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Amorphous Poly[(alkoxy-*n*-alkyl)methylsilane]s and Crystalline Poly[bis(alkoxy-*n*-alkyl)silane]s: The Effect of Side-Chain Flexibility on the Thermochromic Transition

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ABSTRACT: Temperature-dependent UV spectra of three isomeric, amorphous, ether-substituted polymethylsilanes, $(RMeSi)_n$ [R = $(CH_2)_6OCH_3$, $(CH_2)_5OC_2H_5$, and $(CH_2)_4OC_3H_7$], show that, in the solid state, the thermochromic pattern and transition temperature depend on the nature of the ether substitutent. A discontinuous transition from 303 to 330 nm was observed for both methoxyhexyl and ethoxypentyl polymers, whereas the propoxybutyl polymer merely showed a gradually shifted absorption. As the oxygen atom is placed closer to the main chain, the glass transition temperature and ^{29}Si spin-lattice relaxation time decrease, consistent with enhanced side-chain motions. Three symmetrical ether-substituted polysilanes, $(R_2Si)_n$ [R = $(CH_2)_6OCH_3$, $(CH_2)_5OC_2H_5$, and $(CH_2)_4OC_3H_7$], were also investigated. These polymers exist as hexagonal columnar mesophases above their transition temperatures; below the transition temperature, they crystallized and exhibited a distinct thermochromism from 320 to 352 nm.

I. Introduction

The importance of conformational defects in influencing the electronic structure of conjugated polymers is well acknowledged.[1] In the presence of conformational defects, the delocalization of valence electrons is effectively interrupted, and the polymer chain is divided into electronically independent "subchains" with smaller conjugation lengths.[2] As a consequence, the optical absorption of the conjugated polymer chain shifts to higher energies. For the σ-conjugated polysilanes,[3] conformational defects can be formed within the linear silicon chain by rotating the skeletal bonds out of planarity. In the absence of bulky substitutents and strong interchain interactions, the inherently low rotation energy of the silicon−silicon bond (1.1−1.2 kcal/mol)[4] is comparable to ambient thermal energies (RT $\cong$ 0.6 kcal/mol at room temperature), so the conformation of the silicon backbone may be strongly influenced by variations in temperature.

Polysilanes are commonly found to undergo a discontinuous thermochromic transition.[5] The study of poly(*n*-alkylmethylsilane)s[6] indicates that a long, extended alkyl side chain can induce strong dispersion forces, leading to a discontinuous shift in the absorption maximum. During the thermochromic transition, the change in molecular structure from a random coil to a rigid rod allows an increase in the intermolecular interactions via a better interchain packing. It is plausible that a conformationally flexible and, hence, disordered side chain might destabilize the rodlike silicon skeleton[7,8] and so prevent the occurrence of a discontinuous thermochromic transition.

According to earlier studies of ether derivatives,[9] the incorporation of an oxygen atom into a side chain should increase the chain flexibility. This is due to the large rotational freedom of the C−O−C linkage and a strong preference for gauche conformations at the carbon atoms bonded to oxygen. To explore the possible effects of oxygen substitution on side-chain flexibility, three isomeric amorphous ether-substituted polymethylsilanes were prepared and characterized. A series of symmetrical polysilanes, $(R_2Si)_n$, with the same three substitutents were also investigated. In both series of polymers, the side groups are isomeric, containing seven carbon atoms and one oxygen atom; the position of the ether oxygen in the side chain was varied.

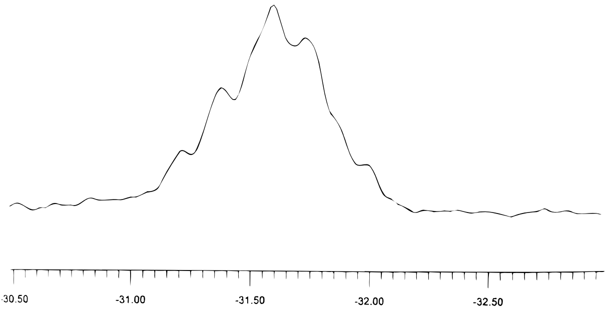

Figure 1. ^{29}Si NMR (99.36 MHz) in benzene-d_6 of poly[(6-methoxy-*n*-hexyl)methylsilane].

II. Results and Discussion

(a) Poly(*n*-octylmethylsilane) and Poly[(alkoxy-*n*-alkyl)methylsilane]s. Three ether-substituted polymethylsilanes, $(RMeSi)_n$ [R = $(CH_2)_6OCH_3$, $(CH_2)_5OC_2H_5$, and $(CH_2)_4OC_3H_7$], were prepared by reducing the corresponding diorganodichlorosilane in the presence of 2 equiv of sodium. The silicon-29 nuclear resonances of the resulting polysilanes clearly indicate a random stereoconfiguration. As an example, the ^{29}Si NMR spectrum for poly[(methoxy-*n*-hexyl)methylsilane] is illustrated in Figure 1. The multiple resonances are resolved at the pentad level, characteristic of an atactic homopolymer. These polymers were examined by wide-angle X-ray diffraction (WAXD) and showed completely amorphous patterns at the study temperatures, consistent with an irregular assembly of silicon units along the backbone. The WAXD pattern for poly[(methoxy-*n*-hexyl)methylsilane], shown in Figure 2, is a representative example.

