Abrupt Thermochromic Transitions in Alcohol-Soluble Ethoxypentyl-Substituted Polysilanes

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In the past decade, organopolysilanes[1] have been extensively studied because of their unusual electronic and photochemical properties, as well as their attractive potential applications such as microlithography,[2] ceramics,[3] photoconductivity,[4] and nonlinear optics.[5] Owing to the extensive delocalization of σ electrons along the silicon backbone, polysilanes display an intense absorption band in the near-ultraviolet region, which is strongly coupled with the polymer conformation.

Dialkylpolysilane exhibit a variety of interesting thermochromic behaviors, depending upon the nature of the alkyl substituents. As the temperature is decreased, bathochromic shifts of the principal σ–σ^* absorption band in the ultraviolet region are often observed, attributed to increased population of trans conformations in the polymer chain. This change may occur gradually, with continuous red-shifting of the ultraviolet absorption band, or abruptly, as the original absorption band decreases in intensity and is replaced by a new band at longer wavelength. This abrupt thermochromic shift may be accompanied by a first-order phase transition attributed to side-chain crystallization. A well-studied example of the latter type is poly(di-*n*-hexylsilane),[6] which undergoes a transition from a columnar liquid-crystalline form to a crystalline phase at ca. 43 °C, with the UV absorption shifting from 315 to 375 nm.

In order to provide greater flexibility while maintaining a linear side-chain structure, we have synthesized two polysilane polymers bearing linear substituent groups with oxygen atoms in the side chain, poly[5-(ethoxypentyl)-*n*-propylsilane] (**1**) and poly[5-(ethoxypentyl)-*n*-hexylsilane] (**2**). Unlike typical dialkylpolysilanes, polymers **1** and **2** are soluble in alcohols such as 2-propanol but are still insoluble in methanol.[7]

The precursors of polymer **1** and **2** were prepared by the coupling of 5-(ethoxypentyl)magnesium bromide[8] with an excess of the corresponding alkyltrichlorosilane in THF, giving quantitatively 5-(ethoxypentyl)-*n*-propyldichlorosilane and 5-(ethoxypentyl)-*n*-hexyldichlorosilane. Polysilanes **1** and **2** were prepared by reductive polymerization of the dichlorosilane precursors with 2 equiv of a sodium dispersion in refluxing toluene and were subsequently precipitated from the solution with methanol. The polymers were purified by repeated precipitation with methanol from a filtered toluene solution of the crude polymer mixture. The resulting high molecular weight polysilanes were characterized by ^{1}H NMR ^{29}Si NMR spectroscopy, size-exclusion chromatography,[9] DSC, and X-ray diffraction.

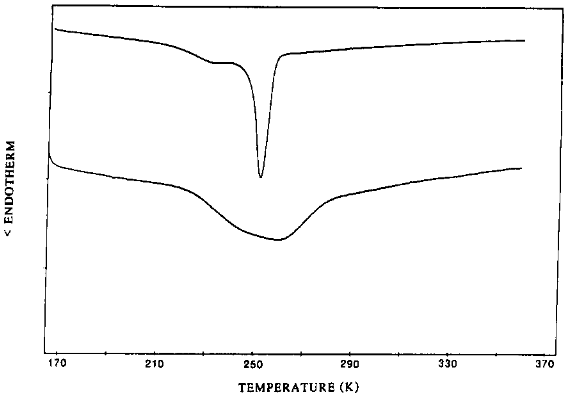

Figure 1. DSC thermograms of polymers **1** (bottom) and **2** (top) at a heating rate of 20 °C/min.

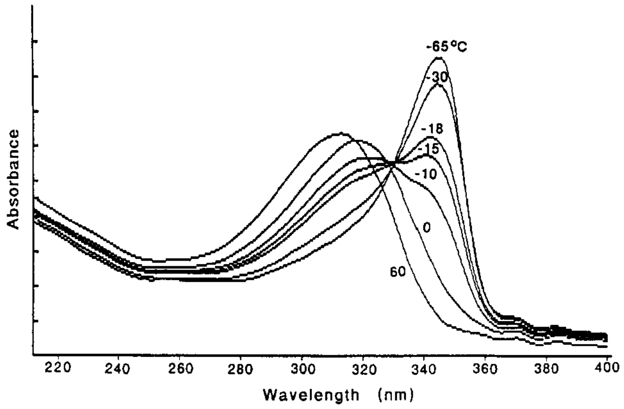

Figure 2. Variable-temperature solid-state UV spectra of polymer **1**.

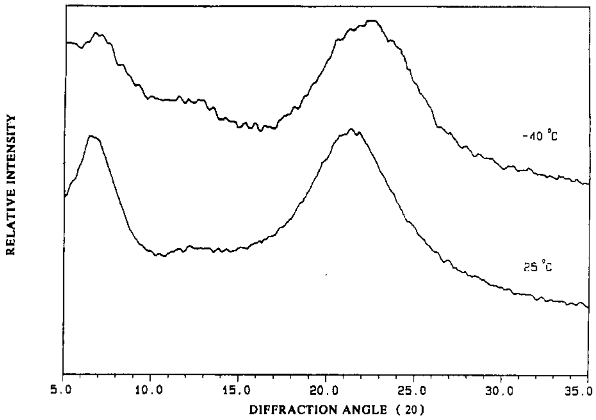

Figure 3. X-ray diffractograms of polymer **1** recorded at the indicated temperature.

