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Structure and Properties of Poly(*n*-pentyl-*n*-alkylsilanes). 2

Bruce M. Klemann*

Materials Science Program, University of Wisconsin—Madison, Madison, Wisconsin 53706

Robert West

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

James A. Koutsky†

Department of Chemical Engineering, University of Wisconsin—Madison,
Madison, Wisconsin 53706

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ABSTRACT: The solid-state electronic properties and structures of poly(*n*-pentyl-*n*-hexylsilane) (C5-C6), poly(*n*-pentyl-*n*-octylsilane) (C5-C8), and poly(*n*-pentyl-*n*-dodecylsilane) (C5-C12) have been investigated using UV absorption, differential scanning calorimetry, and X-ray diffraction. At low temperatures, C5-C6 is semicrystalline with an all-trans backbone conformation. Upon heating, it transforms to the hexagonal, columnar, condis crystalline phase observed in many polysilanes. C5-C8 exhibits the hexagonal, columnar mesophase both above and below its first-order transition temperature of −32 °C. This type of behavior is found to be characteristic of poly(*n*-alkyl-*n*-alkyl′silanes) with a side-chain asymmetry of two or three carbon atoms. The existence of first-order transitions and the observation of UV thermochromic red shifts upon cooling for these polymers which do not crystallize are most likely the result of polarization interactions between the σ-bonded silicon backbone and the alkyl side chains, which is consistent with the predictions of the model of Schweizer for conjugated polymers.

Introduction

Polysilanes, which have a chain backbone composed solely of silicon atoms, are a relatively new class of polymers. They have attracted significant interest as materials for microlithography[1−3] due to their radiation sensitivity[2,4] which is a consequence of electron delocalization along the σ-bonded backbone. Most polysilanes exhibit intense absorption of ultraviolet radiation in the 290−400 nm range, with absorption maxima that depend on backbone conformation.[5] Polysilanes also have shown promise as β-silicon carbide precursors,[6−11] nonlinear optical materials,[12,13] and photoconductors.[14]

Many of the studies of polysilanes have focused on the symmetric poly(di-*n*-alkylsilanes). Several of these polymers, including poly(di-*n*-hexylsilane), C6-C6,[15] the most widely studied of these compounds, exhibit a trans planar conformation of the silicon backbone at room temperature. However, poly(di-*n*-butylsilane), C4-C4,[16] and poly(di-*n*-pentylsilane), C5-C5,[17] have a 7/3 helical backbone conformation. KariKari and Farmer[18] have also recently established that the conformation of the symmetric poly(di-*n*-alkylsilanes) with side-chain lengths of 9−14 carbon atoms have a TGTG′ silicon backbone conformation.

Weber et al.[19] showed that all poly(di-*n*-alkylsilanes) with linear side chains of 4−14 carbon atoms show an order−disorder transition to a hexagonal, columnar liquid crystalline phase upon heating. Two explanations for this transition have been advanced. Kuzmany[15] attributed the ordering of C6-C6 at low temperatures to side-chain crystallization which enforces an all-trans conformation upon the silicon backbone. This explanation was also employed to explain the all-trans or TGTG′ conformations of other long-side-chain poly(di-*n*-alkylsilanes). However, it does not satisfactorily explain the disordering transitions of C4-C4 and C5-C5, for which side-chain crystallization has been demonstrated to be unimportant due to the short length of the side chains.[16] Schweizer,[20,21] on the other hand, developed a model for conjugated polymers that predicts a thermochromic phase transition may occur due to polarization interactions between the polymer backbone and its surroundings. The model, initially developed for dilute solutions, has also now been applied to the solid state of polymers that *do not* crystallize.

Films of the symmetrically-substituted poly(di-*n*-alkylsilanes) are often brittle and tend to crack. The introduction of asymmetry into the side chains should yield polymers that produce thin films that are more flexible and less crack-prone. In order to study the changes in structure and the mechanical and optical properties caused by the introduction of asymmetry into the side chains of the poly(*n*-alkyl-*n*-alkyl′silanes), the following members of the poly(*n*-pentyl-*n*-alkylsilane), or C5-CX, series of polymers have been synthesized: poly(ethyl-*n*-pentylsilane) (C2-C5), poly(*n*-propyl-*n*-pentylsilane) (C3-C5), poly(*n*-butyl-*n*-pentylsilane) (C4-C5), poly(*n*-pentyl-*n*-hexylsilane) (C5-C6), poly(*n*-pentyl-*n*-octylsilane) (C5-C8), and poly(*n*-pentyl-*n*-dodecylsilane) (C5−C12). The UV spectra, DSC, and X-ray diffraction analyses of C2-C5, C3-C5, and C4-C5 have been detailed previously.[22] The characterization of C5-C6, C5-C8, and C5-C12 will be reported here, along with several generalizations regarding the structure and properties of poly(*n*-alkyl-*n*-alkyl′silanes).

Experimental Section

The monomers for these polymers were prepared by Grignard reactions between *n*-pentylmagnesium bromide and alkyltrichlorosilanes (Petrarch Systems) in an argon atmosphere with THF as a solvent. After isolation by two fractional distillations, the resulting dichlorosilanes were polymerized by the usual Wurtz condensation reaction with sodium in toluene at 110 °C.[5] The polymers were purified by repeated

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[*] To whom correspondence should be addressed. Current address: W.H. Brady Co., Milwaukee, WI 53201.

[†] In memoriam.

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precipitation from toluene with 2-propanol and ethyl acetate. The resulting products are white solids that show a large range of physical properties. C5-C6 is hard, waxy, and brittle, C5-C8 is waxy but softer, and C5-C12 is soft and rubbery. These polymers are quite hydrophobic and impervious to water, but they are soluble in toluene and other nonpolar organic solvents.

Molecular weight distributions were determined using a Waters Associates GPC equipped with three Microstyragel columns of porosity 10^4, 10^5, and 10^6 Å. THF was the eluant. Monomodal distributions with M_w values of 53 000 g/mol for C5-C6, 370 000 g/mol for C5-C8, and 430 000 g/mol for C5-C12 were obtained.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-2C. Scans were run in a dry helium atmosphere at a heating rate of 20 °C/min. Each scan was repeated twice, and no changes in transition temperatures of more than 1 °C were observed for any of the three polymers discussed in this paper.

