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Studies of Chain Conformational Kinetics in Poly(di-*n*-alkylsilanes) by Spectroscopic Methods. 1. Poly(di-*n*-hexylsilane), Poly(di-*n*-heptylsilane), and Poly(di-*n*-octylsilane)

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ABSTRACT: A series of poly(di-*n*-alkylsilanes) having hexyl, heptyl, and octyl side chains have been investigated by spectroscopic methods. Whereas the UV spectrum provided information about the electronic structure of the polymer backbone, IR and Raman methods have been used to characterize the molecular conformation of both the main and side chains. These structural studies were correlated with results from thermal analyses and X-ray diffraction measurements. A mechanism involving the melting of the *n*-alkyl side chains with a subsequent disordering of the polymer backbone is proposed.

Introduction

Crystallization has been observed[1-7] in a number of polymers containing long unbranched side chains that can pack together in an ordered array. In many cases[1-6] this side-chain crystallization occurs without a corresponding crystallization of the main chain. X-ray evidence[5,6] suggests that the side chains of poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) are extended at right angles to the main chain, thus enhancing the crystallization process but leaving the main chain amorphous even in materials that exhibit considerable tacticity. On the other hand, there have been studies on isotactic poly(1-alkenes)[7] that have found that both the main chain and the side chain crystallize, presumably due to the structural simplicity of the polymer backbone. Hence, in the absence of a bulky main chain, side-chain crystallization can cause changes in the main-chain conformation, which in turn makes it compatible with the crystal lattice.[5] It is this latter point that became important in understanding the thermally reversible behavior of the poly(di-*n*-alkylsilanes).

Although polysilanes have existed[8] for more than 60 years, there has been very little scientific interest because early materials were intractable and insoluble in all common solvents. Recently, however, there have been a number of reports[9-12] on the synthesis of soluble substituted polysilane derivatives that are processable and can thus be studied by conventional analytical techniques. Most of these polysilanes were unsymmetrically substituted in an atactic configuration, thus giving rise to an amorphous polymeric material. On the other hand, the alkyl derivatives exhibited an intense UV absorption in the range 305-320 nm attributable[13-15] to either a $\sigma\sigma^*$ or a $\sigma 3d\pi_{Si-Si}$ electronic transition, and it was the electronic properties of the unsymmetrically substituted polysilanes that attracted the most attention and eventually led to the development of new applications.[16-19]

A change in the electronic structure with backbone conformation was recently reported[20] for poly(di-*n*-hexylsilane) (PDHexS) in the solid state. The as-polymerized material exhibited an anomalously long wavelength absorption at 374 nm, some 60 nm red-shifted from that of any simple, alkyl-substituted polysilane previously investigated. Subsequent spectroscopic studies revealed that the *n*-hexyl side chains had crystallized, locking the silane backbone into a more ordered conformation, which consequently altered its electronic structure. Although, as mentioned previously, the crystallization of polymers with long unbranched side chains has been known for many years, to date none of those contained a main chain that exhibited such a dramatic change in electronic structure with change in conformation. Thus, the di-*n*-alkyl-substituted polysilanes with side chains of intermediate length represent a novel class of materials that seem to exhibit a unique electronic structure due to conformational rigidity induced by side-chain crystallization.

The present work was undertaken to expand previous studies[20] of the anomalous long-wavelength electronic transition in PDHexS to include poly(di-*n*-heptylsilane) (PDHepS) and poly(di-*n*-octylsilane) (PDOctS), which together seem to form a class of structurally similar materials. The structure of these polysilanes has been further investigated by IR and Raman spectroscopy and correlated with the electronic structure previously described. In addition, wide-angle X-ray diffraction (WAXD) and thermal analysis have been used to better characterize the kinetics of side-chain crystallization.

