Structure and Properties of Poly(*n*-pentyl-*n*-alkylsilanes). 1

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ABSTRACT: We have investigated the solid-state electronic properties and the structures of three asymmetric poly(*n*-pentyl-*n*-alkylsilanes) using UV absorption, calorimetry, and X-ray diffraction. Poly(*n*-butyl-*n*-pentylsilane) (C4–C5) has a 7/3 helical backbone conformation at 25 °C, as has been previously observed for poly(di-*n*-butylsilane) and poly(di-*n*-pentylsilane). The X-ray diffraction pattern of a uniaxially oriented film of C4–C5 may be indexed with an orthorhombic unit cell containing hexagonally packed chains with a = 13.23 Å, b = 22.92 Å, and c = 13.88 Å. At 45 °C a sharp first-order phase transition to a hexagonal, columnar structure with lattice parameter $a = b$ = 13.4 Å is observed. Poly(*n*-propyl-*n*-pentylsilane) (C3–C5) shows a thermochromic shift of its UV absorption maximum from 324 to 339 nm upon cooling. Above the first-order phase transition observed at −2 °C, C3–C5 has a hexagonal, columnar structure with lattice parameter $a = b$ = 12.2 Å. Poly(ethyl-*n*-pentylsilane) is a poorly ordered polymer with a second-order phase transition at −35 °C. The degree of order and the mechanical strength of the materials decrease markedly as the side chain mismatch increases in this series of polymers.

Introduction

Polysilanes, a relatively new class of polymers with an all-silicon backbone, have been attracting considerable attention lately. Much of this interest is due to their radiation sensitivity, which is a consequence of electron delocalization along the σ-bonded backbone. They show intense UV absorption in the 300–400-nm range, with absorption maxima that are dependent upon the backbone conformation.[1] These electronic properties make polysilanes ideal candidates for lithographic materials.

The first poly(alkylsilanes) to be studied have been the symmetric poly(di-*n*-alkylsilanes) because their symmetry leads to high degrees of crystallinity. Most of these polymers, including poly(di-*n*-hexylsilane) (C6–C6),[2] 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)[3] and poly(di-*n*-pentylsilane) (C5–C5)[4] have a 7/3 helical backbone conformation. Films of this homologous series of compounds are often brittle and tend to crack. The introduction of asymmetry into the side chains should yield polymers that produce films that are more flexible and less crack-prone.

In this paper we introduce three new asymmetric poly(*n*-pentyl-*n*-alkylsilanes): poly(*n*-butyl-*n*-pentylsilane) (C4–C5), poly(*n*-propyl-*n*-pentylsilane) (C3–C5), and poly(ethyl-*n*-pentylsilane) (C2–C5). The degree of asymmetry of the side chains influences the conformation of the silicon backbone and greatly affects the physical properties of the polymer.

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 precipitation from toluene with 2-propanol and ethyl acetate. The resulting products are *white solids that show a large range of physical properties.* C4–C5 is hard and waxy, C3–C5 is softer, and C2–C5 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 μ-Styragel columns of porosity 10^4, 10^5, and 10^6 Å. THF was the eluant. Monomodal distributions with M_n's ranging from 100 000 to 400 000 and M_w's ranging from 400 000 to 1 200 000 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 an 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. The polymer crystal structures were analyzed by X-ray diffractometry using nickel-filtered Cu Kα radiation. Both unoriented films and films stretched uniaxially to a draw ratio of approximately 4 were used to obtain both powder and fiber diffraction patterns.

Results and Discussion

(a) Physical Properties of 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. C4–C5 forms strong, tough, but flexible films that feel somewhat similar to low-density polyethylene. Films of C3–C5 are weaker, and C2–C5 is soft and rubbery and films of it tear much more easily. All three of these polymers produce films that are not brittle and that show superior fracture toughness when compared with the symmetric poly(di-*n*-alkylsilanes).

Films of C4–C5 can be stretched to moderately high draw ratios. A film with a draw ratio of 4.0 was obtained for X-ray diffraction, although the film broke and had to be regripped three times during the drawing process. Films of C3–C5 and C2–C5 are less cohesive and tend to retract rather than retain their elongation when the tension on them is removed.

