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Synthesis and Mesomorphism of α,ω-Diphenylpermethyl-oligosilanes

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α,ω-Diphenylpermethyloligosilanes, $Ph(SiMe_2)_nPh$ where n = 12 (**3**), and 13 (**4**), showed the mesophases in the range of 126–139 and 127–155 °C, respectively. In the mesophases, 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 the silicon chain were interdigitated between the neighboring layers.

Keywords: oligosilane; mesophase; interdigitated structure

INTRODUCTION

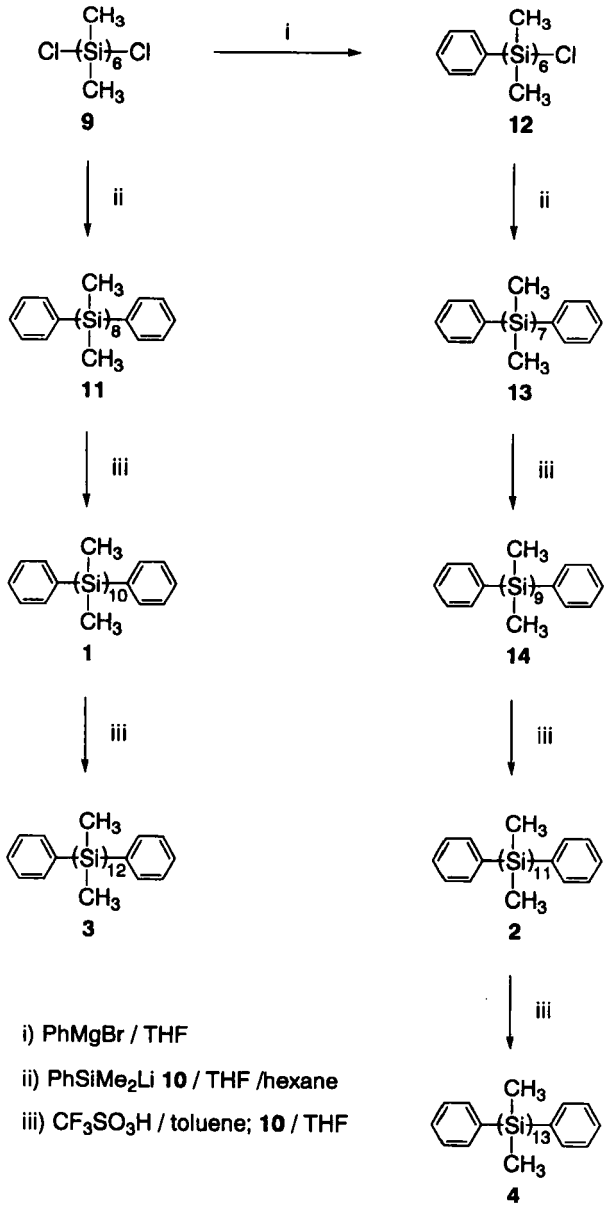
Linear oligosilanes, $R(SiR_2)_nR$ where R = organic groups, are a new class of interesting organic optoelectronic materials because of their

mesomorphism[1-3] and photoconductive properties[4,5]. We found that a series of permethyloligosilanes, $Me(SiMe_2)_nMe$ where n = 9 (**5**), 10 (**6a**), 11 (**7**), and 12 (**8**), possess the smectic B phase, where the molecular axes are perpendicular to the layer plane and hexagonally packed within each layer[2]. Reflecting such an ordered structure, permethyldecasilane **6a** demonstrates high charge carrier mobility exceeding 1 x 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 with the odd-even effect for longer silicon chains (54-86, 82-114, 70-131, and 95-147 °C for **5**, **6a**, **7**, and **8**, respectively). The replacement of the Me end groups of the decasilane **6a** with longer alkyls, $R(SiMe_2)_{10}R$ where R = Et (**6b**), Pr (**6c**), and Bu (**6d**), 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 (82-114, 50-105, 22-87, 23-69 °C for **6a-d**, respectively). 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 a series of α,ω-diphenylpermethyloligosilanes, $Ph(SiMe_2)_nPh$ where n = 10 (**1**), 11 (**2**), 12 (**3**), and 13 (**4**).

RESULT AND DISCUSSION

Synthesis

The diphenyl-substituted oligosilanes **1-4** were synthesized according to Scheme 1. 1,6-Dichloropermethylhexasilane (**9**)[6] was treated with 2 equiv. of (dimethylphenylsilyl)lithium (**10**) at 0 °C to give 1,8-diphenyl-



SCHEME 1

phenylpermethyloctasilane (**11**) in 83% yield. Treatment of 1,8-diphenyloctasilane **11** in toluene cooled to 20 °C with 2 equiv. of trifluoromethanesulfonic acid, followed by addition of 2 equiv. of phenylsilyllithium **10** in THF gave 1,10-diphenydecasilane **1** in 88% yield. This reaction should be important because of the substitution of phenyl end groups with dimethylphenylsilyl units in a moderate yield. 1,12-Diphenyldodecasilane **3** was prepared form 1,10-diphenyldecasilane **1** in a similar manner, in 70% yield. The deca- and dodecasilanes **1** and **3** were purified by silica gel chromatography with hot heptane and subsequently by high performance liquid chromatography (HPLC) with toluene. **1**: ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, δ) –5.28, -4.38, -4.08, -4.03, -2.92, 127.69, 128.30, 133.74, 139.90. **3**: ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, δ) –5.29, -4.39, -4.09, -4.02, -3.99, -2.93, 127.68, 128.29, 133.73, 139.90.