Films for X-ray diffraction and UV absorption spectra were cast from concentrated solution in toluene and dried in a vacuum oven at 130 °C for 24 h. UV absorption spectra of these films were measured with a Perkin-Elmer Lambda Array 3840 UV/VIS spectrophotometer. A Dewar flask with quartz windows was employed as a cooling stage for subambient variable-temperature spectra.

Thin film samples were cut and stacked or folded and mounted in a sample holder for X-ray diffraction. For subambient investigations, the samples were mounted onto the side of the cold-finger of a closed-cycle cryostat equipped with a Be-windowed vacuum shroud. Temperatures as low as −80 °C were accessible with the cryostat.

A 15 kW Elliot GX-21 rotating anode X-ray generator with a Cu target fitted with a bent graphite monochromator was utilized as a source of Cu Kα (λ = 1.542 Å) radiation. The cross-sectional area of the incident beam on the sample was adjusted to 4 mm^2. A Huber D424/D511 computer-controlled diffractometer was employed, with a refrigerated silicon diode array (EG&G XR 1412) and associated electronics (EG&G M1461) serving as the position sensitive array detector. The detector, containing 960 25 μm × 2 mm pixels, was set at approximately 30 cm from the sample for resolution of the scattered radiation over a 2θ arc of 4.5°. Radial 2θ scans were conducted.

Physical Properties of Thin Films

Films of these polymers are hazy, and the amount of light transmission is dependent upon film thickness and the degree of crystallinity. The degree of order decreases markedly as the side-chain mismatch increases. This reduction in order manifests itself as a decrease in the mechanical strength of films. Thus, films of C5-C12 are much weaker and tear more easily than films of C5-C8. Both of the aforementioned polymers produce films that are not brittle and that show superior fracture toughness when compared with the symmetric poly(di-*n*-alkylsilanes). Films of C5-C6 are waxy and brittle, because of the low molecular weight of our sample of this polymer.

Thermal Properties

The DSC traces of C5-C6 and C5-C8 (Figures 1 and 2) are quite similar. For both polymers, a relatively broad first-order transition is observed. The transition enthalpy of 3.9 cal/g (3.5 kJ/mol) for C5-C8 is relatively small, while that of C5-C6 is 6.9 cal/g (5.3 kJ/mol). This indicates that a greater change in structure occurs at the first-order transition for C5-C6 than for C5-C8. Wallraff et al.[23] had reported two first-order transitions for C5-C6, with transition temperatures of −2 and 19 °C for DSC heating scans. It is thought that the transition seen in Figure 1 for C5-C6, with a transition onset of −13 °C (260 K) and a peak at −6 °C (267 K), corresponds to the lower transition seen by Wallraff (who did not publish transition enthalpies), but with the transition temperature decreased somewhat due to the low molecular weight of the sample.

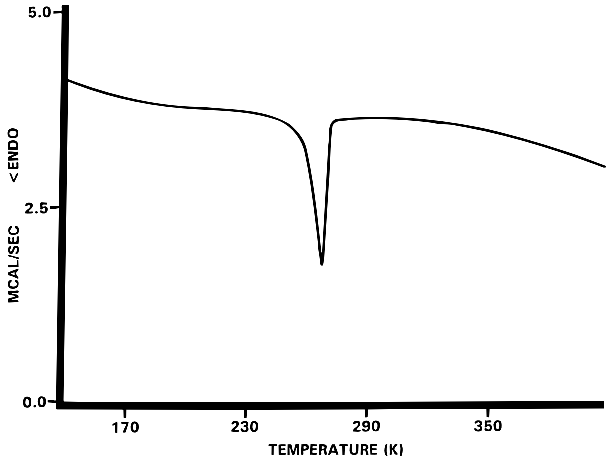

Figure 1. DSC thermogram of C5-C6 at a heating rate of 20 °C/min.

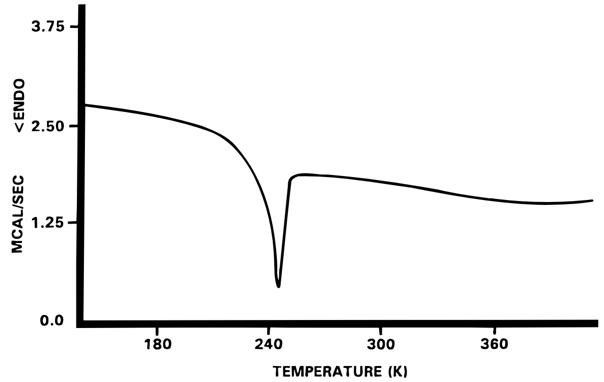

Figure 2. DSC thermogram of C5-C8 at a heating rate of 20 °C/min.

Table 1. DSC of Poly(*n*-pentyl-*n*-alkylsilanes)

polymer	order	T_{onset}	T_{peak}	$T_{midpoint}$	ΔH (cal/g)[a]
C2-C5	2			−35	
C3-C5	1	−2	6		3.1
C4-C5	2			−44	
	1	45	48		2.5
C5-C6	1	−13	−6		6.9
C5-C8	1	−36	−28		3.9
C5-C12	1	−35	−24		6.9[b]
	1	−20	−10		

[a] All data is for a heating rate of 20 °C/min. Transition temperatures in in °C. [b] Combined transition enthalpy for the two peaks.

The thermal analysis of the poly(*n*-pentyl-*n*-alkylsilanes) is summarized in Table 1. Data for C2-C5, C3-C5, and C4-C5 are included, as the information in Table 1 is more complete than that reported previously.[22]

Figure 3A contains the DSC analysis of a sample of C5-C12 as polymerized. Although the scan was run from 140 to 400 K, only the 180−300 K region is shown here, as all subsequent scans were conducted over this temperature range. Two overlapping endotherms with peaks at −24 and −10 °C are visible, with the latter endotherm somewhat sharper and larger. The combined transition enthalpy is 6.9 cal/g (7.7 kJ/mol).

