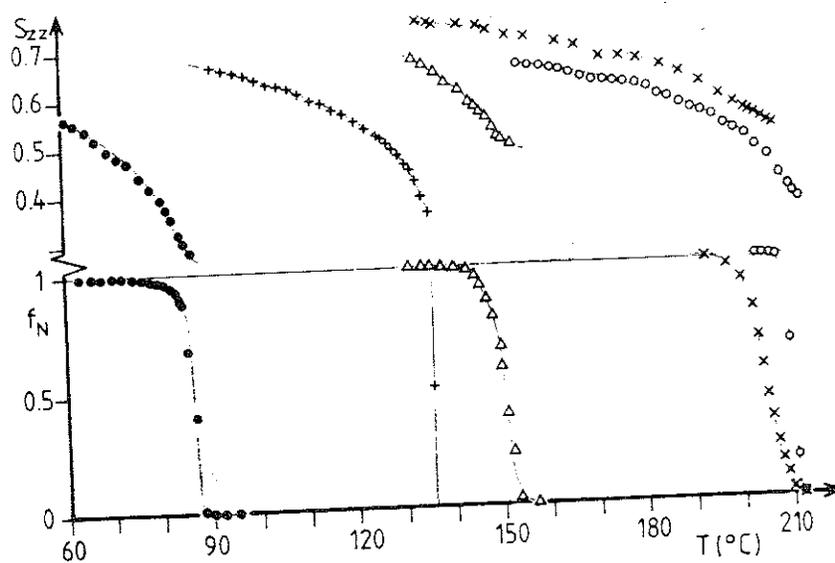


FIGURE 3 Order parameters  $S_{zz}$  and the nematic fraction of the biphas  $f_N$  as a function of temperature  $T$  for twin diesters containing the azoxy benzene mesogen (mesogen 8) and different spacers. From left to right:  $II_m$ , PAA,  $X_m$ ,  $VIII_m$ ,  $IX_m$  (see Table III).

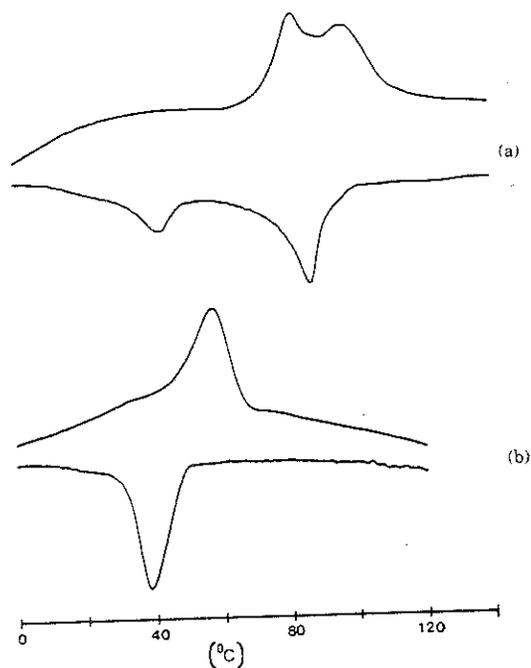


FIGURE 4 Thermograms of Polymer  $II_p$  (a) and  $IV_p$  (b) (2nd heating and cooling).

to the layer normal). However, a complete trans configuration of the spacer is unlikely and most certainly the discrepancy between the measured and calculated length of the spacer is smaller than the one based on the completely extended model. The "schlieren" texture observed for  $II_p$  under polarizing microscope is quite frequently encountered with smectic C phases<sup>14</sup> and we are therefore inclined to favor a smectic C phase for  $II_p$  with a rather small angle of tilt. Figure 5 a,b,c,d gives the diffraction patterns of the polymer  $II_p$  in its mesomorphic state.

Polymer  $I_p$  did not show any mesophases. Strong crystallinity was persistent on heating until the isotropization on melting. Polymer  $III_p$  crystallized with difficulty. The isotropic phase could be easily supercooled and the DSC thermograms displayed no sizable enthalpic effects (even on slow cooling at 5°C/min). Annealing overnight at room temperature (20–25°C above  $T_g$ ) induced crystallinity. The rather slow crystallization process of this polymer can be explained by a strongly distorted molecular configuration of the substituted mesogen which is known to impede easy packing and rapid crystallization.

Polymer  $IV_p$  showed crystallinity persistent until melting. Thermograms showed two overlapping peaks on the first heating and only one broad peak on the subsequent heating and cooling, see Figure 4(b). After overnight annealing the large peak at 63–64°C was preceded by a very small peak at 47°C. The X-ray data (see Table V) indicated persistent crystallinity. Similarly, polymer  $V_p$  did not show presence of any mesophase possibly because of its relatively high crystalline melting point. It is worth to note however that both transition temperatures C/C.L. and L.C./I are lower for the polymers than for the corresponding diesters (Tables II and IV). This is most unusual since macromolecular liquid crystals have higher clearing temperatures than their low molecular analogues and models. This may be due to the destabilizing influence of the siloxane bonds introduced into the spacer.