(b) Thermal Properties. The differential scanning calorimetry (DSC) analysis of poly(*n*-butyl-*n*-pentylsilane)

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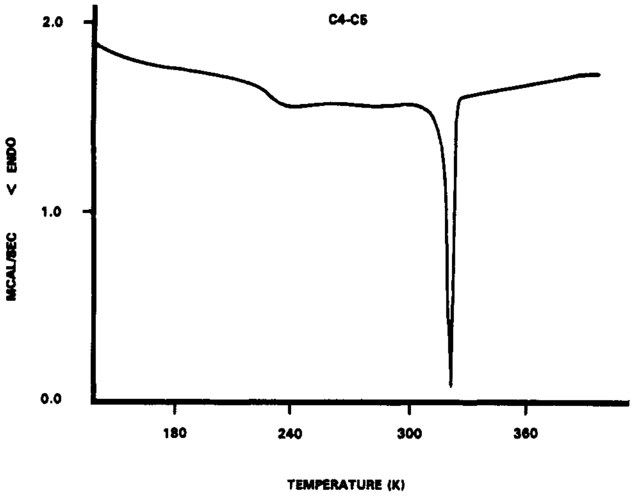

Figure 1. DSC thermogram of C4–C5 at a heating rate of 20 °C/min.

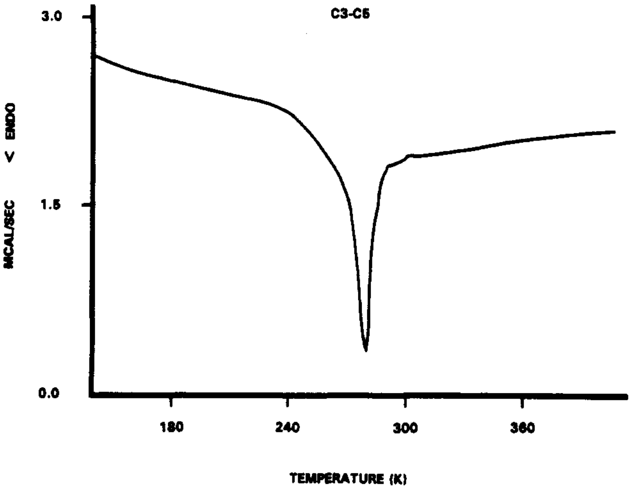

Figure 2. DSC thermogram of C3–C5 at a heating rate of 20 °C/min.

(C4–C5) (Figure 1) is very similar in appearance to those reported for C4–C4[3] and C5–C5.[4] A second-order transition is observed at −44 °C, followed by a sharp endotherm at 45 °C possessing a heat of transition of 2.5 cal/g. This sharp endotherm corresponds to a solid-state disordering transition seen[6] in poly(di-*n*-alkylsilanes) with side chains longer than three carbon atoms. It is seen that the asymmetry of C4–C5 lowers the temperature of the disordering transition relative to those of C4–C4 (87 °C) and C5–C5 (70 °C).[4] The transition enthalpies of these three compounds, however, are nearly identical.

The DSC of poly(*n*-propyl-*n*-pentylsilane) (C3–C5) (Figure 2) shows only a first-order transition at −2 °C. This endotherm is broader than that of C4–C5, but the transition enthalpy of 3.1 cal/g is comparable. Only a second-order transition at −35 °C is present in the DSC scans of C2–C5. The DSC analyses of the three polymers are summarized in Table I.

(c) Solid-State UV Spectra. The subambient variable-temperature UV spectrum of a C4–C5 film is shown in Figure 3. At 25 °C the sample gives a relatively sharp absorption maximum at 314 nm, which lies in the range (305–325 nm)[1] usually characteristic of a helical or disordered conformation of the silicon backbone. When cooled to −45 °C, a very small shoulder appears at 338 nm, but the intensity of the 314-nm band does not diminish as the temperature is lowered further. Upon warming, the shoulder disappears.

Table I
DSC of Poly(*n*-pentyl-*n*-alkylsilane) Films

polymer	transition temp[a] (°C)	order	ΔH (cal/g)
C4–C5	−44	2	
	45	1	2.5
C3–C5	−2	1	3.1
C2–C5	−35	2	

[a] Heating rate of 20 °C/min.

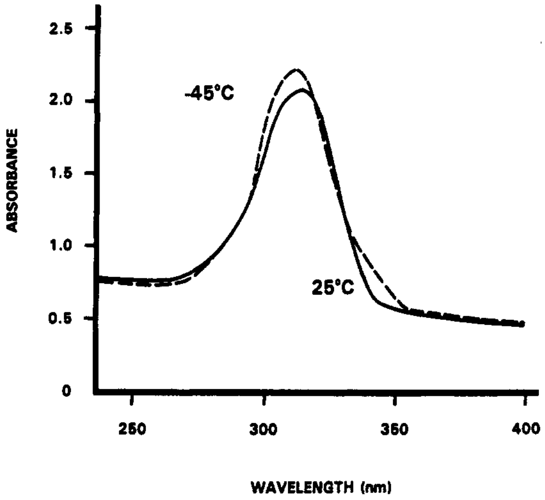

Figure 3. Variable-temperature solid-state UV absorption spectra of C4–C5.