The optical spectra of the three ether-substituted polymethylsilanes as a function of temperature are

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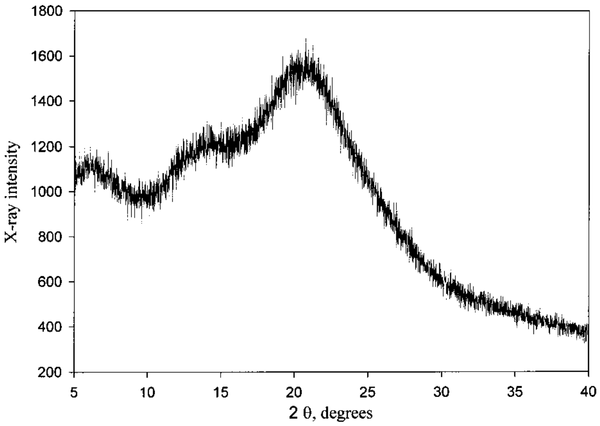

Figure 2. WAXD pattern for $[CH_3O(CH_2)_6SiMe]_n$, showing amorphous halo. The patterns for the isomeric polymers are very similar.

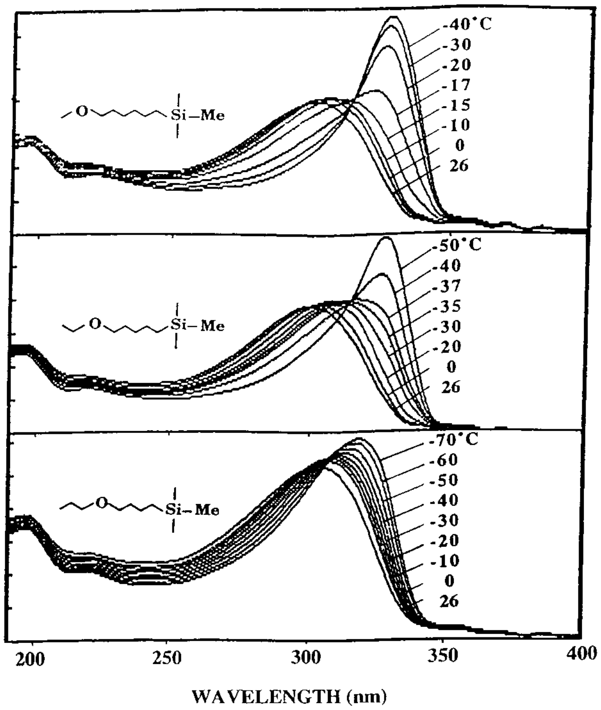

Figure 3. Temperature evolution of the UV spectra of $(RSiMe)_n$ films, with R = $(CH_2)_6OCH_3$ (top), $(CH_2)_5OC_2H_5$ (middle), and $(CH_2)_4OC_3H_7$ (bottom). The analogous spectra for $(MeSiOct)_n$[6] are similar in appearance to those for $[MeSi(CH_2)_6OCH_3]$.

shown in Figure 3. Analogous to poly(octylmethylsilane),[6] which has a similar side-chain length, the methoxyhexyl- and ethoxypentyl-substituted polymers absorb at λ_{max} = 303 nm at ambient temperature and undergo a red shift to 330 nm upon cooling. A discontinuity with an isosbestic point is visible in the thermochromism of each polymer. The onset temperatures of their thermochromic transitions are, however, lower than those for $(OctMeSi)_n$ and decrease from methoxyhexyl to ethoxypentyl. The absorption spectra of the propoxybutyl-substituted polymer merely show a gradual red shift in the absorption maximum and a smaller bathochromic displacement from 302 to 318 nm.

It has been previously demonstrated that thermal analysis is useful in monitoring thermochromic transitions and provides a result parallel to the discontinuous changes in the optical absorption.[6] The DSC cooling scans of methoxyhexyl and ethoxypentyl polymers (Figure 4) showed an exotherm at a temperature corresponding well with the discontinuous shifts in UV spectra. The onset temperature (T_o) decreases with substitution of an ether functionality and depends on the position of the oxygen atom in the isomeric ether substitutent [T_o(octyl) = −9 °C, T_o(methoxyhexyl) = −18 °C, and T_o(ethoxypentyl) = −37 °C]. The exotherm becomes smaller as well: ΔH(octyl) = 0.24 kcal/mol (per mole of monomeric units), ΔH(methoxyhexyl) = 0.16 kcal/mol, and ΔH(ethoxypentyl) = 0.05 kcal/mol. Only a second-order transition is detected in the thermogram of the propoxybutyl polymer, corresponding to the glass transition. This is in agreement with the observation of a gradually shifted absorption in the variable-temperature UV spectra. The changes in the thermochromism and thermal behavior with different ether substitutents closely match those found in the poly(*n*-alkylmethylsilane)s[6] with heptyl, hexyl, and butyl side chains.