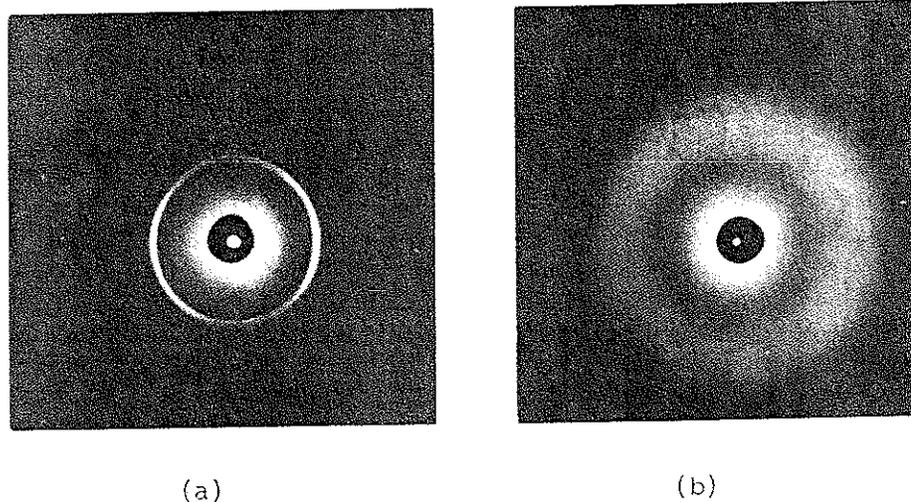


FIGURE 5 X-ray diffraction pictures of the polymer  $II_p$  at 85°C a) low angle and b) wide angle.

TABLE V  
X-ray Spacings of Polymers at Room and Elevated  
Temperatures

Polymer	d(spacings in Å)	
	Room Temperature	Elevated Temperature
I <sub>p</sub>	4.2(s);4.7(w);5.3(w)	90°C: 4.3(vs)
	6.3(w);10.7(vw);14.3(vw)	4.8(s);5.3(s) 6.2(s);6.9(vw) 10.3(s)
II <sub>p</sub>	4.0(m);4.4(s);5.4(m)	85°C: 24.4(s)
	6.1(w);6.9(w);7-8(vw)	4-5 (halo)
IV <sub>p</sub>	3.9(w);4.2(m);4.4(s)	59°C: 3.9(w)
	5.6(m);6.3(w);9.7(vw)	4.2(w);4.4(s)
	14.0(vw);19.3(s)	5.5(w);19.3(s)
V <sub>p</sub>	3.0(vw);3.9(m);4.3(m):	121°C: 3.81(w);4.1(m)
	4.7(m);5.1(s);6.0(w)	4.4(w);5.4(m) 6.0(w)

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

In conclusion, this study indicates that the introduction of a short tetramethyl-disiloxane moiety into an otherwise rather long spacer dramatically lowers the transition temperatures in both the low molecular (twin) diesters and polymers. In the twin model compounds the mesogen order parameter is decreased by insertion into the spacer of a  $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$  sequence of bonds. Enantiotropic mesophases of smectic or nematic type appear to be destabilized as is suggested by the appearance in all cases studied here of a monotropic nematic mesophase even in the case of mesogens such as azobenzene known to give in twin diesters smectic mesophases.<sup>15</sup> In contradistinction to diesters the mesophase changes from nematic to smectic C when a  $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$  sequence is inserted into a flexible polymethylene sequence for polymers with a similar mesogen such as polymer II<sub>p</sub> and poly(4,4'-dioxazyoxybenzene dodecanediyl) (DDA-8).<sup>16</sup> Such nematic to smectic change due to insertion of two siloxane bonds into the repeat unit of the polymer may well be due to microphase separation of the rigid and flexible portions of the repeating unit and a concomitant layer formation. The driving force for such microphase separation is apparently insufficient in the twin diester in which mesogen dominates the property of the molecule.

Interestingly, while as a general rule for compounds based on C—C backbone polymerization appears to stabilize the mesophase displayed by the corresponding monomer (side chain systems<sup>17,18</sup> and main chain systems<sup>19</sup>) in compounds investigated here and containing siloxane bonds it appears to hamper rather than to further liquid crystallinity. Thus the diesters I<sub>m</sub> and IV<sub>m</sub> display a monotropic nematic mesophase while the corresponding polymers are crystalline and this despite of rather low crystalline melting points.

The above results show clearly that the introduction of even a very small number of siloxane bonds into the repeating unit of a main chain liquid crystalline polymers has a strong effect on its mesomorphic behavior. Much more work with different well characterized systems is necessary to fully understand this phenomenon.

### Acknowledgment

This work was supported by the National Science Foundation Polymer Program under Grant DMR-8600029 and Grant INT-871501. Thanks are expressed to Dr. F. Volino for helpful discussions and assistance with NMR studies. Thanks are also due to Dr. Rita B. Blumstein and Dr. C. H. Lin for helpful discussions.

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