A mixture of 1,6-dichlorohexasilane **9** and 1 equiv. of phenylmagnesium bromide in THF was heated under reflux to give 1-chloro-6-phenylpermthylhexasilane (**12**) in 43% yield. A THF solution of silyllithium **10** was added to a hexane solution of 1-chloro-6-phenylhexasilane **12** cooled to 0 °C, giving 1,7-diphenylpermethylheptasilane (**13**) in 70% yield. Treatment of a toluene solution of 1,7-diphenylheptasilane **13** cooled to 10 °C with 2 equiv. of trifluoromethanesulfonic acid, followed by addition of 2 equiv. of silyllithium **10** gave 1,9-diphenypermethylnonasilane (**14**) in 59% yield. 1,11-Diphenylundecasilane **2** and 1,13-diphenyltridecasilanes **4** were prepared by repeating this reaction in 73 and 66% yields, respectively. Silica gel chromatography with hot hexane and subsequently by HPLC with toluene gave pure products. **2**: ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, δ) –5.29, -4.38, -4.09, -4.02, -3.99, -2.93, 127.68, 128.29, 133.73, 139.90. **4**: ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, δ) –5.29, -4.38, -4.08, -4.00, -3.97 (x 2), -2.93, 127.68, 128.29, 133.73, 139.90.

Mesomorphism

The thermal properties of the oligosilanes **1-4** were investigated by differential scanning calorimetry (DSC) measurements and polarizing microscopy. The transition temperatures and the associated enthalpies are summarized in Table 1. Deca- and undeca- silanes **1** and **2** did not show any mesophases unlike decasilanes **6a-d** with alkyl end groups. In contrast, dodeca- and trideca-silanes **3** and **4** with longer silicon chains showed enantiotropic mesophases; a texture similar to a lancet texture typical of a smectic B phase[7] was observed both on heating and on cooling. For the dodecasilane **3** the mesomorphic state occurred in

TABLE 1 Transition temperatures and enthalpies (ΔH) for oligosilanes **1-4**, $Ph(SiMe_2)_nPh$

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

the range of 126-139 °C on heating and 138-122 °C on cooling. For the tridecasilane **4** it was 127-155 °C on heating and 155-123 °C on cooling. Compared with the permethyl-substituted dodecasilane **8** (smectic B: 95-147 °C), the 1,12-diphenyl-substituted dodecasilane **3** exhibited the lower clearing point and the narrower mesomorphic range.

Intermolecular and interlayer distances for the oligosilanes **3** and **4** in the mesophase were obtained by X-ray diffractometry. The *d*-spacings are listed in Table 2. For the dodecasilane **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, $\gamma = 120$ deg. 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 the permethyl-substituted dodecasilane **8** (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]. The peaks assigned to d_{001} and d_{003} were not observed because of the extinction rule of reflection[8]. 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 the permethyl-substituted dodecasilane **8**, for which they coincide. The interlayer distance for the tridecasilane **4** (30.0 Å) was longer by 2.0 Å than that for the dodecasilane **3**. These distances are in good agreement with the values calculated by the use of an equation: $(n-1)d_{SiSi} + 2d_{SiC1} + 2d_{C1C2} + d_{C2C3} + d_{C3C4}$, where n is the number of silicon atoms and d_{XY} is the spacing between atoms X and Y

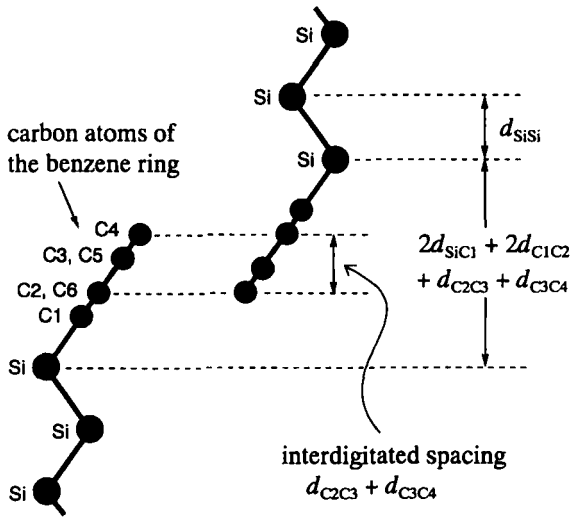


FIGURE 1 Schematic illustration of the interdigitated structure for oligosilanes **3** and **4** in the mesophase. Carbon atoms of the methyls on the silicon atoms are omitted.

projected onto the axis of the silicon chain having the all-*trans* conformation: d_{SiSi} = 1.99; d_{SiC1} = 1.52; d_{C1C2} = d_{C3C4} = 0.61; d_{C2C3} = 1.15 Å, as estimated from a molecular model shown in Figure 1. 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. Such interdigitated B phases observed in the oligosilanes **3** and **4** with phenyl end groups are similar to those of the decasilanes **6b-d** with alkyl chains (Et, Pr, and Bu) and mark a difference from the permethyl-substituted oligosilanes **5**, **6a**, **7**, and **8**.

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