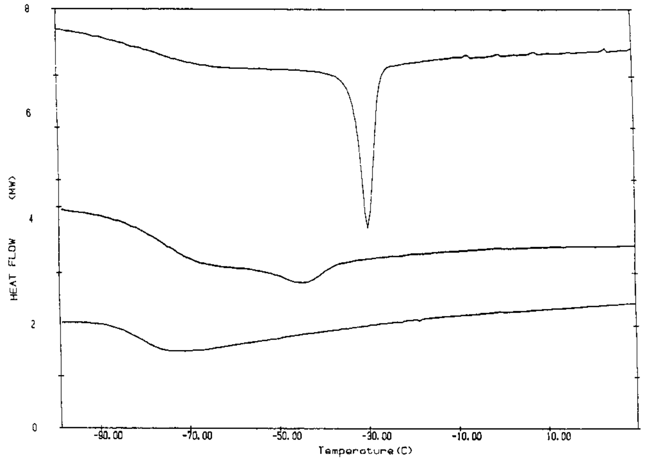

Figure 4. DSC of $(RSiMe)_n$, with R = $(CH_2)_6OCH_3$ (top), $(CH_2)_5OC_2H_5$ (middle), and $(CH_2)_4OC_3H_7$ (bottom).

Inspection of the thermograms of $(OctMeSi)_n$ and three ether-substituted polysilanes reveals that there is a pronounced change in glass transition temperatures [T_g(octyl) = −57 °C, T_g(methoxyhexyl) = −67 °C, T_g(ethoxypentyl) = −76 °C, and T_g(propoxybutyl) = −82 °C] (Figure 4). In comparison with that of $(OctMeSi)_n$, the lower glass transition temperature of the methoxyhexyl polymer indicates that polymer flexibility is enhanced by introducing the ether group. Moving the ether functionality closer to the silicon backbone further increases polymer chain flexibility, leading to a progressive decrease in T_g.

To gain insight into the local chain motions at ambient temperature, we measured the spin-lattice relaxation time of the silicon nucleus (T_1) in the three ether-substituted polymers using the standard inversion−recovery pulse sequence[10] with magic angle spinning. The T_1's for the three polymers are T_1(methoxyhexyl) = 15.3 s, T_1(ethoxypentyl) = 12.4 s, and T_1(propoxybutyl) = 11.3 s. The fluctuation of local magnetic fields caused by the motions of side-chain protons is primarily responsible for the relaxation of the silicon nucleus;[11] a shorter T_1 reflects increased local motion of the silicon chain, largely arising from the greater motion of the side chains. The enhanced relaxation of the silicon nuclei indicates that displacing the oxygen atom in the ether substitutent closer to the main polysilane chain causes an increase in local side-chain motions.[12] The glassification of the propoxybutyl

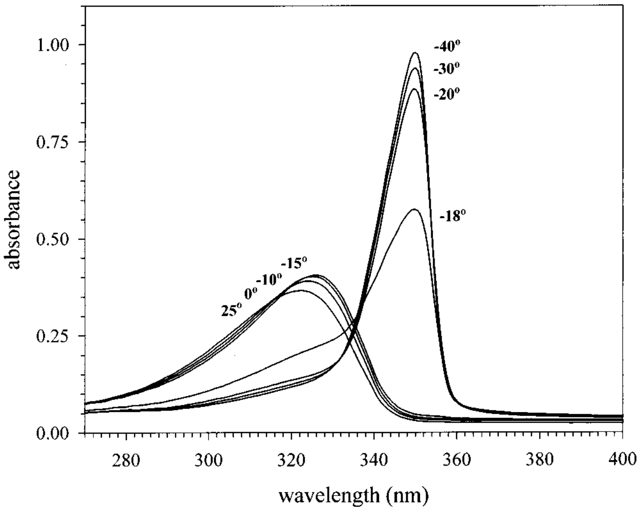

Figure 5. UV spectrum of solid poly[bis(propoxy-*n*-butyl)silane] at various temperatures, showing the abrupt thermochromic transition near −17 °C.

isomer at a lower temperature confirms that the mobility of polymer molecules is closely coupled with increased side-chain motions.

In agreement with the model for thermochromism of conjugated polymers proposed by Schweizer,[7] the polysilane with the least flexible methoxyhexyl substitutent allows the induction of strong intermolecular forces (strong coupling) and promotes a discontinuous thermochromic transition. The isomeric ethoxypentyl polysilane shows a much weaker response toward a change in temperature, which is reflected by a lower transition temperature and a smaller exotherm. In spite of having a long propoxybutyl substitutent, the thermochromic transition of the poly[(*n*-propoxy-*n*-butyl)methylsilane] behaves like that of (BuMeSi)$_n$, which corresponds to a “weak coupling” case.

(b) Symmetrical Poly[bis(alkoxy-*n*-alkyl)silane]s. Among polysilane polymers, the symmetrically substituted poly(di-*n*-alkylsilane)s have been especially well characterized, in part because of their diverse features of thermochromism[3] and piezochromism[13] associated with intriguing phase transitions. Studies of symmetrical poly(dialkylsilane)s[14] showed that the solid-state structure depends strongly on the length of the linear alkyl chain, but little attention has been paid to the nature of the side group apart from a theoretical discussion.[15]

In this section, the isomeric symmetric polymers (R$_2$Si)$_n$, where R = (CH$_2$)$_6$OCH$_3$, (CH$_2$)$_5$OC$_2$H$_5$, and (CH$_2$)$_4$OC$_3$H$_7$, are described. The flexibility of the polysilane chain again appears to depend on the position of the oxygen atom in the isomeric ether substitutent.