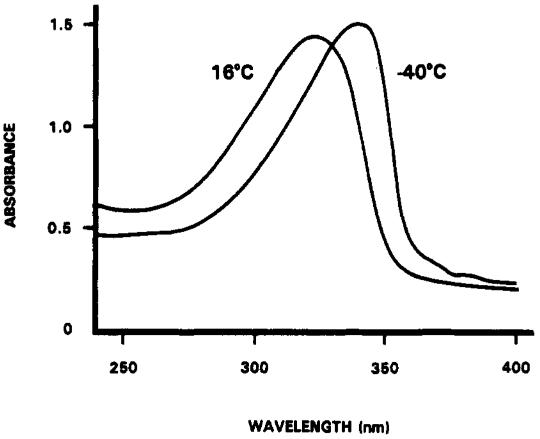

Figure 4. Variable-temperature solid-state UV absorption spectra of C3–C5.

C3–C5 shows a different type of behavior (Figure 4). A red shift from 324 to 339 nm corresponding to the DSC endotherm is seen in the UV spectra upon cooling. This shift implies that a conformational change occurs at the transition.

The variable-temperature UV spectrum (Figure 5) of C2–C5 is quite interesting. At ambient conditions a somewhat broad absorption maximum is centered at 306 nm. A shoulder at 330 nm becomes perceptible upon cooling to −15 °C. This 330-nm band grows as the temperature is lowered, and an isosbestic point is reached at −42 °C. At −50 °C, the 330-nm band is just a little more intense than the original absorption peak (which has shifted slightly to 310 nm). Surprisingly, the ratio of these two peak intensities is unchanged upon further cooling to −80 °C. Evidently, the backbone conformations are frozen in due to lack of mobility at temperatures below −50 °C. The behavior described above is fully reversible. Upon heating, the isosbestic point changed only 1 °C and the second band disappeared at −15 °C. The solid-state UV data are summarized in Table II.

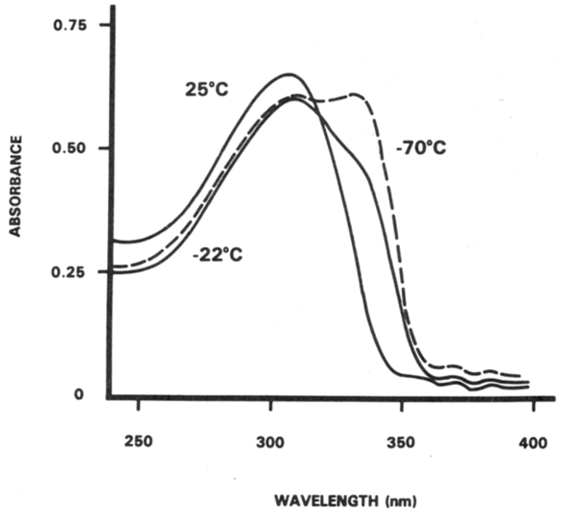

Figure 5. Variable-temperature solid-state UV absorption spectra of C2–C5.

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

	transition temp (°C)		λ_{max} (nm)	
polymer	cooling	heating	25 °C	−50 °C
C4–C5	−45	−45	314	314, 338[a]
C3–C5	3	4	324	339
C2–C5	−42	−43	306	310, 330

[a] Shoulder.

(d) X-ray Diffraction and Chain Conformations. It has been shown that symmetric poly(alkylsilanes) with 4–14 methylene units in their side chains all exist as hexagonal, columnar liquid crystals[6] at temperatures above their disordering transitions. Hexagonal, columnar mesophases have also recently been reported for the following asymmetric poly(alkylsilanes): C4–C6,[7] C5–C6, and C6–C7.[8] Thus it is expected that C4–C5, C3–C5, and C2–C5 may also exhibit similar mesophases.

C4–C5 Polymer. At 100 °C, the X-ray diffraction pattern (Figure 6A) of an unoriented film of C4–C5 has a very strong reflection at 11.6 Å, followed by a weak reflection at 6.75 Å. The reciprocals of these *d*-spacings are in the ratio $1{:}\sqrt{3}$, which is indicative of hexagonal packing.[6] The lattice parameter is $a = b = 13.4$ Å.

