Mesomorphic Properties of Oligosilanes with Phenyl End Groups

Tetsuo Yatabe,* Nobutsugu Minami, Hajime Okumoto, and Katsuhiko Ueno
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565

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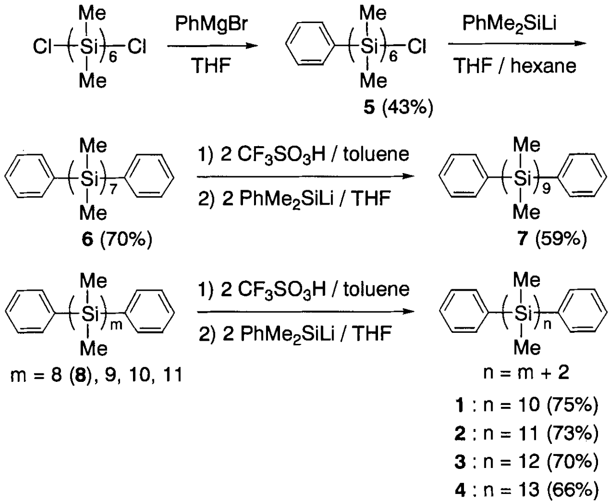
Oligosilanes with phenyl end groups, $Ph(SiMe_2)_nPh$ where n = 10, 11, 12 and 13, were synthesized and their thermal and structural properties were studied. Dodecamer and tridecamer possessed mesophases showing the interdigitated structure in the range of 126–139 and 127–155 °C, respectively. In the mesophase, the silicon chains adopted the all-*trans* conformation.

Linear oligosilanes, $R(SiR_2)_nR$ where R = organic groups, are a new class of interesting organic optoelectronic materials because of their mesomorphism[1–3] and photoconductive properties.[4,5] We found that a series of permethyloligosilanes, $Me(SiMe_2)_nMe$ where n = 9, 10, 11, and 12, possess smectic B phase, where the molecular axes are perpendicular to the layer plane and hexagonally packed within each layer.[2,6] Reflecting such an ordered structure, $Me(SiMe_2)_{10}Me$ demonstrates high charge carrier mobility exceeding 1×10^{-3} cm^2/Vs in its crystalline phase that is formed by annealing via the mesophase.[5] Moreover, our series of works established that their mesomorphic properties can be tuned by manipulating the molecular structure. The mesomorphic transition temperature becomes higher for longer Si chains. The replacement of the Me end groups of permethyldecasilane with longer alkyls (Et, Pr, and Bu) results in the occurrence of the interdigitated B phase, where the oligosilane molecules are hexagonally ordered and the alkyl chains are interdigitated between the neighboring layers.[3] In addition, the use of Pr and Bu end groups here considerably lowers the mesomorphic transition temperature (Me: 82–114; Pr: 22–87; Bu: 23–69 °C). On the other hand, from the viewpoint of optoelectronic applications, the use of phenyl end groups is intriguing because the π-interaction between the end groups might facilitate intermolecular carrier hopping. Herein we report the synthesis and the thermal and structural properties of oligosilanes with phenyl end groups, $Ph(SiMe_2)_nPh$ where n = 10 (**1**), 11 (**2**), 12 (**3**), and 13 (**4**).

Oligosilanes **1**–**4** were synthesized according to Scheme 1. 1,6-Dichloropermethylhexasilane[7] was treated with 1 equiv of PhMgBr to give hexasilane **5**. Heptasilane **6** was prepared by treatment of hexasilane **5** with $PhMe_2SiLi$. Treatment of heptasilane **6** with 2 equiv of CF_3SO_3H, followed by addition of 2 equiv of $PhMe_2SiLi$ gave nonasilane **7**. Undeca- and trideca-silanes **2** and **4** were prepared by repeating this reaction. Deca- and dodecasilanes **1** and **3** were obtained from octasilane **8**[3] in a similar manner. The products were purified by silica gel chromatography and subsequently by HPLC.[8]

The thermal properties of oligosilanes **1**–**4** were studied using polarizing microscopy and DSC. The transition temperatures and the associated enthalpies are summarized in Table 1. Deca- and undecasilanes **1** and **2** did not show any mesophases unlike decasilanes with alkyl end groups. In contrast, oligosilanes **3** and **4** showed enantiotropic mesophases; a texture similar to a lancet texture typical of a smectic B phase[9] was observed both on heating and on cooling. For **3** the mesomorphic state occurred in the range of 126–139 °C on heating and 138–122 °C on cooling. For **4** it was 127–155 °C on heating



Scheme 1.