As shown in Figure 1, the thermogram of polymer **1** exhibits a broad first-order-like phase transition from 0 to −60 °C associated with an endotherm having $\Delta H = 0.92$ kcal/mol. The temperature-dependent UV of a thin film of polymer **1**, shown in Figure 2, initially displays a continuous bathochromic shift with decreasing temperature, behaving like highly unsymmetrical dialkylpolysilanes.[10] Below 0 °C, no further continuous migration is observed; instead the original absorption band diminishes and a new narrow peak grows at lower energy. For normal dialkylpolysilanes this kind of abrupt electronic transition has been ascribed to side-chain crystallization inducing an order–disorder transition.[11] The X-ray analyses of polymer **1** (Figure 3), however, only gave a patternless halo both below and above the phase transition temperature. Similar thermochromic behavior is observed for polymer **2** which shows an abrupt bathochromic shift in a narrow temperature range from −17 to −25 °C (Figure 4). The thermochromic shift is associated with a first-order-like phase transition centered at −21 °C, with an endothermic enthalpy of 0.93 kcal/mol, according to the DSC thermogram shown in Figure 1. However, this polymer shows an X-ray diffraction pattern characteristic for a columnar liquid-crystalline structure, both above and below the transition temperature (Figure 5). Similar

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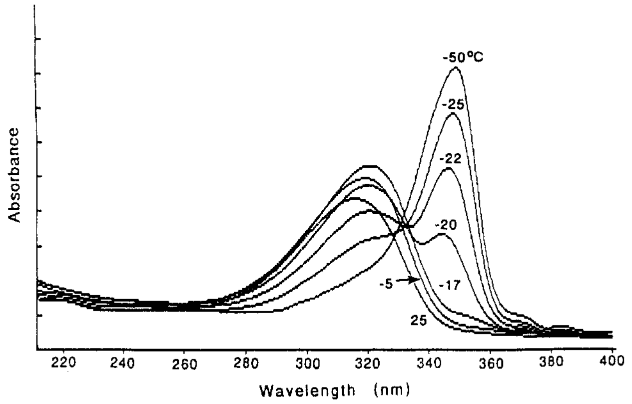

Figure 4. Variable-temperature solid-state UV spectra of polymer 2.

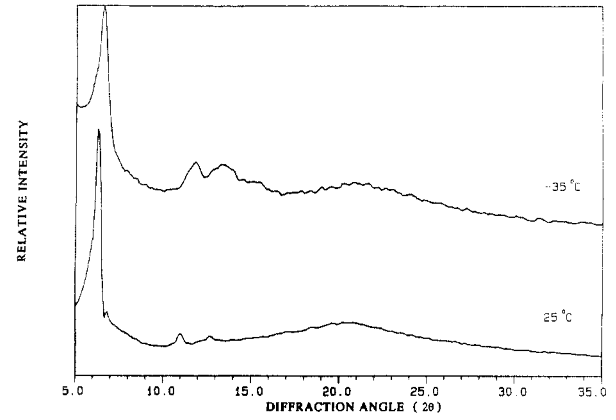

Figure 5. X-ray diffractograms of polymer 2 recorded at the indicated temperature.

results have been observed for poly(*n*-hexyl-*n*-butylsilane) both by us[12] and others.[10]

Schweizer[13] has proposed that the thermochromic phenomena can arise from the dispersion interaction of delocalized electrons along the polymer backbone with the surrounding polarizable medium, which can be the appended side chains, surrounding polymer molecules or solvent. The transition between the ordered and disordered conformation is controlled by a competition between the dispersion interaction for fully conjugated chain segments, V_D, and the rotational defect energy, ϵ. According to this model, the ratio V_D/ϵ determines the type of thermochromic behavior, leading to either continuous shifts or an abrupt transition. For low values of V_D/ϵ ("weak coupling"), a continuous, gradual red shift of the absorption band may take place as the temperature is decreased, due to the gradual reduction of nonplanar defects with cooling. With high values of V_D/ϵ ("strong coupling"), an abrupt order–disorder transition is triggered in which the polymer chain becomes straightened, producing long fully-conjugated segments. Polymers 1 and 2 exhibit initially a gradual red shift of the σ–σ^* absorption band as temperature is decreased and then an abrupt thermochromic shift at the temperature of the pseudo-first-order transition.

It is evident that the thermochromic phase transition in polymers 1 and 2 takes place without side-chain crystallization and for polymer 1 without any crystalline order whatsoever. We propose that the transformation in these polymers is electronically driven, according to the model suggested by Schweizer. At the transition temperature one amorphous or liquid-crystalline phase must give way to another; the trans conformations probably become more numerous in the lower temperature phase.[14] Analogous behavior has been observed for π-conjugated polymers of the polydiacetylene[15] and polythiophene[16] series, which also show abrupt thermochromism over a wide temperature range without crystallization.

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(9) A bimodal molecular weight distribution was generally observed in GPC traces of these polymers. The high molecular weight fraction of polymer 1 was obtained in 6% yield (M_w = 901 200; PD = 2.5, relative to polystyrene standard). ^{1}H NMR (C_6D_6): δ 1.18 (t, 3H, OCH_2CH_3), 1.33 (br, 7H, $SiCH_2$ + CH_3), 1.84 (br, 8H, CH_2), 3.45 (q, 2H, OCH_2CH_3), 3.48 (br, 2H, CH_2O). ^{29}Si NMR (C_6D_6): δ −24.2. The methanol-soluble low molecular weight fraction was recovered in 90% yield (M_w = 3400; PD = 1.3). The high molecular weight fraction of polymer 2 (M_w = 980 000; PD = 1.9) was obtained in 13% yield. ^{1}H NMR: δ 1.17 (t, 3H, CH_3), 1.21 (t, 3H, OCH_2CH_3), 1.58, 1.90 (br, 18H, $SiCH_2$ + CH_2), 3.45 (q, 2H, OCH_2CH_3), 3.53 (br, 2H, CH_2O). ^{29}Si NMR: δ −23.7. The low molecular weight fraction (M_w = 4000; PD = 1.2) was recovered in 85% yield.

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