Liquid Crystalline Behavior of Linear Permethyloligosilanes

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Permethyloligosilanes, $Me(SiMe_2)_nMe$ where n = 9, 10, 11, and 12, show the enantiotropic smectic B phase. In the liquid crystalline state, the silicon chains of these oligosilanes adopt all-*trans* conformation.

Linear oligosilanes show the unique electronic and optical properties, which are attributed to the σ-electrons delocalized along the silicon main chains[1,2] and thus anisotropic with respect to the silicon chain direction.[3] Liquid crystalline oligosilanes are very interesting as a new class of materials because the physical properties in the liquid crystalline phase are expected to be different from those in solution and in the liquid and solid phases.[4] In addition, the physical properties would be anisotropically controlled by the application of magnetic and electric fields in the liquid crystalline state. Very recently, we have synthesized the first liquid crystalline oligosilanes with alkoxybiphenyl groups, $ROC_{12}H_8(SiMe_2)_6C_{12}H_8OR$ (R = C_8H_{17} (**1**) and $C_{10}H_{21}$ (**2**)).[5] Oligosilanes **1** and **2** show the monotropic smectic B and the enantiotropic smectic E phases, respectively. On the other hand, we have recently prepared the first vacuum-deposited film of permethyloligosilane, $Me(SiMe_2)_{12}Me$ (**3**).[3] In the thin film, the oligosilane molecules form a multilayer structure similar to that observed in a smectic B phase. In the course of our studies on oligosilanes, we have found the liquid crystalline properties of oligosilane **3**, which has no mesogen such as a biphenyl unit. DSC thermograms (only on heating) [6] and melting points [7a-c] of permethyloligosilanes have been given so far, but there has been no study on their liquid crystalline behavior. Herein, we report the liquid crystalline behavior of a series of permethyloligosilanes, $Me(SiMe_2)_nMe$ where n = 9 (**4**), 10 (**5**), 11 (**6**), and 12 (**3**), together with their molecular structures in the mesophase.

Oligosilanes **3** and **4** were prepared by treatment of a mixture of 1-chlorotrisilane and 1,3-dichlorotrisilane with sodium in toluene, in a similar manner to the literature procedure,[7] as shown in Scheme 1. Oligosilanes **5** and **6** and permethyloctasilane (**7**) were also obtained from the corresponding α-chlorooligosilane and α,ω-dichlorooligosilane in a similar way. The crude yield of each oligosilane was *ca.* 10%, and these oligosilanes were successfully purified with a preparative HPLC.

The thermal properties of oligosilanes **3**-**7** were examined by the combination of DSC measurements and polarizing microscopy. The values for the transition temperatures and the associated enthalpies for these compounds are summarized in Table 1. Octasilane **7** does not show any liquid crystalline phase; only the crystalline-isotropic transition occurs at 61 °C on heating and at 52 °C on cooling. In contrast to **7**, oligosilanes **3**-**6** with longer silicon chains exhibit the enantiotropic liquid crystalline phase. For dodecasilanes **3**, two endothermic peaks (ΔH = 24.4 and 18.9 $kJmol^{-1}$) are observed at 95 and 147 °C on heating, respectively. Upon cooling, two exothermic peaks (ΔH = 18.2 and 22.3 $kJmol^{-1}$) appear at 150 and 88 °C. The transition peaks at 95 and 88 °C are attributable to the crystalline-mesophase transitions, whereas the peaks at 147 and 150 °C are ascribable to the mesophase-isotropic transitions.[6] Thus, a lancets texture typical of the smectic B phase [8a] is observed in the range of 95-147 °C on heating and 150-88 °C on cooling, as shown in Figure 1. Oligosilanes **4**-**6** also show a lancets texture, like **3**, indicating the smectic B mesophase. Nonasilane **4** forms the mesophase from 54 to 86 °C on heating and from 84 to 50 °C on cooling, while decasilanes **5** are smectic from 82 to 114 °C on heating and from 111 to 74 °C on cooling. For undecasilanes **6**, the meso-

Table 1. Transition temperatures and enthalpies (ΔH) for permethyloligosilanes **3**-**7**, $Me(SiMe_2)_nMe$

compd	n	transition temperatures / °C [ΔH / $kJmol^{-1}$] [a]
7	8	$K \underset{52\ [29.8]}{\overset{61\ [28.3]}{\rightleftharpoons}} I$
4	9	$K \underset{50\ [17.0]}{\overset{54\ [18.9]}{\rightleftharpoons}} S_B \underset{84\ [11.0]}{\overset{86\ [11.4]}{\rightleftharpoons}} I$
5	10	$K \underset{74\ [24.3]}{\overset{82\ [24.2]}{\rightleftharpoons}} S_B \underset{111\ [15.6]}{\overset{114\ [15.5]}{\rightleftharpoons}} I$
6	11	$K \underset{67\ [17.8]}{\overset{70\ [20.0]}{\rightleftharpoons}} S_B \underset{131\ [15.8]}{\overset{131\ [16.2]}{\rightleftharpoons}} I$
3	12	$K \underset{88\ [22.3]}{\overset{95\ [24.4]}{\rightleftharpoons}} S_B \underset{150\ [18.2]}{\overset{147\ [18.9]}{\rightleftharpoons}} I$

[a] K: crystalline, S_B: smectic B, I: isotropic.