Experimental Section

Synthesis of Poly(di-*n*-hexylsilane) (PDHexS). The procedure described here is specifically for PDHexS, but it is general, and the same technique has been used for the preparation of PDHepS and PDOctS. A detailed description of the preparation and characterization of symmetrical dialkyl polysilanes will appear elsewhere.[21] The polymerization was carried out as follows. All glassware was dried overnight and assembled hot under argon. Into the dried flask was weighed 7.76 g (0.135 mol, 40% in odorless mineral spirits) of sodium dispersion, and a mixture of 70 mL of toluene and 28 mL of diglyme was added. The reaction mixture was heated to 135 °C in an oil bath with strong stirring and 18.17 g (0.0675 mol) of distilled dichlorodihexylsilane was added over 10–15 min. The exotherm of the reaction was moderated somewhat by controlling the position of the heating bath. After the addition was complete, the viscous, purple mixture was heated for 5 h and then cooled with stirring overnight. The reaction was quenched by the addition of 42 mL of 2-propanol. The polymer was precipitated by pouring the reaction mixture into 830 mL of 2-propanol. The polymer was then filtered by gravity filtration and air dried in the dark. The solid was dissolved in 420 mL of warm toluene, which was washed 5 times with 170 mL of water and dried over Na_2SO_4. Removal of the solvent yielded 4.5 g (34%) of white solid polymer. The polymer as obtained showed a bimodal molecular weight distribution $\bar{M}_w = 2.15 \times 10^6$ and 4.16×10^4 (ratio ~ 1:1). The material was fractionated by repeated precipitation of the polymer from toluene with 2-propanol. In this manner, monomodal molecular weight fractions were obtained. A similar procedure was used for the preparation of PDHepS and PDOctS with yields of 34 and 36%, respectively.

Thermal Analysis. All thermal measurements were made on powdered samples with a Du Pont 1099 thermal analyzer. Heating and cooling rates during DSC (differential scanning calorimetry) measurements were varied between 1 and 10 °C/min. All melting points reported correspond to the endotherm minima observed in a DSC thermogram. The enthalpies of transition were calculated by digitally integrating the area of the melting endotherm and expressing the ΔH_T in units of cal/mol of repeat unit.

Raman Scattering. Raman spectra were recorded by using a Jobin-Yvon HG-2S double monochromator equipped with concave holographic gratings and a spatial filter to enhance stray light rejection. A cooled RCA 31034A-02 photomultiplier tube operating at −1500 V was used to detect the scattered photons because of its high sensitivity and low dark count. Laser excitation was provided by either the 514.5-nm line of a Spectra Physics 165-08 argon ion laser or the 647.1-nm line of a Spectra Physics 165-11 krypton ion laser. All data were collected and processed digitally by a Nicolet 1180 data system. Unless otherwise noted, the Raman spectra shown have not been analogue or digitally smoothed.

Variable temperature measurements were made in a vertical Harney–Miller cell especially constructed for operation in the −150 to +150 °C range. With this flow cell, the sample could be maintained to within ±2 °C of the desired temperature.

Infrared Spectroscopy. IR measurements were made on films of approximately 200-nm thickness supported on silver-coated (~200 nm Ag) microscope slides and investigated in reflection at grazing incidence,[22] which preferentially gives spectra with the electric field vector normal to the surface when compared with the corresponding spectra obtained in transmission. A variation in the relative intensity of bands was observed, indicating orientation in the film plane. A comprehensive study of oriented PDHexS is in progress, with the results to be published elsewhere. Heating of these films to elevated temperatures was accomplished[23] by a flat-plate heater held in contact with the sample slide. Temperature control was provided by a thermistor-controlled feedback system attached to the flat-plate heater. Temperatures could be accurately controlled to within ±1.5 °C.

Results and Discussion

UV Absorption Spectra. Although the UV spectrum of PDHexS in solution at room temperature[24] shows only the typical featureless absorption maximum at 317 nm., its spectral behavior in thin-film form was quite spectacular, as shown in Figure 1. It was this dramatic thermal behavior illustrated in Figure 1 that first[20] aroused our scientific interest. As shown in Figure 1a when the PDHexS film was heated for 2 min at 100 °C, the band at 317 nm characteristic of the simple, alkyl-substituted polysilanes mentioned previously was observed. After 90 min at 30 °C, spectrum b was observed, indicating a partial return of the species that absorbs at 374 nm. Finally, after 120 min a complete return to the initial spectrum c was observed, indicating that this conversion process was totally reversible. It was determined that this behavior was independent of the casting solvent or the molecular weight of the sample, although the kinetics of the regeneration of the 374-nm band were molecular weight dependent.