Table 1. Thermal Data for Symmetrically Ether-Substituted Polysilanes

substitutent	T_o (°C)[a]	T_c (°C)[b]	T_h (°C)[c]	T_m (°C)[d]	Δ*H* (kcal/mol)
methoxyhexyl	−4	−10	31	−12	2.9
ethoxypentyl	−15	−18	−5	−21	1.9
propoxybutyl	−14	−15	4	−17	1.7

[a] Onset temperature in DSC cooling scan. [b] Minimum of first-order transition in DSC cooling scan. [c] Minimum of first-order transition in DSC heating scan. [d] Approximate temperature of the midpoint of the UV thermochromic transition (thin films).

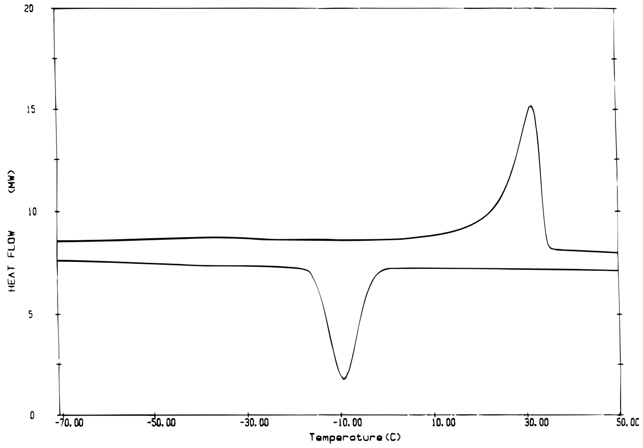

Figure 6. DSC of poly[bis(methoxy-*n*-hexyl)silane] obtained at heating (top) and cooling (bottom) rate of 10 °C/min.

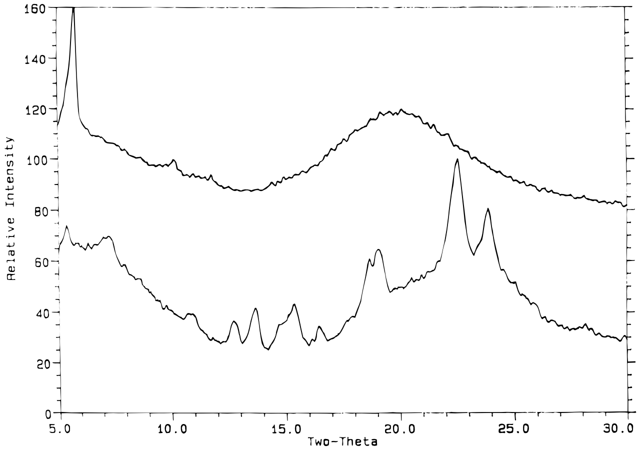

Figure 7. X-ray diffractograms of poly[bis(methoxy-*n*-hexyl)silane] at 80 (top) and −30 °C (bottom).

The UV spectra of fresh solution-cast films of all three polymers exhibit a broad band at 320 nm, characteristic for a random helical chain in a disordered mesophase. On cooling, an abrupt shift in spectral absorption from 320 to 352 nm takes place. As a typical example, the temperature evolution of the UV spectrum for poly[bis(propoxy-*n*-butyl)silane] is shown in Figure 5. For this polymer and for poly[bis(ethoxy-*n*-pentyl)silane], the thermochromism is readily reversible when the films are heated slightly above their transition temperatures. For the methoxyhexyl homologue, the spectral shift takes place at a slightly higher temperature (Table 1) and is much less easily reversible. The 352-nm absorption persists even after long standing of this film at 25 °C. However, when the film was annealed at 80 °C and recooled to room temperature, the UV spectrum again showed a broad band at 320 nm.

Thermal analysis for all three polymers showed a significant exothermic phase transition at a temperature near that for the thermochromic change. The methoxyhexyl polymer showed the largest heat of transition and the highest transition temperature (Figure 6). The other two polymers had very similar thermal properties, as shown in Table 1.

The X-ray diffraction pattern (Figure 7) for the methoxyhexyl polymer displays a reflection pattern consisting of a major peak ($2\theta = 5.77°$) and two minor ones ($2\theta = 10.12°$ and $11.75°$). The ratio of the observed d-spacings ($1, 1/3^{1/2}, {}^1/_2$) is consistent with a hexagonal mesomorphic phase in which the random-helical silicon chains form a quasi-hexagonal array.[16] The X-ray diffractogram recorded at about −30 °C is also shown

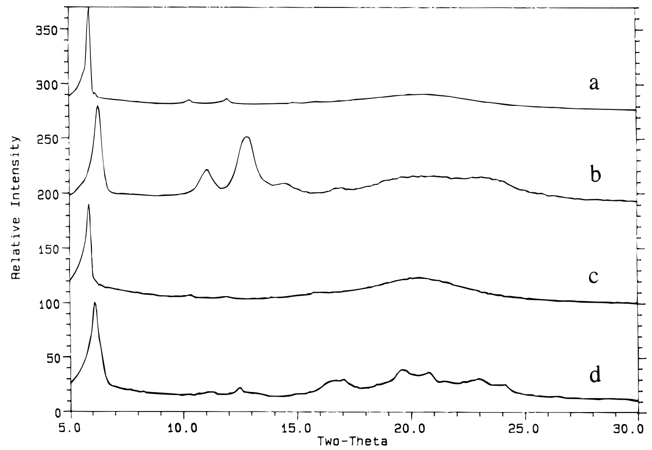

Figure 8. X-ray diffractograms of poly[bis(ethoxy-*n*-pentyl)-silane] at (a) 25 and (b) −40 °C and poly[bis(propoxy-*n*-butyl)-silane] at (c) 25 and (d) −40 °C.