In several of the poly(di-*n*-alkylsilanes) (C4-C4, C5-C5, C8-C8, and C12-C12), both Weber[19] and Klemann[27]

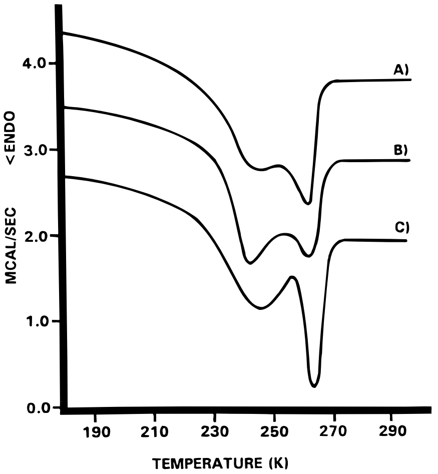

Figure 3. DSC thermogram of C5-C12 at a heating rate of 20 °C/min; (A) as polymerized; (B) after 70 min at 230 K (−43 °C); (C) after 15 min at 252 K (−21 °C).

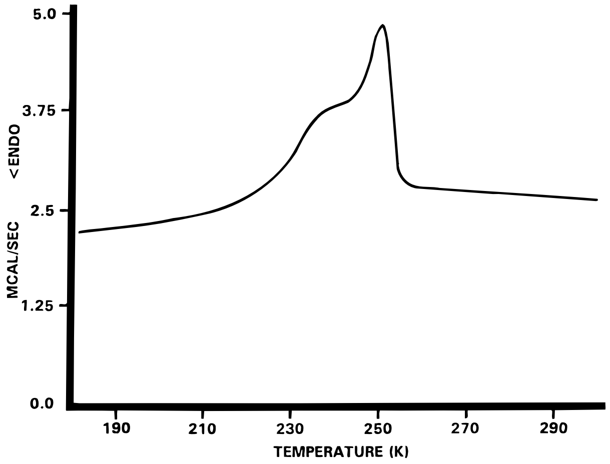

Figure 4. DSC thermogram of C5-C12 at a cooling rate of 20 °C/min.

have observed that the transition peaks were split into two peaks upon heating, whereas only a single peak was seen upon cooling. In each case, the total enthalpy of transition was the same for heating and cooling scans. For C5-C12, however, both peaks are still present in DSC scans run at a cooling rate of −20 °C/min (Figure 4). A supercooling of 12 °C (difference of peak temperatures) is seen in the cooling DSC scan relative to the heating scan.

Annealing experiments were performed in an attempt to isolate the two endotherms of C5-C12. First, the sample was annealed at −43 °C (230 K) for 70 min, quenched at a cooling rate of −180 °C/min to −93 °C (180 K), and subsequently heated at 20 °C/min. In the resulting DSC trace (Figure 3B), the first peak became slightly larger than the second. The combined enthalpy of 6.7 cal/g (7.5 kJ/mol) was virtually unchanged by this annealing at −43 °C. When the sample was held between the peaks for 15 min at −21 °C (252 K) and then quenched, the second peak became much larger and sharpened considerably (Figure 3C). Again, the total transition enthalpy was virtually unchanged (6.8 cal/g, 7.6 kJ/mol). In both annealing experiments one peak grew at the expense of the other with no significant change in the overall transition enthalpy. Since the ratio of the enthalpies of the two peaks changed in these experiments, the two peaks cannot represent two successive transitions of all of one crystalline phase to a second phase followed by the transformation of all of the second phase to a third phase. Instead, this may indicate the presence of multiple phases or conformations at low temperatures.

In order to determine whether or not the two peaks represent separate equilibrium transitions, DSC was conducted at several heating rates. If equilibrium were maintained during the DSC experiment, the DSC thermograms at different heating rates could be superimposed if all endotherms and exotherms corresponded to equilibrium phase transitions.[24] Often, however, a series of overlapping or closely-spaced endotherms and exotherms are observed at slow heating rates due to rearrangement of metastable crystals of the same structure. Upon rapid heating, only one endotherm is seen for these systems. Reorganization processes and fusion of the perfected crystals are only observed at slow heating rates.[24] Figure 5 illustrates the effect of heating rate variations upon the thermal analysis of C5-C12. Although the scales of the *y*-axes of the three thermograms in Figure 5 are different, the total enthalpy of the endotherms is similar for all three heating rates. Note that the different scales serve to roughly equalize the peak heights of the four scans because the Perkin-Elmer DSC-2C displays thermograms with units of power (mcal/s) on the *y*-axes; units of energy (cal/g) would have to be used in order for the curves to be superimposable. As the heating rate is increased, the two peaks are observed to merge into one broad endotherm. Thus, the two peaks present in scans at 20 °C/min probably do not represent two equilibrium phase transitions but may correspond to one equilibrium phase transition along with some rearrangement and perfection of the structure present at low temperatures. Other experiments in which the cooling rate between heating scans was varied revealed no discernable changes in the DSC thermograms for a heating rate of 20 °C/min.

Solid-State UV Absorption Spectra

As is true of the DSC, the UV spectra of C5-C6 (Figure 6) only indicates a single first-order thermal transition. The DSC heating scan gives a peak temperature of −6 °C while the UV spectra (both heating and cooling) show the transition at lower temperatures. Since C5-C6 was the only polymer of the poly(*n*-pentyl-*n*-alkylsilanes) that was studied for which the UV transition temperatures upon heating and cooling differed by more than 1 °C, both heating and cooling scans are shown in Figure 6. A discontinuous red shift in which the 314 nm absorption band present at room temperature is replaced by a peak at 344 nm is observed at −25 °C upon cooling. Again, this corresponds to the lower-temperature transition found by Wallraff et al. (they did not see any thermochromism at the higher-temperature transition[23]).

C5-C8 also shows an abrupt, discontinuous red shift upon cooling (Figure 7). The isosbestic point of this transition, in which the 320 nm absorption band is replaced by a more intense band at 351 nm, occurs at −32 °C. For both C5-C6 and C5-C8, these abrupt thermochromic shifts may be interpreted as manifestations of transitions to more extended silicon backbone conformations. Indeed, KariKari and Farmer[18] have shown by X-ray diffraction that the conformation of C5-C6 at −40 °C is all-trans.