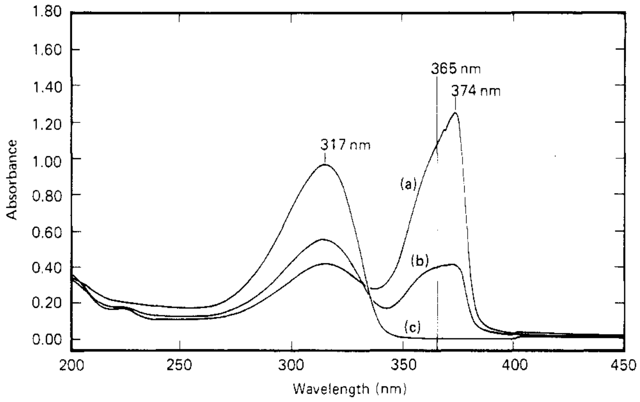

Figure 1. UV spectrum of a thin film of PDHexS on a quartz wafer: (a) film heated and then returned to 30 °C for 120 min; (b) film heated and then returned to 30 °C for 90 min; (c) film heated at 100 °C for 2 min, spectrum recorded immediately.

Similar results have also been observed for high molecular weight samples of poly(di-*n*-heptylsilane) (PDHepS) and poly(di-*n*-octylsilane) (PDOctS) in the solid state. Each sample, when cast as a thin film and baked at 100 °C to remove the casting solvent, shows a typical polysilane electronic transition centered around 317 mm. When the sample is held at 22 °C under vacuum in the cryostat, the intensity of this peak gradually diminishes and is replaced by a more narrow absorption at ~373 nm in a similar fashion to that described for PDHexS. In each case the original absorption at 317 mm, while significantly decreased, never completely disappears. The long-wavelength absorption of PDHepS and PDOctS rapidly disappears upon heating above 45 °C and the original spectra are restored. These thermal effects are reversible, as is also the case for PDHexS.

Infrared and Raman Spectroscopy. Correlations between changes in electronic spectra and the structure of both the main and side chain of the polysilanes were made with IR and Raman spectroscopy. Since vibrations of *n*-alkyl side chains give rise[27] to large changes in the dipole moments of individual bonds, bands associated with the side chain should be intense in the infrared. On the other hand, vibrations of the silicon backbone cause large deformations in the electron cloud, thus giving a large change in polarizability[28] resulting in intense Raman bands. Thus, the use of both IR and Raman spectroscopy provided a method to follow the thermal behavior of both the side chain and the main chain independently.

The IR spectra (3400–600 cm^{-1}) of PDHexS, PDHepS, and PDOctS at 30 °C are shown in Figure 2. Although the general features are the same, there is a considerable variation in relative intensities of bands due to the increasing CH_2/CH_3 ratio as the side chain gets longer. For example, in the CH stretching region, the symmetric CH_2 stretching band at 2854 cm^{-1} is seen to increase, becoming the most intense in PDOctS. Similarly, the band at 2961 cm^{-1}, which remains constant in all three spectra, can be assigned[27] to the asymmetric stretching of the CH_3 group. In a likewise fashion, most of the observed bands have been

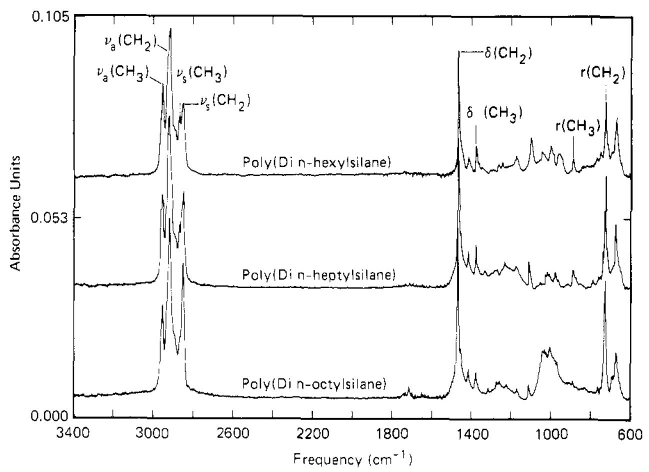

Figure 2. IR spectra of PDHexS, PDHepS, and PDOctS: ν_a, asymmetric stretch; ν_s, symmetric stretch; δ bend; r, rock. The broad feature in the vicinity of 1000-cm^{-1} in the spectrum of PDOctS is an artifact resulting from incomplete cancellation of the reflection spectra obtained from bare metal and PDOctS-coated metal substrates.