in Figure 7. Many reflections are observed over wide angles of $2\theta = 10-25°$, consistent with the existence of a three-dimensional crystalline phase. The X-ray manifestations of the phase transition from a mesomorphic phase to a crystalline packing are in good agreement with the observed thermochromism. In the diffraction patterns of the ethoxypentyl and propoxybutyl polymers (Figure 8) recorded below their transition temperatures, the appearance of several new reflections also indicates that these polymers partially crystallize on going through the thermochromic transition.

The thermal behavior of poly[bis(methoxyhexyl)-silane] was reversible but with strong supercooling (ΔT = 41 °C). A similar, but much smaller, thermal hysteresis was found for poly(di-*n*-hexylsilane)[14a] (ΔT = 11 °C). A careful X-ray diffraction study in the temperature range of supercooling (−4−25 °C) indicates that the crystallites of methoxyhexyl polymer persist even at ambient temperature. The disordered mesophase is recovered only by heating beyond 40 °C. This explains the existence of the 352-nm absorption at ambient temperature found in the UV measurement. The rigid nature of the side chain and strong interchain interactions in this polymer may contribute to the stabilization of the crystal lattice and, therefore, a much higher melting point.

The similar thermal properties for the ethoxypentyl and propoxybutyl polymers are unexpected, since the side-chain flexibility should be greater in the latter polymer. The X-ray diffraction pattern of crystalline poly[bis(ethoxypentyl)silane] shows an amorphous halo in the 19−23° 2θ region, where reflections are generally observed due to side-chain crystallization.[17] This indicates irregular packing between the ethoxypentyl side chains and, therefore, a lower symmetry for this polymer, which may account for its low transition temperature.

The UV spectra of these polymers were also studied in THF solution, which provides a quasi-unimolecular environment without the perturbation of molecular packing. In each case, an abrupt thermochromic shift was observed from a broad band at 325 nm to a sharp peak at 354 nm. The spectra for the ethoxypentyl polymer are shown in Figure 9 as an example. As also observed for some symmetrical poly(dialkylsilanes),[18] the low-temperature absorption is stable for some time, but eventually sudden precipitation is observed, causing a rapid decrease in absorbance. The solution transition temperatures for all three polymers were obtained without any appreciable precipitation. As the isomeric ether substitutent is changed, the transition temperatures decrease regularly with increasing side-chain flexibility, from −28 to −42 to −50 °C for the methoxyhexyl, ethoxypentyl, and propoxybutyl polymers, respectively.

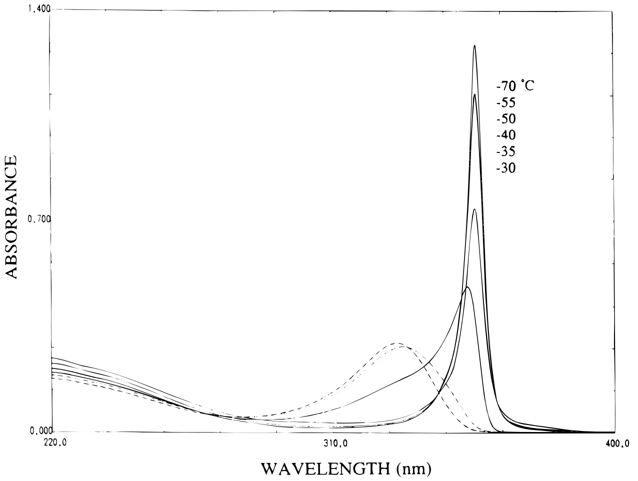

Figure 9. UV spectrum of a solution of poly[bis(ethoxy-*n*-pentyl)silane] in THF: (a) −30, (b) −35, (c) −40, (d) −50, (e) −55, (f) −70 °C.

III. Conclusion

The examination of ether-substituted polysilanes by X-ray diffraction indicates that the unsymmetrical polymers are fully amorphous and that some undergo an amorphous-to-amorphous phase transition, accompanied by a discontinuous thermochromism. Measurements of glass transition temperatures and relaxation of silicon nuclei reveal increased side-chain and polymer mobility as the oxygen atom of the ether substitutents is moved closer to the silicon backbone.

For the symmetrical oxygen-containing polysilanes, a phase transition from a liquid crystalline mesophase to a polycrystalline polymer dominates the conformational change, leading to an abrupt shift in spectral absorption.

The changes in the thermochromic behavior of these polysilanes are also consistent with variations in side-chain flexibility, although the phase transitions are somewhat complicated by molecular packing. Evidently, a flexible substitutent associated with considerable randomness has the effect of preventing the ordering of side chains and is unfavorable to the induction of a discontinuous thermochromic transition.