In contrast to the DSC thermograms for slow heating rates, the variable-temperature UV spectra of a C5-C12 film (Figure 8) upon slow cooling (cooling rate of

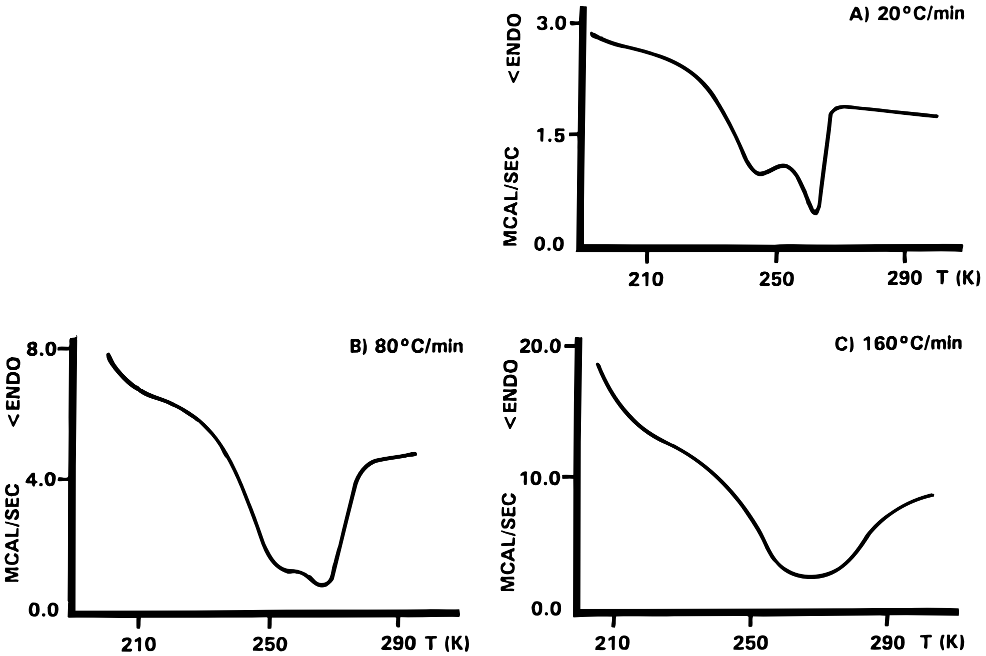

Figure 5. DSC thermograms of C5-C12 at different heating rates; (A) 20 °C/min; (B) 80 °C/min; (C) 160 °C/min.

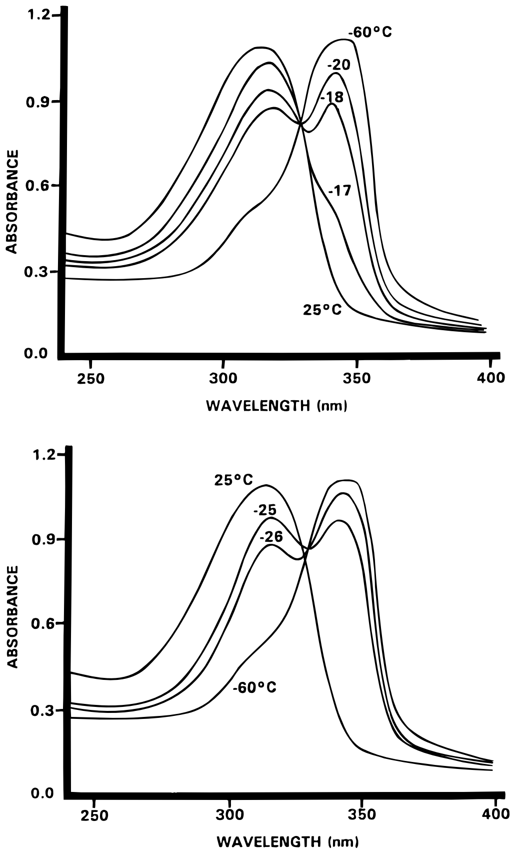

Figure 6. Variable-temperature solid-state UV spectra of C5-C6 upon (A) heating and (B) cooling.

approximtely −1 °C/min, with scan durations of 1 s) only shows one broad transition. At 25 °C a relatively broad peak is seen with a maximum at 320 nm, which is characteristic of a helical backbone conformation. Upon cooling, a shoulder on the 320 nm absorption band develops between −25 and −40 °C. Below −40 °C, it is apparent that there are at least two overlapping absorption bands, as may be seen in the −50 °C spectrum of C5-C12 in Figure 8. Hence, it is thought that two or more different conformations are present in C5-C12 at

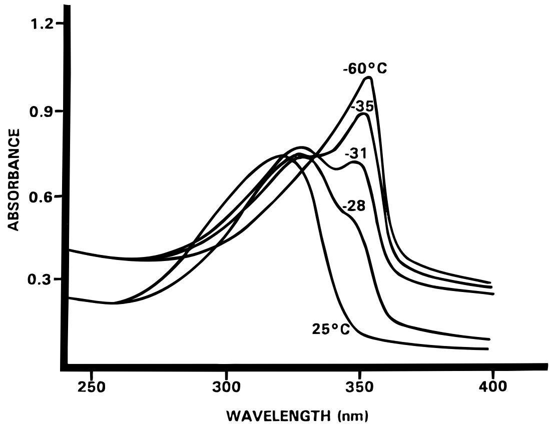

Figure 7. Variable-temperature solid-state UV spectra of C5-C8.

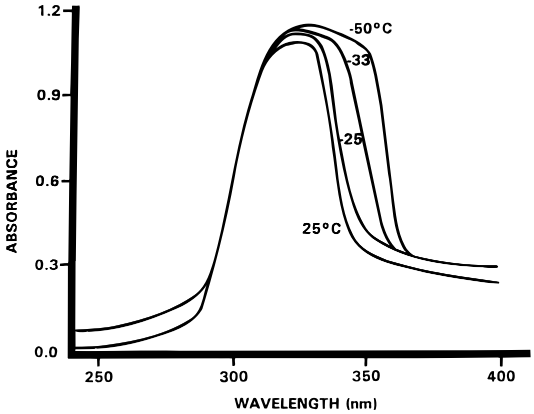

Figure 8. Variable-temperature solid-state UV spectra of C5-C12.

low temperatures. The solid-state UV spectral data are summarized in Table 2.