Table I
Observed IR Bands of Poly(di-*n*-alkylsilanes) and Their Assignment

frequency, cm^{-1}	assignment[a]
2961 s	$\nu_a(CH_3)$
2924 vs	$\nu_a(CH_2)$
2871 s	$\nu_s(CH_3)$
2854 s	$\nu_s(CH_2)$
1471 vs	$\delta(CH_2)$
1417 m	
1379 m	$\delta_s(CH_3)$
1233 w 1175 w	$\gamma(CH_2) + w(CH_2)$
1110 w 977 w	$\nu(CC)$
889	$r(CH_3)$
727 s	$r(CH_2)$
673 s	$\nu(CSi)$

[a] ν stretch; δ, bend; r, rock; γ, twist; w, wag.

assigned to vibrations of either the CH_2 or CH_3 groups since vibrations of the silicon atoms occur below 700 cm^{-1}.[28-30] In Table I is found a summary of the observed bands with their respective assignments. It should be pointed out that in addition to the observed changes in intensity, some bands shift in frequency with increasing side-chain length. This variation in frequency with alkyl chain length reflects the shape of the phonon dispersion curves and has been observed previously in both *n*-alkanes[31] and perfluoro-*n*-alkanes.[32]

The effect of temperature on both the CH_2 and CH_3 vibrations are shown in the IR spectra of PDHexS in Figure 3. As seen, the sample history parallels that of Figure 1. The sample is heated to 100 °C, all the intense sharp bands characteristic of an ordered trans planar hydrocarbon chain become broad with a concomitant decrease in intensity similar to that observed for *n*-alkane chains in the melt phase.[33] As Figure 3c indicates, after 50 min at room temperature partial ordering of the hydrocarbon side chain occurs, but it is not until after 75 min (Figure 3d) that the IR bands return to their original intensity and bandwidth indicative of molecular order. Similar behavior was noted for the PDHepS and PDOctS samples. These observations suggest that there is also a temporal component associated with this order–disorder transition and any proposed mechanism must take this into account.

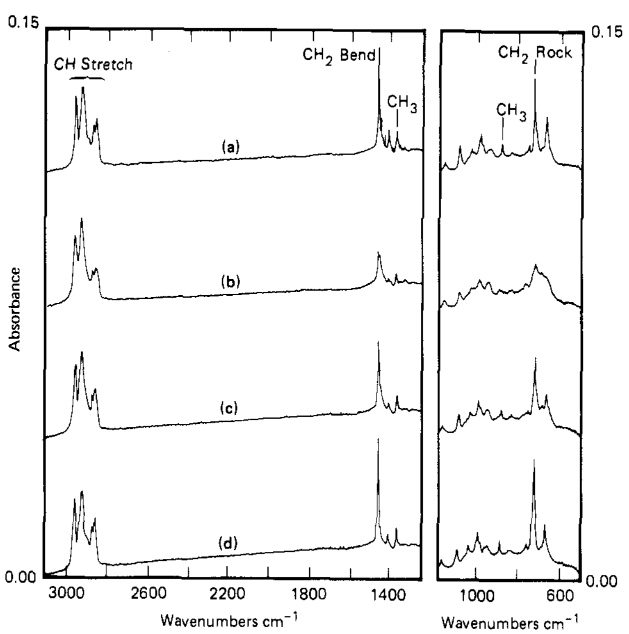

Figure 3. IR spectra of a thin film of PDHexS: (a) as-prepared film, 30 °C; (b) heated to 100 °C and run immediately; (c) 50 min after cooling; (d) 75 min after cooling.