IV. Experimental Section

General Procedure for the Preparation of Monomers. All reactions were carried out under a dry nitrogen atmosphere. The standard Williamson method was used to synthesize 6-methoxyhexyl bromide. In a typical reaction, methanol (200 mL) was slowly added into a 250-mL three-necked flask containing Na metal (23.4 g, 1 mol). After the completion of addition, the mixture was heated to reflux for 24 h. The solution was then slowly dropped into 1,6-dibromohexane (220 g, 0.9 mol), and the reaction mixture was stirred for 24 h. The reaction solution was quenched with 4 mL of water. The organic layer was washed twice prior to drying over anhydrous K_2CO_3. Fractional distillation of the organic mixture under vacuum gave 124 g of 6-methoxybromohexane; the purity according to gas chromatography was >94%.

The monomer, (6-methoxyhexyl)methyldichlorosilane, was prepared by the reaction of methyltrichlorosilane with (6-methoxyhexyl)magnesium bromide according to the method described.[19] The coupling of excess methyltrichlorosilane with the corresponding Grignard reagent prepared from 124 g (0.65 mol) of 6-methoxybromohexane gave the corresponding dichlorosilane (102 g, 0.43 mol, 66%).

Analytical data for (6-methoxy-*n*-hexyl)methyldichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.39$ (Si-CH_3, 3H), 0.75 (Si-αCH_2-, 2H), 1.05−1.35 (Si-βCH_2-γCH_2-δCH_2-, 6H), 1.46 (Si-ϵCH_2-, 2H) 3.13 (O-CH_3, 3H), 3.17 (O-CH_2-, 2H); ^{13}C NMR (C_6D_6) δ 4.88 (Si-CH$_3$), 21.56 (Si-αCH$_2$-), 22.65 (Si-βCH$_2$-), 26.02 (Si-δCH$_2$), 29.89 (Si-ϵCH$_2$-), 32.37 (Si-γCH$_2$-), 58.32 (O-CH$_3$), 72.77 (O-CH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = 33.30$ ppm.

Analytical data for (5-ethoxy-*n*-pentyl)methyldichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.41$ (Si-CH_3, 3H), 0.78 (Si-αCH_2-, 2H), 1.10 (O-CH$_2$CH_3, 3H), 1.2−1.35 (Si-βCH_2-γCH_2-, 4H), 1.41 (Si-δCH_2-, 2H) 3.20 (Si-ϵCH_2-, 2H), 3.26 (O-CH_2-CH$_3$, 2H); ^{13}C NMR (C_6D_6) δ 4.95 (Si-CH$_3$), 15.57 (O-CH$_2$CH$_3$), 21.65 (Si-αCH$_2$-), 22.58 (Si-βCH$_2$-), 29.38 (Si-γCH$_2$), 29.71 (Si-δCH$_2$-), 66.21 (O-CH$_2$CH$_3$), 70.45 (Si-ϵCH$_2$-); ^{29}Si NMR (C_6D_6) $\delta =$ 33.22 ppm.

Analytical data for (4-n-propoxy-*n*-butyl)methyldichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.39$ (Si-CH_3, 3H), 0.79 (Si-αCH_2-, 2H), 0.87 (O-CH$_2$CH$_2$CH_3, 3H), 1.44 (Si-βCH_2-γCH_2-, 4H), 1.49 (O-CH$_2$CH_2CH$_3$, 2H), 3.15 (Si-δCH_2-, 2H), 3.18 (O-CH_2CH$_2$CH$_3$, 2H); ^{13}C NMR (C_6D_6) δ 4.84 (Si-CH$_3$), 10.96 (O-CH$_2$CH$_2$CH$_3$), 19.65 (Si-βCH$_2$-), 21.47 (Si-αCH$_2$-), 23.45 (O-CH$_2$CH$_2$CH$_3$), 32.67 (Si-γCH$_2$), 70.10 (Si-δCH$_2$-), 72.70 (O-CH$_2$CH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) $\delta = 33.18$ ppm.

Analytical data for bis(6-methoxy-*n*-hexyl)dichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.83$ (Si-αCH_2-, 2H), 1.10−1.30 (Si-βCH_2-γCH_2, 4H), 1.35 (Si-δCH_2-, 2H), 1.45 (Si-ϵCH_2-, 2H), 3.12 (O-CH_3, 3H), 3.16 (O-CH_2-, 2H); ^{13}C NMR (C_6D_6) δ 20.44 (Si-αCH$_2$-), 22.71 (Si-βCH$_2$-), 26.07 (Si-δCH$_2$), 29.92 (Si-ϵCH$_2$-), 32.56 (Si-γCH$_2$-), 58.36 (O-CH$_3$), 72.79 (O-CH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = 33.88$ ppm.

Analytical data for bis(5-ethoxy-*n*-pentyl)dichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.82$ (Si-αCH_2-, 2H), 1.09 (O-CH$_2$CH_3, 3H), 1.2−1.35 (Si-βCH_2-γCH_2-, 4H), 1.41 (Si-δCH_2-, 2H) 3.21 (Si-ϵCH_2-, 2H), 3.26 (O-CH_2-CH$_3$, 2H); ^{13}C NMR (C_6D_6) δ 15.60 (O-CH$_2$CH$_3$), 20.49 (Si-αCH$_2$-), 22.61 (Si-βCH$_2$-), 29.52 (Si-γCH$_2$), 29.75 (Si-δCH$_2$-), 66.22 (O-CH$_2$CH$_3$), 70.47 (Si-ϵCH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = 33.78$ ppm.