Several different types of thermochromic behavior were detailed in the preceding discussion. Similar observations have also been made for many other symmetric[15,16] and asymmetric[23,26] poly(*n*-alkyl-*n*-alkyl′-silanes). It is found that the UV thermochromism

Table 2. Solid-State UV Absorption Spectra of Poly(*n*-pentyl-*n*-alkylsilanes)

	T_{trans} (°C)		$\lambda_{\max}$ (nm)	
polymer	cooling	heating	25 °C	−50 °C
C2-C5	−42	−43	306	310, 330
C3-C5	3	4	324	339
C4-C5	−45, 45[b]	−45, 45[b]	314	314, 338[a]
C5-C6	−25	−19	314	344
C5-C8	−32	−32	320	351
C5-C12	−30	−22	320	327, 347[a]

[a] Shoulder. [b] No shift at transition, peak only narrows.

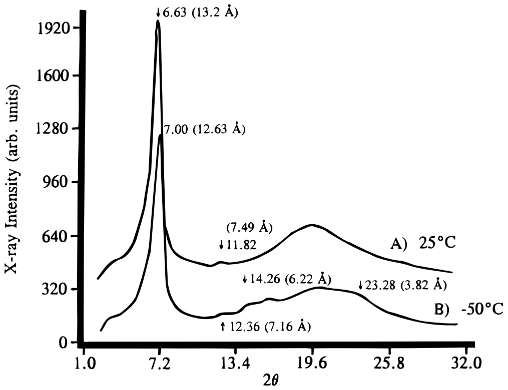

Figure 9. X-ray diffractogram of an unoriented film of C5-C6 at (A) 25 °C and (B) −50 °C.

observed upon cooling of alkyl polysilane films can be arranged into four categories: (1) A discontinuous transition occurs over a small temperature range. An absorption band at a longer wavelength grows to replace the original absorption band, which decays away (C5-C6, C5-C8). (2) One or more shoulders grow on the long-wavelength side of the original absorption band, which changes little in intensity (C4-C5,[22] C5-C12, C2-C5).[22] (3) The UV absorption band quickly shifts to a longer wavelength over a narrow temperature range (C3-C5).[22] (4) The UV absorption band very gradually and smoothly increases its wavelength (C1-C4).[27]

X-ray Diffraction and Chain Conformation

It has been shown that symmetric poly(di-*n*-alkylsilanes) with 4−14 methylene units in their side chains all exist as hexagonal, columnar liquid crystals[19] at temperatures above their disordering transitions. Hexagonal, columnar mesophases have also recently been reported for the following asymmetric poly(alkylsilanes): C4-C6,[26] C5-C6,[18] C6-C7,[18] C3-C5,[22] and C4-C5.[22]

C5-C6 Polymer. At 25 °C, the diffraction pattern of C5-C6 (Figure 9A) shows two reflections: a sharp peak at 13.2 Å (6.63°) followed by a weak peak at 7.49 Å (11.8°). The ratio of these d-spacings is 1.76, slightly greater than $\sqrt{3}$. Consequently, the structure is that which is expected at high temperatures—hexagonal, columnar condis crystalline with $a = b = 15.1$ Å. This compares well with the value of 14.9 Å determined by KariKari and Farmer.[18] Figure 10 illustrates the disordered conformation and the cylindrical packing of the polymer chains in the hexagonal, columnar mesophase.

At −40 °C, below the first-order transition, KariKari and Farmer[18] indexed a diffraction pattern of an oriented film of C5-C6. The flat-film photograph revealed a low degree of crystallinity, due to the lack of sharpness of the reflections. A strong equatorial reflection at 12.63 Å and four weaker equatorial at 7.16, 6.29, 5.87, and 5.31 Å, along with a sharp reflection at 3.81 Å on the first layer line, were present. The d-spacings were indexed by a monoclinic unit cell with $a = 14.7$ Å, $b = 25.4$ Å, $c = 4.0$ Å, and $\gamma = 120°$. The 4.0 Å repeat distance is consistent with an all-trans backbone conformation. The lack of crystallinity seen by KariKari is borne out by the weakness of the peaks in Figure 9B, the diffractometer scan which we obtained for an unoriented film of C5-C6 at −50 °C. Except for the sharp peak at 12.63 Å, all of the peaks are very weak. The four peaks at 12.63, 7.16, 6.22, and 3.82 Å each correspond to reflections seen by KariKari. The broad peak at 5.1−5.9 Å (15.0−17.4°) probably is a superposition of the two reflections seen by KariKari at 5.86 and 5.31 Å. Hence, it is concluded that our X-ray diffraction pattern at −50 °C is consistent with the monoclinic unit cell and trans backbone conformation determined by KariKari.

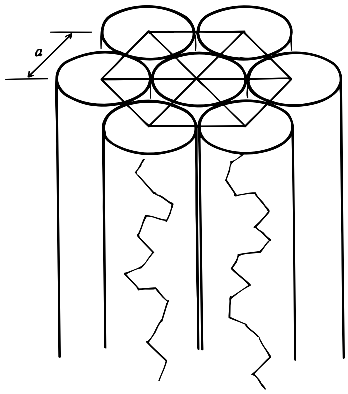

Figure 10. Packing of polymer chains in the hexagonal, columnar mesophase.

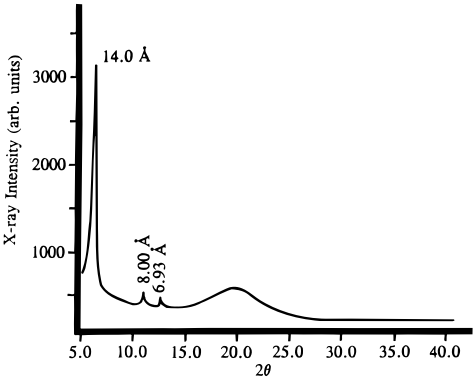

Figure 11. X-ray diffractogram of an unoriented film of C5-C8 at 25 °C.