At 25 °C C4–C5 is highly crystalline. Six sharp Bragg peaks, along with several weaker peaks, are present in the diffractometer trace of an unoriented film, as shown in Figure 6B. In addition to this, a fiber pattern is needed to determine the crystal structure.

Figure 7 is a contour map of reflected intensity of one quadrant of a diffraction pattern obtained from a uniaxially oriented film of C4–C5 with a draw ratio of 4.0. These data were obtained digitally with a diffractometer and then contoured. The horizontal axis shows the reflections from the equatorial plane; the vertical axis corresponds to the meridional reflections. There are three main features: an extremely intense equatorial reflection at 7–9°, a strong near-meridional reflection at 19° followed by several other near-meridional reflections, and a diffuse meridional reflection centered at 46°. The equatorial reflections at 43° and 50° are artifacts due to a copper rod of the sample holder.

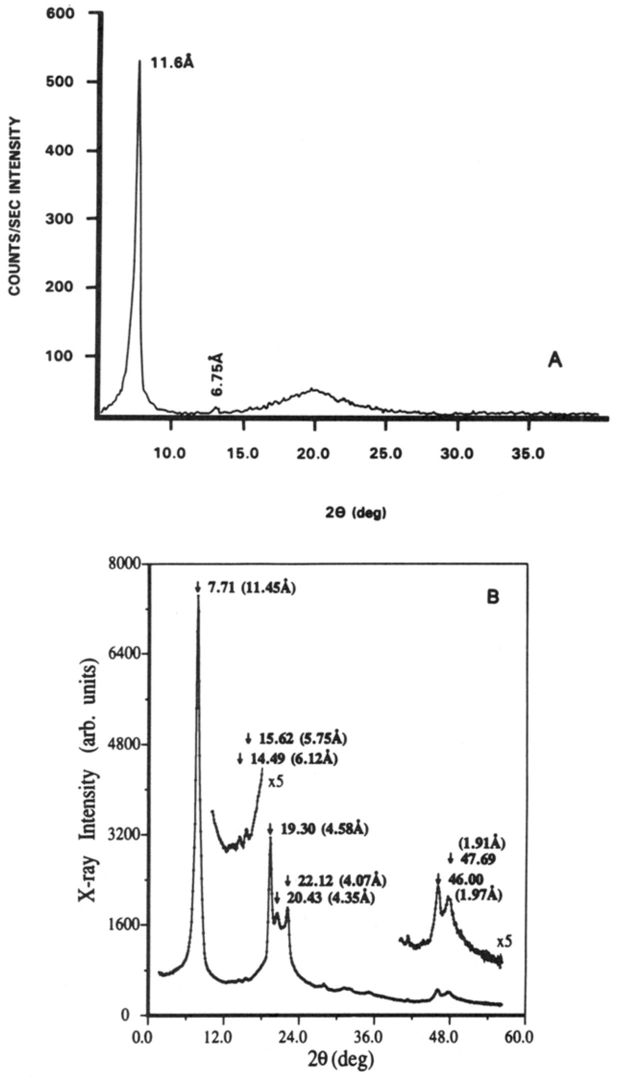

Figure 6. X-ray diffractograms of an unoriented film of C4–C5 at (A) 100 °C and (B) 25 °C.

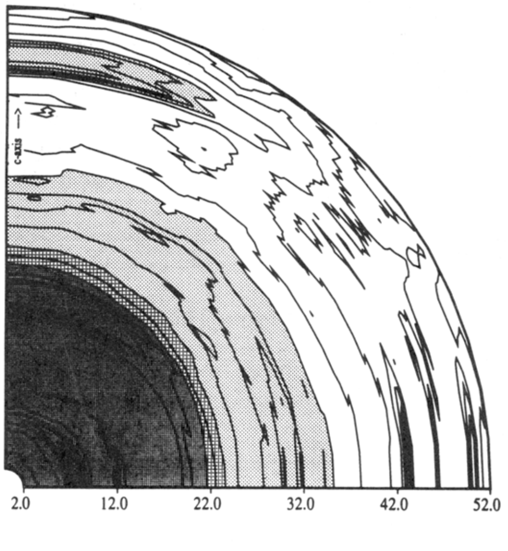

Figure 7. Contour map of constant X-ray intensity between the equatorial (*hk*0) plane and the *c*-axis for an oriented film of C4–C5 at 25 °C. The *c*-axis is vertical.