Analytical data for bis(4-n-propoxy-*n*-butyl)dichlorosilane: ^{1}H NMR (C_6D_6) $\delta = 0.80{-}0.9$ (Si-αCH_2-, O-CH$_2$-CH$_2$CH_3, 5H), 1.40−1.55 (Si-βCH_2-γCH_2-, O-CH$_2$CH_2CH$_3$, 6H), 3.15 (Si-δCH_2-, 2H), 3.17 (O-CH_2CH$_2$CH$_3$, 2H); ^{13}C NMR (C_6D_6) δ 10.97 (O-CH$_2$CH$_2$CH$_3$), 19.67 (Si-βCH$_2$-), 20.26 (Si-αCH$_2$-), 23.45 (O-CH$_2$CH$_2$CH$_3$), 32.67 (Si-γCH$_2$), 70.13 (Si-δCH$_2$-), 72.71 (O-CH$_2$CH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) $\delta = 33.69$ ppm.

Polymerization. In a typical synthesis of poly(6-methoxy-*n*-hexyl)methylsilane, a dried 250-mL three-necked flask was fitted with a water-cooled condenser, a high-speed mechanical stirrer, and a 20-mL pressure-equalized addition funnel. In the flask was placed 4.83 g (0.21 mol) of Na metal and 60 mL of toluene. Under constant stirring and gentle refluxing, 22.9 g (0.1 mol) of (6-methoxy-*n*-hexyl)methyldichlorosilane was slowly syringed into the refluxing toluene solution. After addition, the viscous, purple solution was allowed to reflux for an additional 1 h. The crude polymer was obtained by precipitation from the toluene solution with 500 mL of methanol. The precipitate was redissolved in toluene and washed twice with water. After removal of insoluble material by filtration, the polymer solution was subsquently added into 500 mL of methanol to precipitate the product. Removal of solvent was carried out in a vacuum oven at 50 °C for 48 h and gave polymer in yields ranging from 8% to 15%.

Analytical data for poly(6-methoxy-*n*-hexyl)methylsilane: $M_w = 468\,000$, PD = 3.5; ^{1}H NMR (C_6D_6) $\delta = 0.63$ (Si-CH_3, 3H), 1.22 (Si-αCH_2-, 2H), 1.58 (Si-γCH_2-δCH_2-, 4H), 1.46 (Si-βCH_2-, Si-ϵCH_2, 4H), 3.20 (O-CH_3, 3H), 3.33 (O-CH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = -3.3$ (SiCH$_3$), 15.8 (Si-αCH$_2$-), 26.7 (Si-δCH$_2$-), 27.8 (Si-βCH$_2$-), 30.4 (Si-ϵCH$_2$-), 34.9 (Si-γCH$_2$-), 58.4 (O-CH$_3$), 73.0 (O-CH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = -31.6$ ppm.

Analytical data for poly[(5-ethoxy-*n*-pentyl)methylsilane]: $M_w = 455\,000$, PD = 3.7 (bimodal distribution); ^{1}H NMR (C_6D_6) $\delta = 0.61$ (Si-CH_3, 3H), 1.19 (Si-αCH_2-, O-CH$_2$CH_3, 5H), 1.67 (Si-βCH_2-γCH_2-, 4H), 1.80 (Si-δCH_2-, 2H), 3.39 (O-CH_2-CH$_3$, 2H), 3.43 (Si-ϵCH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = -3.4$ (SiCH$_3$), 15.7 (O-CH$_2$CH$_3$), 15.8 (Si-αCH$_2$-), 27.6 (Si-βCH$_2$-), 30.4 (Si-δCH$_2$-), 31.6 (Si-γCH$_2$-), 66.3 (O-CH$_2$CH$_3$), 70.9 (Si-ϵCH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = -31.5$ ppm.

Analytical data for poly[(4-*n*-propoxy-*n*-butyl)methylsilane]: $M_w = 504\,000$, PD = 2.8; ^{1}H NMR (C_6D_6) $\delta = 0.64$ (Si-CH_3, 3H), 0.98 (O-CH$_2$CH$_2$CH_3, 3H), 1.22 (Si-αCH_2-, 2H), 1.65 (O-CH$_2$CH_2CH$_3$, 2H), 1.85 (Si-βCH_2-γCH_2-, 4H), 3.35 (O-CH_2CH$_2$CH$_3$, 2H), 3.52 (Si-δCH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = -3.4$ (SiCH$_3$), 11.1 (O-CH$_2$CH$_2$CH$_3$), 15.6 (Si-αCH2-), 23.6 (O-CH$_2$CH$_2$CH$_3$), 24.4 (Si-βCH$_2$-), 35.0 (Si-γCH$_2$-), 70.7 (Si-δCH$_2$-), 72.8 (O-CH$_2$CH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) $\delta = -23.6$ ppm.