Table 1. Transition temperatures and enthalpies (Δ*H*) for oligosilanes with pheny end groups **1**-**4**, $Ph(SiMe_2)_nPh$

Compd	n	Transition temperatures / °C [Δ*H* / kJmol^{-1}]^a
1	10	$K \underset{115\,[56.0]}{\overset{118\,[56.1]}{\rightleftarrows}} I$
2	11	$K \underset{122\,[57.1]}{\overset{125\,[57.8]}{\rightleftarrows}} I$
3	12	$K \underset{122\,[38.6]}{\overset{126\,[38.1]}{\rightleftarrows}} M \underset{138\,[23.8]}{\overset{139\,[24.2]}{\rightleftarrows}} I$
4	13	$K \underset{123\,[38.1]}{\overset{127\,[37.7]}{\rightleftarrows}} M \underset{155\,[25.8]}{\overset{155\,[26.1]}{\rightleftarrows}} I$

^{a}K: crystalline, M: mesophase (interdigitated B), I: isotropic.

Table 2. The *d*-spacings / Å and the lattice constant *a* / Å for oligosilanes **3** and **4**, $Ph(SiMe_2)_nPh$, in the mesophase

Compd	n	d_{002}	d_{004}	d_{100}	d_{110}	d_{200}	*a*
3	12	28.0	14.0	6.81	3.97	-	7.86
4	13	30.0	15.0	6.92	4.00	3.46	7.99

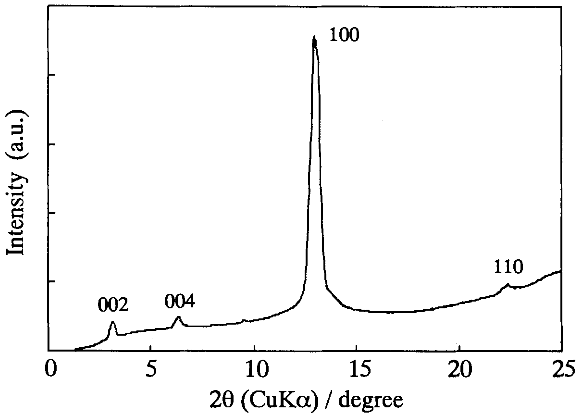


Figure 1. X-Ray diffraction pattern of dodecasilane **3** at 130 °C.

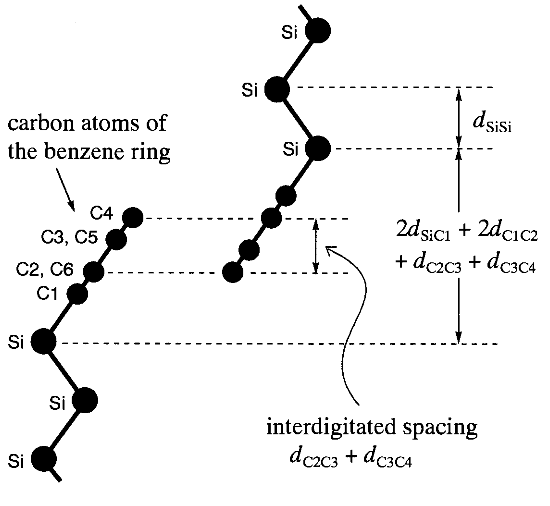


Figure 2. Schematic illustration of the interdigitated structure for oligosilanes **3** and **4** in the mesophase. Carbon atoms of the methyls on the silicon atoms are omitted.

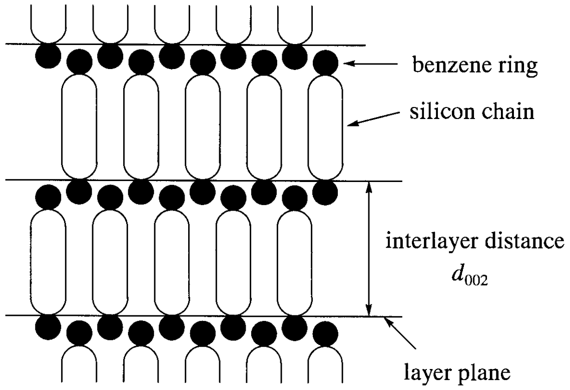


Figure 3. Schematic illustration of the interdigitated structure for oligosilanes **3** and **4** in the mesophase.

and 155–123 °C on cooling. Compared with permethyldodecasilane **9** (smectic B: 95–147 °C),[2] **3** exhibited the lower clearing point and the narrower mesomorphic range.