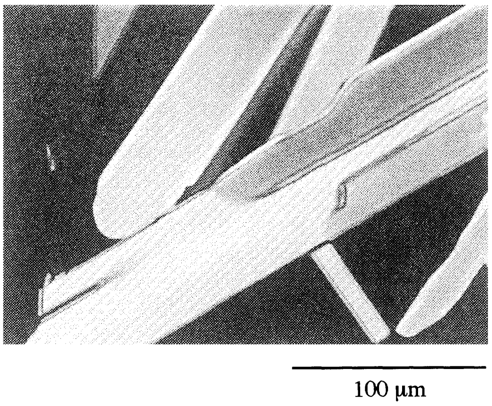
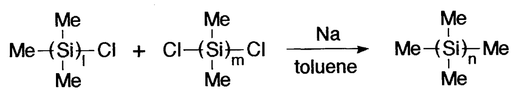


Figure 1. Optical texture of oligosilane **3** at 120 °C on cooling.



$$Me\!-\!(\underset{Me}{\overset{Me}{Si}})_l\!-\!Cl + Cl\!-\!(\underset{Me}{\overset{Me}{Si}})_m\!-\!Cl \xrightarrow[\text{toluene}]{\text{Na}} Me\!-\!(\underset{Me}{\overset{Me}{Si}})_n\!-\!Me$$

4: n = 9; **3**: n = 12 (l = 3, m = 3); **5**: n = 10 (l = 3, m = 4)
7: n = 8; **6**: n = 11 (l = 4, m = 3)

Scheme 1.

phase is formed in the range of 70-131 °C on heating and 131-67 °C on cooling. When the number of dimethylsilylene units is increased from eight to twelve, the isotropization temperature increases monotonously from 61 to 147 °C.[7a] In contrast, the crystalline-mesophase transition temperature increases alternately with an even-odd effect, with increasing length of the silicon chain (54, 82, 70, and 95 °C for **4**, **5**, **6**, and **3**, respectively).

Furthermore, the structures of the mesophase for oligosilanes **3**-**6** were investigated by X-ray diffraction method. The *d*-spacings found are listed in Table 2. The X-ray pattern for **3** shows only sharp peaks at 25.5 Å (d_{001}) and 12.8 Å (d_{002}) corresponding to the first and second order reflections of the smectic layer in the small angle region (Figure 2). This interlayer distance is in excellent agreement with the long spacing of 25.7 Å observed for the vaccum-deposited film of **3**, in which the silicon chains with all-*trans* conformation are oriented perpendicular to the substrate.[3] An intense peak at 6.86 Å (d_{100}), followed by a weak peak at 3.99 Å (d_{110}) corresponding to $d_{100}/\sqrt{3}$, is observed in the wide angle region. These peaks are attributed to the reflections of the hexagonal lattice with $a = b = 7.92$ Å, $\gamma = 120°$ and the lattice constants a and b ($d_{100} \times 2/\sqrt{3}$) correspond to the intermolecular distance between the nearest molecular chains.[8] While the intermolecular distances are almost the same in all the compounds (7.82, 7.91, and 7.84 Å for **6**, **5**, and **4**, respectively), the interlayer distances decrease regularly by 2.0 Å per silicon unit with decreasing length of the silicon chain (23.5, 21.5, and 19.5 Å for **6**, **5**, and **4**). The Δd_{100} values are the same as the *d*-spacing of 1.99 Å corresponding to the sub-cell 002 in the deposited film of **3**.[3] These results indicate that in all the compounds the silicon chains with all-*trans* conformation are perpendicular to the smectic laylers and hexagonally ordered within the layers. Interestingly, the silicon chains of these permethyloligosilanes adopt all-*trans* conformation in the smectic B phase, whereas the conformation of silicon backbones is disordered for polysilanes with alkyl chains in the hexagonal columnar mesophase.[9]

Table 2. The *d*-spacings / Å and the lattice constant *a* / Å for permethyloligosilanes **3-6**, $Me(SiMe_2)_nMe$, in the mesophase

compd	n	d_{001}	Δd_{001}	d_{002}	d_{100}	d_{110}	a
4	9	19.5	2.0	9.8	6.77	-	7.82
5	10	21.5	2.0	-	6.85	-	7.91
6	11	23.5	2.0	11.7	6.79	3.92	7.84
3	12	25.5		12.8	6.86	3.99	7.92

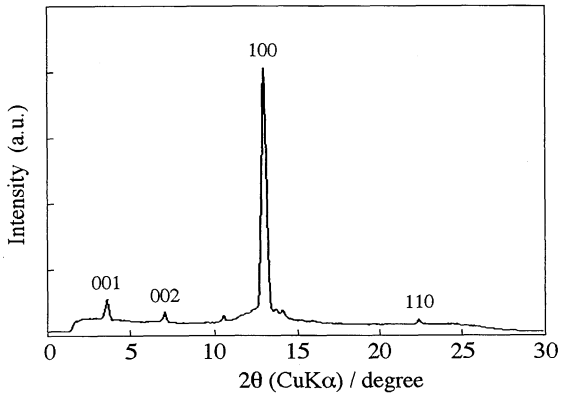


Figure 2. X-ray diffraction pattern of oligosilane **3** at 120 °C.

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