C5-C8 Polymer. The structure of C5-C8 is very similar to that of C3-C5.[22] Both of these polymers maintain hexagonal, columnar packing both above and below the order−disorder transition. At 25 °C, the X-ray diffractometer scan of an unoriented film of C5-C8 (Figure 11) displays a strong, sharp reflection at 14.0 Å, followed by weak but relatively sharp reflections at 8.00 and 6.93 Å. The latter two reflections are the d/$\sqrt{3}$ and d/$\sqrt{4}$ peaks expected for the hexagonal lattice. There is very little change in the diffraction pattern upon cooling. Due to thermal contraction, the main peak gradually shifts to a smaller d-spacing as the temperature is decreased. At −40 °C it appears at 13.6 Å. The halo also shifts to a slightly longer diffraction angle and sharpens somewhat as the temperature decreases.

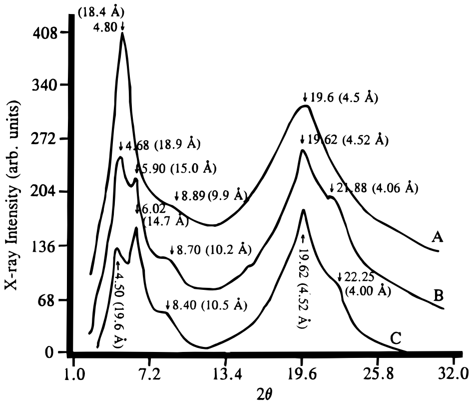

Figure 12. X-ray diffractogram of an unoriented film of C5-C12 at (A) 25 °C, (B) −25 °C and (C) −50 °C.

Asuke[26] found that poly(*n*-butyl-*n*-hexylsilane) (C4-C6) also exhibits hexagonal, columnar packing at all temperatures. It appears that this is a general feature of poly(*n*-alkyl-*n*-alkyl′silanes) with relatively long side chains and a side-chain asymmetry of two or three methyl groups. The asymmetry of these polymers is too great to permit crystallization, so the structure in which the molecules pack as cylinders in a hexagonal lattice is retained at low temperatures.

C5-C12 Polymer. The X-ray diffraction pattern of an unoriented film of C5-C12 at 25 °C (Figure 12A) consists of a broad but sharp-tipped maximum at 18.4 Å (4.8°), a barely discernable shoulder on this peak around 10 Å (9°), and a broad amorphous halo at 4.5 Å (19.6°). The polymer has little order. The low angle peak is probably a manifestation of a partial alignment of the molecules as in a nematic phase, but the degree of order is significantly diminished with respect to the hexagonal, columnar liquid crystalline structure seen in so many poly(*n*-alkyl-*n*-alkyl′silanes) at high temperatures.

When the polymer is cooled, the X-ray diffraction pattern changes somewhat. The changes seen in the diffraction pattern upon cooling occur at about −20 °C, which corresponds to the higher-temperature peak seen in the DSC cooling scan in Figure 4. The onset of this DSC transition is at −19 °C with the peak at −23 °C. Below −25 °C, very little change is seen in the diffraction pattern, as evidenced by the similarity of the patterns at −25 and −50 °C (Figures 12B and 12C, respectively). At −50 °C, the broad, sharp-tipped reflection observed at 18.4 Å at 25 °C is split into two peaks at 19.6 and 14.7 Å. There also may be one or more weaker peaks present between these maxima, as there is some structure to this region. This corroborates what is suggested by the low-temperature UV spectra—there must be several backbone conformations present in C5-C12 at low temperatures. The presence of a shoulder on the high-angle side of the amorphous halo may indicate multiple preferred conformations of the alkyl side chains as well, because the d-spacing of the amorphous halo for alkyl polysilanes is approximately that of the interchain distance commonly seen for alkyl chains.

The diffraction pattern as a whole does not display enough order to be considered indicative of a crystalline structure. For C5-C12, C3-C5,[22] and C5-C8 the same scenario is observed. First-order transitions are seen by DSC, along with corresponding thermochromic shifts in the UV spectra. However, these materials are shown by X-ray diffraction not to crystallize at these transitions. What, then, is the nature of the transitions? To attempt to answer this question, we must examine the model of Schweizer for order−disorder transitions of conjugated polymers.

Model of Schweizer for Order−Disorder Transitions of Conjugated Polymers

In addition to polysilanes, several other types of conjugated polymers exhibit order−disorder phase transitions. Poly(diacetylenes)[28] and alkyl-substituted poly(thiophenes)[29] have displayed this type of transition both in solution and in the solid state. Schweizer attempted to ascertain the mechanism or driving force for these transitions.

The model[20] was originally developed for a conjugated polyene (i.e., polyacetylene) in solution. The reader is referred to refs 20 and 21 for a detailed description of the model, but a brief summary of the pertinent aspects follows. In conjugated polymers, electrons are delocalized along the axis of the chain backbone. The delocalization is maximized by an all-trans, planar backbone conformation. Since the presence of non-trans conformers disrupts the electron delocalization by decreasing the amount of π-orbital overlap, Schweizer modeled the non-trans conformers as noninteracting “defects”. All defects were assumed to be characterized by the same dihedral angle and energy of creation, ϵ.

Upon cooling, the conjugated polymer orders as the conformation extends and defects are frozen out. This increases the amount of electron delocalization and enhances the polarizability of the backbone. For nonpolar systems, the dispersion interaction (i.e. van der Waals forces due to instantaneous dipoles) between the backbone and the surrounding medium is the dominant attractive interaction. The energy of this interaction scales with the polarizability of the polymer backbone and the surrounding medium, which physically signifies that it scales with the ability of the electrical charge to adjust to the local electric field by deforming and lowering the mutual potential energy. The enhancement of the backbone polarizability with increasing ordering stabilizes the rod-like trans planar conformation via the attractive dispersion interaction and is a driving force for structural transitions.[20]

In this model a summation of the contributions of the solvent and the electronically-decoupled side chains to the dispersion is used for polymer solutions. In the solid state, the side chains are the only media that are assumed to interact with the polymer backbone. Schweizer characterized the backbone−side chain/solvent dispersion interaction by using the backbone delocalized-electron contribution to the dispersion interactions for an all-trans conformation. This energy of the dispersion interaction is denoted as V_D, and the ratio V_D/ϵ has been termed the “coupling constant”. This dimensionless group largely controls the qualitative trends of the model. Three regimes of behavior are observed.[20,21]

Small V_D/ϵ, or “weak coupling”, generally means that the polymer backbone is either stiff or has a low polarizability. For these systems, a slow, continuous increase in the mean conjugation length (a length scale for electron delocalization along the polymer backbone), ξ_M, and λ_{max} occurs as the temperature is increased. The free energy surface is unimodal at all temperatures, and no abrupt transition is observed.