Intermolecular and interlayer distances for **3** and **4** in the mesophase were obtained by X-ray diffractometry. The *d*-spacings are listed in Table 2. For **3**, a intense peak at 6.81 Å (d_{100}) and a very weak peak at 3.97 Å (d_{110}) are attributed to the reflections from the hexagonal lattice with $a = b = 7.86$ Å, $\gamma = 120°$ (Figure 1). The lattice constant a corresponds to the intermolecular distance between the nearest molecules within the layer. Its value was almost the same as that of permethyldecasilane **9** (7.92 Å).[2] Two peaks at 28.0 Å (d_{002}) and 14.0 Å (d_{004}) are attributed to the reflections from the smectic layer.[3,10] It should be noted that the interlayer distance (28.0 Å) was shorter by 3.4 Å than the extended molecular length estimated form a molecular model; this is different from **9**, for which they coincide. The interlayer distance for **4** (30.0 Å) was longer by 2.0 Å than that for **3**. These distances are in good agreement with the values calculated by the use of an equation: $(n\text{-}1)d_{\mathrm{SiSi}} + 2d_{\mathrm{SiC1}} + 2d_{\mathrm{C1C2}} + d_{\mathrm{C2C3}} + d_{\mathrm{C3C4}}$, where n is the number of silicon atoms and d_{XY} is the spacing between atoms X and Y projected onto the axis of the silicon chain having the all-*trans* conformation: $d_{\mathrm{SiSi}} = 1.99$; $d_{\mathrm{SiC1}} = 1.52$; $d_{\mathrm{C1C2}} = d_{\mathrm{C3C4}} = 0.61$; $d_{\mathrm{C2C3}} = 1.15$ Å, as estimated from a molecular model shown in Figure 2. These results indicate that the silicon chains adopted the all-*trans* conformation and were perpendicular to the layer plane and hexagonally ordered within the layer. Furthermore, the phenyls at both ends of a silicon chain were shown to be interdigitated between the neighboring layers, as illustrated in Figure 3. Such interdigitated B phases of **3** and **4** are similar to those of the decasilanes with alkyl chains (Et, Pr, and Bu) and mark a difference from permethyldodecasilane **9**.

References and Notes

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8 **1**: ^{1}H MNR ($\mathrm{CDCl_3}$, δ) 0.08 (12 H, s), 0.12 (12 H, s), 0.14 (12 H, s), 0.16 (12 H, s), 0.38 (12 H, s), 7.27–7.35 (6 H, m), 7.39–7.47 (4 H, m); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) –5.28, –4.38, –4.08, –4.03, –2.92, 127.69, 128.30, 133.74, 139.90. **2**: ^{1}H MNR ($\mathrm{CDCl_3}$, δ) 0.07 (12 H, s), 0.12 (12 H, s), 0.14 (12 H, s), 0.16 (12 H, s), 0.17 (6 H, s), 0.37 (12 H, s), 7.28–7.34 (6 H, m), 7.39–7.46 (4 H, m); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) –5.29, –4.38, –4.09, –4.02, –3.99, –2.93, 127.68, 128.29, 133.73, 139.90. **3**: ^{1}H MNR ($\mathrm{CDCl_3}$, δ) 0.07 (12 H, s), 0.12 (12 H, s), 0.14 (12 H, s), 0.16 (12 H, s), 0.17 (12 H, s), 0.37 (12 H, s), 7.26–7.35 (6 H, m), 7.38–7.46 (4 H, m); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) –5.29, –4.39, –4.09, –4.02, –3.99, –2.93, 127.68, 128.29, 133.73, 139.90. **4**: ^{1}H MNR ($\mathrm{CDCl_3}$, δ) 0.08 (12 H, s), 0.12 (12 H, s), 0.14 (12 H, s), 0.17 (12 H, s), 0.18 (18 H, s), 0.38 (12 H, s), 7.28–7.34 (6 H, m), 7.39–7.46 (4 H, m); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) –5.29, –4.38, –4.08, –4.00, –3.97 (× 2), –2.93, 127.68, 128.29, 133.73, 139.90.
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