Table III[9] shows the indexing of the diffraction pattern. The main peak at 11.45 Å (7.71°), which is the intense equatorial reflection of the fiber pattern, is indexed as a superposition of the 110 and 020 reflections of an orthorhombic lattice with hexagonally packed chains. The diffuse meridional reflection at 1.97 Å (46.00°) is indexed as 007. Then, the strong near-meridional reflection at

Table III
Indexing of X-ray Diffraction Pattern of C4–C5 at 25 °C[a]

intensity	2θ	d_{exp} (Å)	d_{calc} (Å)	index
vs	7.71	11.45	11.46	110, 020
vw	14.49	6.12	6.15	102
vw	15.62	5.75	5.73	220
s	19.37	4.58	4.54	013
w	20.43	4.35	4.37	103
m	21.86	4.07	4.08	123
m	22.20	4.01	3.96	033
w	46.00	1.97	1.98	007

[a] Unit cell parameters: a = 13.23 Å, b = 22.92 Å, c = 13.88 Å, γ = 90°. d_{exp} = experimental positions of diffraction maxima; d_{calc} = calculated values of diffraction maxima for the above unit cell.

4.58 Å (19.37°) may be indexed as 013. The indexing corresponds to an orthorhombic unit cell with a = 13.23 Å, b = 22.92 Å, and c = 13.88 Å. When the polymer is cooled to −80 °C, only minor changes in the region between 4.1 and 4.5 Å are seen in the diffraction pattern. These changes are probably due to a reduction of mobility of the alkyl side chains around the second-order transition temperature of −44 °C.

The near-meridional reflection at 1.90 Å (47.69°) is not included in Table III. It may be indexed as the 127 reflection of the orthorhombic unit cell, but the intensity is greater than that which was shown for a 127 reflection in our structure factor calculations. Thus it has been omitted from Table III. It should also be noted that 1.90 Å is approximately the position at which a 002 reflection would be seen for a polymer with an all-trans backbone conformation. However, attempts to index the diffraction pattern for an all-trans conformation failed.

It is somewhat surprising that the meridional 007 reflection is seen for an oriented film that has not been tilted. It was noted that the intensity of this reflection in a diffractometer scan along the meridian was weaker than that of the reflection in the powder pattern. However, sufficient chain alignment to cause the complete disappearance of the meridional reflection evidently was not attained. We should reiterate that the oriented film was drawn multiple times in order to achieve the desired draw ratio, and significant retraction due to relaxation processes occurred each time that the film fractured.

The presence of a 007 reflection confirms that the silicon backbone conformation of the low-temperature form of C4–C5 is 7/3 helical. This is not surprising, as both C4–C4 and C5–C5 also exhibit this same conformation. It should be noted that the first-order transition enthalpy of 2.5 cal/g for C4–C5 is quite similar to the enthalpies of the disordering transitions of C4–C4[3] and C5–C5[4] (2.1 and 2.6 cal/g, respectively). These latter two polymers show no side chain melting, but only the disordering of the 7/3 helices at the transition. In contrast, C6–C6 has a large transition enthalpy of 20 cal/g, because both side chain melting and a conformational change from trans planar to disordered helical occurs.[2] Even C3–C3, which has side chains too short to crystallize but has the trans-planar conformation at ambient temperature, has a transition enthalpy as large as 5.6 cal/g.[10] Thus, the side chains of C4–C5 have some mobility at temperatures above −44 °C. In attempts at computer modeling of the crystal structure, it was observed that the best results were obtained when the helix was treated as cylindrically symmetric.

There is no indication of any layer lines in the contour map for C4–C5 other than the near-meridional reflections at 19–22 °C. In our computer modeling, the intensity of all of the other layer line reflections quickly decayed away as the polymer chains were given more rotational freedom.

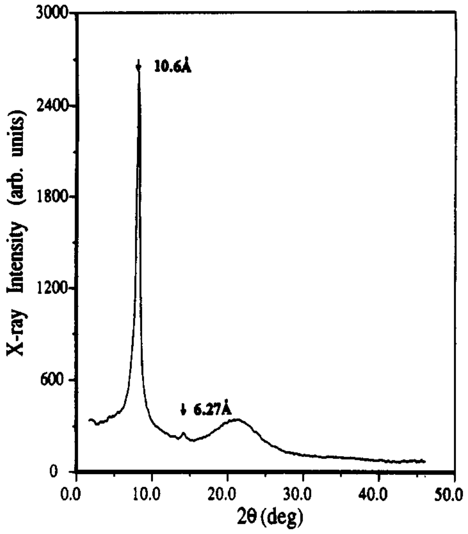

Figure 8. X-ray diffractogram of an unoriented film of C3–C5 at 25 °C.