As V_D/ϵ increases, the free energy surface begins to flatten out over a small temperature range. In this temperature range, the minimum free energy shifts from one end of the flattened region to the other. The result is that intermediate values of the coupling constant V_D/ϵ result in a rapid increase in ξ_M and λ_{max} over a small temperature range.

Eventually a critical value of V_D/ϵ is reached, and the free energy surface becomes bimodal over a small temperature range. The regime above this critical value of the coupling constant is called “strong coupling” and is characteristic of polymer backbones that are highly polarizable and, usually, relatively flexible. The bimodal free energy surface is manifested in the UV spectra as an abrupt thermochromic shift centered at T_c, the critical temperature.

All three of these types of behavior predicted are seen in the solution and solid-state UV absorption spectra of conjugated polymers. Also note that these types of behavior account for three of the four types of UV spectra discussed above for the poly(*n*-alky-*n*-alkyl′silanes).

It should be noted here that quantum chemical calculations[30] have revealed that the silicon backbone is even more polarizable than that of the polyene and that *gauche*-like defects appear to almost totally disrupt the σ-conjugation of the polysilane backbone. Thus, although quantitative differences between the behavior of σ- and π-conjugated polymers are possible, Schweizer resolved that the physical circumstances in these two types of systems are similar enough that the model should be at least qualitatively applicable to polysilanes.[21]

Schweizer successfully applied the model to predict the transition temperatures and UV absorption maxima of polysilanes in solution, and it appears that solid films show the same types of relationships, although different values of V_D and ϵ must be employed. Since most of the solvents used by Schweizer and the side chains of the poly(*n*-alkyl-*n*-alkyl′silanes) are composed of saturated entities, large differences in the polarizabilities would not be expected. V_D depends mainly on the polarizabilities, so one of the major quantitative differences that would be expected is that due to the enhanced interactions that result from the close proximity in the solid state of the side chains and backbones of neighboring molecules to the polymer backbone. It is expected that changes in side-chain structure and the corresponding changes in interchain packing may have quite complex effects on the dispersion interactions. It is also possible that packing effects may result in a series of discrete values for the dispersion interaction instead of a continuum of values as would be expected for a polymer in solution. Nonetheless, if a conjugated polymer is not capable of crystallization, then first-order transitions due to polarization interactions are a very real possibility. In any system with sufficient regularity to crystallize, this phenomenon will be overshadowed. The polymer will probably organize into a crystalline structure upon cooling at, or somewhat before, T_c is reached.[20] Any thermochromic shifts upon crystallization correspond to a change of the disordered backbone conformation characteristic of the high-temperature liquid crystalline state to the backbone conformation characteristic of the crystal structure, which may or may not be more extended than the conformation present at higher temperatures.

Discussion

The effects of changes in side-chain asymmetry on the structures and properties of the poly(*n*-alkyl-*n*-alkyl′silanes) are much clearer when the possibility of polarization-driven transitions is taken into account. For large side-chain asymmetries and long side chains, conformational changes are most likely induced by polarization interactions, whereas crystallization is the dominant force that effects conformational changes in alkyl polysilanes that are symmetric or have an asymmetry of one methyl group. In the foregoing discussion, the following nomenclature will be used. The length of the longer side chain in carbon atoms will be denoted R_L, while the length of the shorter side chain will be designated R_S. The side-chain asymmetry, *A*, is simply the difference between R_L and R_S.

All poly(*n*-alkyl-*n*-alkyl′silanes) with $A = 0$ or 1 are crystalline at low temperatures. If $R_S \geq 3$, an order–disorder transition from the crystalline solid to a hexagonal, columnar mesophase occurs upon heating. The magnitude and direction of the thermochromic shift is determined by the conformation present in the crystal structure. For C4-C5 there is little conformational change at the 45 °C first-order transition.[22] Upon cooling of the mesophase, the backbone conformation changes from the disordered chain conformation of the columnar structure to a 7/3 helix. Since both of these conformations absorb in the same range of wavelengths, the only change in the UV absorption spectra is a narrowing of the 314 nm band, which reflects the ordering of the system due to the presence of only a single backbone conformation at low temperatures. On the other hand, for C5-C6 a large conformational change occurs from the disordered conformation to an all-trans conformation. Consequently, the UV absorption maximum shifts from 314 to 344 nm upon cooling. For C4-C5, the only polymer of the C5-CX series that showed a glass transition,[22,31] there is also a minute change in the UV spectra at T_g. A very small shoulder develops on the long-wavelength side of the 314 nm band. The explanation for this change is not clear.

The behavior of poly(*n*-alkyl-*n*-alkyl′silanes) with $A = 2$ or 3 depends upon R_S. There seem to be separate regimes for polymers with $R_S \geq 4$ and for $R_S = 2$ or 3. For the case of long R_S, the behavior is that found in C4-C6[26] and C5-C8. There is hexagonal, columnar packing at all temperatures, with a first-order transition and corresponding abrupt thermochromic shift in the UV absorption maximum most probably caused by the polarization interaction between the silicon backbone and the electronically decoupled alkyl side chains.