Analytical data for poly[bis(6-methoxy-*n*-hexyl)silane]: $M_w = 525\,000$, PD = 3.1; ^{1}H NMR (C_6D_6) $\delta = 1.43$ (Si-αCH_2-, 2H), 1.70 (Si-γCH_2-δCH_2-, 4H), 1.81 (Si-βCH_2-, Si-ϵCH_2, 4H), 3.25 (O-CH_3, 3H), 3.42 (O-CH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = 16.0$ (Si-αCH$_2$-), 27.0 (Si-δCH$_2$-), 28.5 (Si-βCH$_2$-), 30.6 (Si-ϵCH$_2$-), 35.5 (Si-γCH$_2$-), 58.4 (O-CH$_3$), 73.1 (O-CH$_2$-); ^{29}Si NMR (C_6D_6) $\delta = -24.0$ ppm.

Analytical data for poly[bis(5-ethoxy-*n*-pentyl)silane]: $M_w = 751\,000$, PD = 3.3; ^{1}H NMR (C_6D_6) $\delta = 1.24$ (O-CH$_2$CH_3, 5H), 1.42 (Si-αCH_2-, 2H), 1.80 (Si-γCH_2-, 4H), 1.92 (Si-δCH_2-, Si-βCH_2-, 4H), 3.47 (O-CH_2-CH$_3$, 2H), 3.56 (Si-ϵCH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = 15.8$ (O-CH$_2$CH$_3$), 15.9 (Si-αCH$_2$-), 28.4 (Si-βCH$_2$-); 30.6 (Si-δCH$_2$-), 32.0 (Si-γCH$_2$-), 66.3 (O-CH$_2$CH$_3$), 71.1 (Si-ϵCH$_2$-), ^{29}Si NMR (C_6D_6) $\delta = -23.8$ ppm.

Analytical data for poly[bis(4-*n*-propoxy-*n*-butyl)silane]: $M_w = 523\,000$, PD = 2.9; ^{1}H NMR (C_6D_6) $\delta = 1.04$ (O-CH$_2$CH$_2$CH_3, 3H), 1.43 (Si-αCH_2-, 2H), 1.72 (O-CH$_2$CH_2-CH$_3$, 2H), 1.80−2.15 (Si-βCH_2-γCH_2-, 4H), 3.48 (O-CH_2CH$_2$-CH$_3$, 2H), 3.67 (Si-δCH_2-, 2H); ^{13}C NMR (C_6D_6) $\delta = 11.1$ (O-CH$_2$CH$_2$CH$_3$), 15.7 (Si-αCH$_2$-), 23.7 (O-CH$_2$CH$_2$CH$_3$), 24.9 (Si-βCH$_2$-), 35.4 (Si-γCH$_2$-), 71.1 (Si-δCH$_2$-), 73.9 (O-CH$_2$CH$_2$CH$_3$); ^{29}Si NMR (C_6D_6) $\delta = -23.6$ ppm.

Gel Permeation Chromatography. Molecular weights were measured by gel-permeation chromatography using a Waters Associates model 6000A liquid chromatograph equipped with three American Polymer Standards Co. Ultrastyragel columns in series with porosity indexes of 10^3, 10^4, and 10^5 Å, and THF as eluant. The polymers were detected with a Waters Model 440 ultraviolet absorbance detector at a wavelength of 254 nm, and the data were manipulated using a Waters Model 745 data module. Molecular weights were determined relative to a calibration with polystyrene standards.

Wide-Angle X-ray Diffraction (WAXD). Polymer films were cast from a concentrated toluene solution and dried under vacuum for 24 h at 50 °C. Measurements of polymer samples were carried out on a Nicolet I2/V diffractometer at 0.6° 2θ/min using Ni-filtered Cu Kα radiation.

UV−Vis Spectroscopy. UV absorption spectra were recorded on a Perkin-Elmer Lambda array model 3840 spectrometer interfaced with a Motorola series 7000 computer. Thin films of the polysilanes were cast from hexane solution onto quartz plates and dried under vacuum for 24 h to remove residual solvent. Variable-temperature measurements were conducted under vacuum with a cryostat having two quartz windows. The solution variable-temperature absorption spectra were recorded for THF solutions approximately 10^{-4} M in monomer units. The specimens were scanned at a cooling rate of ca. 2 °C/min.

Thermal Analysis. Thermal measurements were performed with a Perkin-Elmer DSC-7 thermal analyzer and a 3700 data station using mass samples of 8−12 mg in a dry helium atmosphere. All DSC thermograms were collected at a heating and cooling rate of 10 °C/min under a dry helium atmosphere over the temperature range of from 100 to −100 °C. The enthalpy of transition and temperature were calibrated with mercury and indium standards.

NMR Spectroscopy. In addition to the measurement of ^{1}H (300 MHz) spectra carried out on a Bruker AC-300, ^{13}C(125

MHz) and ^{29}Si (100 MHz) NMR spectra in solution were measured on a Bruker AM-500 with ca. 10% (w/w) solutions of monomers and polymers in benzene-d_6 using TMS as reference. The magic angle spinning 59.591-MHz ^{29}Si NMR spectra were recorded on a Varian Unity 300 spectrometer equipped with a variable-temperature Doty Scientific magic angle spinning probe and Al_2O_3 rotors, and were externally referenced to $Si(SiMe_3)_4$. A sample spinning rate of 1-kHz was employed.

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