It is possible that C4–C5 has two phases present below the disordering transition. In both C4–C4[3] and C5–C5[4] some of the high-temperature hexagonal, columnar phase is present below the transition temperature. In Figure 6B a reflection at 8.4° is present as a small shoulder on the main peak at 7.71°. This reflection is more visible in diffractometer scans of oriented films midway between the meridian and the equatorial *hk*0 plane. We speculate that this reflection may be indicative of the presence of a second phase in C4–C5 below the disordering transition. Another possibility is that this peak is due to rings or low molecular weight species present in the polymer.

C3–C5 Polymer. At 25 °C, an unoriented film of C3–C5 yields an X-ray diffraction pattern with a strong peak at 10.6 Å and a very weak reflection at 6.27 Å (Figure 8). The ratio of these d-spacings is approximately $\sqrt{3}$, so the unit cell is hexagonal with $a = b$ = 12.2 Å. In addition to the two aforementioned peaks, a broad peak centered at 3.8 Å of width 0.4 Å is present at temperatures below 0 °C. This signifies that an imperfect side chain ordering occurs at the first-order transition temperature of −2 °C. As the heat of transition is only 3.1 cal/g, the side chains probably have significant mobility in this partially ordered state. Since the low-temperature diffraction pattern shows only two-dimensional order, little can be said definitively about the conformational change that occurs when the UV absorption maximum shifts from 324 to 339 nm upon cooling. Disordered helical and 7/3 helical conformations generally result in absorption maxima in the 305–325-nm range. In many symmetric poly(di-*n*-alkylsilanes) with long side chains of six or more methylene units, side chain crystallization forces the backbone into an all-trans conformation; these polymers show UV absorption around 374 nm.[2,11] However, other poly(alkylsilanes) with all-trans conformations absorb UV at significantly shorter wavelengths. The low-temperature form of C5–C6 has an absorption maximum of 344 nm.[12] The UV absorption peak of poly(dimethylsilane) is even lower, 340 nm.[13] An all-trans conformation does not seem likely for C3–C5, however, because there is no change in the spacing of the hexagonal packing at the transition. A more likely explanation for the relatively long UV absorption maximum below the transition is that there are a significant number of trans conformers in a more open disordered helix.

C2–C5 Polymer. The diffraction pattern of C2–C5 at 25 °C shows only a strong reflection at 10.9 Å. A $d\sqrt{3}$

peak is probably buried in the background noise of the diffractometer scan, and this compound is probably a hexagonal, columnar liquid crystal as most poly(alkylsilanes) are in their high-temperature states.

Conclusions

We have demonstrated that hexagonal, columnar mesophases are observed for three asymmetric poly(*n*-pentyl-*n*-alkylsilanes), C4–C5, C3–C5, and C2–C5, at temperatures above 45 °C. This behavior has been seen previously in the symmetric poly(di-*n*-alkylsilanes) with side chains longer than three carbon atoms and in some other asymmetric poly(alkylsilanes). At lower temperatures, hexagonal packing is maintained in all three polymers, but the degree of order is strongly influenced by the side chain mismatch.

C4–C5, which has a side chain mismatch of only one carbon atom, is quite crystalline below its disordering transition temperature of 45 °C. It has a 7/3 helical backbone conformation below its disordering transition, the same conformation seen in C4–C4 and C5–C5. We found the X-ray diffraction pattern of an oriented film of C4–C5 to be consistent with an orthorhombic unit cell with hexagonal chain packing and $a = 13.23$ Å, $b = 22.92$ Å, and $c = 13.88$ Å.

C3–C5 has a hexagonal, columnar crystal structure at all temperatures studied. This is analogous to poly(*n*-butyl-*n*-hexylsilane), which also has a side chain mismatch of two methylene units and has been found by Asuke[7] to exhibit a hexagonal, columnar structure at all temperatures.

An increase in side chain asymmetry was found to decrease the mechanical strength of films. The films of these three asymmetric poly(alkylsilanes) are flexible and extensible, in contrast to the relatively brittle films produced by the symmetric poly(di-*n*-alkylsilanes).

Future work and work currently in progress include dynamic mechanical analysis, optical microscopy, X-ray diffraction of fibers, investigations of the fracture of thin polysilane films, and studies of other asymmetric poly(alkylsilanes).

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