The behavior of those polymers with $R_S < 4$ is more complex. C3-C5[22] exhibits hexagonal packing at all temperatures. However, the thermochromic transition of C3-C5 is not abrupt. Instead of a new absorption band growing to replace the original band, the λ_{max} red shifts rapidly over a temperature range of approximately 10 °C upon cooling. This may be interpreted to signify that C3-C5 falls into the intermediate coupling regime of Schweizer’s model. The polarization interaction seems to be somewhat larger when the length of the alkyl side chain is at least four carbon atoms long, as C4-C6 and C5-C8 show the characteristics of the strong coupling regime. An explanation for this which may be postulated is that approximately four carbon atoms are needed for the side chains to loop back into close proximity with their own silicon backbone (as is seen in some “back-biting” reactions). Thus, more dispersion interaction is possible when the side chains can exist in conformations that have one or more carbon atoms in close proximity to the conjugated silicon backbone. While the first three carbon atoms of the side chain would not participate in this mechanism, several of the atoms from C4 on out could curl back into close proximity with their own silicon backbone, which would increase the polarization interaction somewhat as the side-chain length increases. A second effect may also limit the dispersion interactions in highly asymmetric polymers. Since the interchain spacing is largely determined by the longer side chain, it follows that for a large side-chain asymmetry the shorter side chain may not be able to reach neighboring polymer backbones even if it adopts an extended all-trans conformation. Consequently only the longer side chain would contribute to polarization interactions with other polymer backbones.

In any case, it is evident that the criterion that $R_S \geq 4$ must be fulfilled in order for a poly(*n*-alkyl-*n*-alkyl′-silane) to exhibit the characteristics expected for the strong coupling regime. This also has been shown to be the minimum side-chain length for which the hexagonal mesophases have been observed in the symmetric poly(di-*n*-alkylsilanes), the only homologous series of poly(*n*-alkyl-*n*-alkyl′silanes) for which all of the members up to $R_L = 14$ have been investigated.

Wallraff et al.[23] reported that C3-C6 shows only a gradual shift in λ_{max} upon cooling, which is the behavior typical of the weak coupling regime. C2-C5[22] is amorphous and shows no first-order transition in the DSC. Its thermochromic behavior, in which a second peak forms upon cooling without the disappearance of the original absorption band, does not exactly fit any of the regimes of the conjugated polymer model. This type of thermochromic behavior has been observed for several poly(*n*-alkyl-*n*-alkyl′silanes) with $A \geq 2$, but is not well understood. It can occur for polymers that appear amorphous by DSC like C2-C5, but it also is seen in polysilanes that have first-order transitions in their DSC thermograms such as C5-C12.

An attentive reader may have noticed that the preceding discussion of polymers with $A = 2$ or 3 did not address the case of $R_S = 1$. The reason for this omission is that one of the materials that fits this description, poly(methyl-*n*-propylsilane) (C1-C3) is crystalline at room temperature.[18,27] Hence, C1-C3 should be classified with the short-side-chain polysilanes with $A = 0$ or 1 instead of those with $A = 2$ or 3.

Poly(*n*-alkyl-*n*-alkyl′silanes) with $A \geq 4$ and $R_L \geq 6$ show first-order transitions that are probably caused by the polarization interactions. There is only partial ordering and alignment of the chain axes rather than hexagonal, columnar packing, due to the destabilizing effect of the great asymmetry. Many of these compounds show an abrupt thermochromic shift at the first-order transition, but in others like C5-C12 the original UV absorption band does not decrease in intensity when the new absorption band forms. The reason for this is unknown. When $A \geq 4$ and $R_L < 6$ the polysilane is amorphous and only shows a gradual thermochromic shift as the temperature decreases. Both C1-C5[32] and the less highly asymmetric C1-C4[27] show this type of behavior because they are too asymmetric to crystallize and because the C1 side chains are too short to contribute to polarization interactions with other polymer backbones.

Conclusions

It has been demonstrated that the structure and properties of the poly(*n*-alkyl-*n*-alkyl′silanes) can be classified according to the side-chain asymmetry and the lengths of the shorter and longer alkyl side chains. These polymers may be categorized into several groups: (1) For $A = 0$ or 1 and $R_L \geq 4$, the polymers are crystalline at low temperatures and undergo an order−disorder transition to a hexagonal, columnar mesophase upon heating. When the mesophase is cooled, if the crystallization results in a large conformational change, there is an abrupt UV thermochromic red shift at the disordering transition. (2) For $A = 2$ or 3 and $R_S \geq 4$, a hexagonal, columnar mesophase is present at all temperatures. A first-order transition and abrupt UV thermochromic red shift corresponding to a change to a more extended conformation is observed upon cooling. This shift is most likely due to the polarization interaction between the conjugated silicon backbone and the electronically decoupled alkyl side chains. (3) For $A \geq 4$ and $R_L \geq 6$, only partial ordering and chain alignment occur. Again, an observed first-order transition is probably due to the polarization interaction between the conjugated silicon backbone and the alkyl side chains. The UV thermochromic shift at the first-order transition always involves the formation of a new absorption band at higher λ_{max} upon cooling, but the original room temperature absorption band does not decay away in all cases.

For polysilanes with shorter side chains, the behavior is often more complicated, although some generalizations can be made. When the asymmetry is large, the polymers tend to be amorphous and show only a gradual red shift in the UV spectra as the temperature is decreased. When the asymmetry is small, the polymers are crystalline at low temperatures and often show an imperfect columnar packing at high temperatures.

It has been demonstrated that the solid-state behavior of polysilanes with linear alkyl side chains is consistent with the model of Schweizer[20,21] for conjugated polymers. All three of the regimes of thermochromic behavior predicted by the model are observed in this class of polysilanes. As a caveat, however, it should be noted here that no attempt has been made to estimate the values of the dispersion interactions between the conjugated silicon backbone and the alkyl side chains or the characteristic defect energies. These calculations were deemed to be beyond the scope of this investigation. The intention is only to assert that polarization interactions are a *likely cause* of the thermochromic transitions manifested by several of these polysilanes and that the results do not disprove this postulate.

The structures and conformations of a series of poly(*n*-pentyl-*n*-alkylsilanes) have been determined. As is common for alkylpolysilanes, most of these polymers exhibit hexagonal, columnar mesophases at temperatures above 45 °C. C5-C8 has the hexagonal, columnar structure at all temperatures. C5-C6 crystallizes only to a small degree. The trans conformation and monoclinic unit cell found by KariKari and Farmer[18] are confirmed by our results.

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