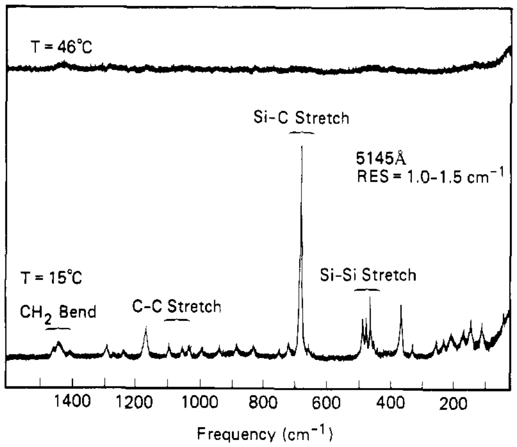

Figure 4. Raman spectra of PDHexS at 15 and 46 °C. (Resolution = 1.5 cm^{-1}, λ_{ex} 514.5 nm.) As noted by noise level, amplification of spectra are the same.

The Si backbone conformation was followed as a function of temperature with Raman spectroscopy as shown in Figure 4. The lower trace was recorded at 15 °C and contains a number of intense bands associated with the vibrations of the Si atoms. In the 1500–700-cm^{-1} region, a number of weak bands are found that are characteristic of the ordered paraffinic side chain.[27]

Bands below 700 cm^{-1} are attributable to vibrations of the silicon backbone. Those in the 450–500-cm^{-1} range are characteristic of the Si–Si bond stretch. In fact, Vora et al.[30] observed a strong Raman band at 480 cm^{-1} in polysilane and assigned it to the asymmetric Si–Si stretching vibration calculated at ~520 cm^{-1}. Likewise the symmetric Si–Si band was calculated to occur at 370 cm^{-1} and corresponds to the medium band at 380 cm^{-1} observed in our spectrum of PDHexS. The presence of three distinct bands in the 500-cm^{-1} region is puzzling, and although at least one can be assigned to the symmetric stretching of the Si–C bond, the origin of the third band is unclear and perhaps arises from the presence of a second backbone conformation. The intense band at 689 cm^{-1} can be tentatively assigned to the asymmetric Si–C stretch. Studies of ^{13}C enriched PDHexS are currently in progress and should provide added insight into the exact assignment

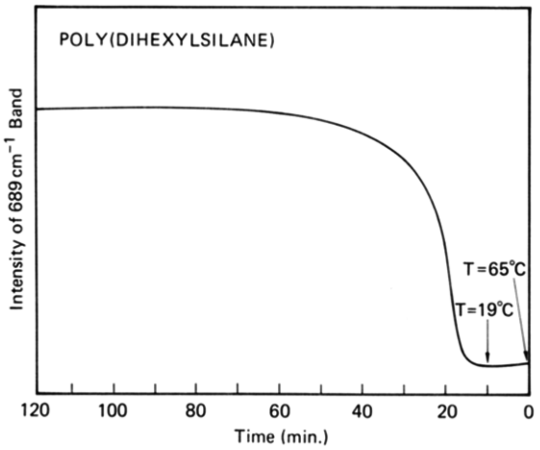

Figure 5. Recovery of the intensity of the 689-cm^{-1} Raman band as a function of time.

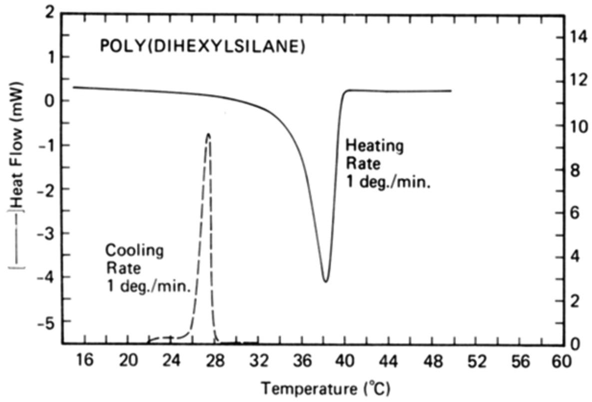

Figure 6. DSC thermogram of PDHexS obtained upon heating and cooling at 1 °C/min.

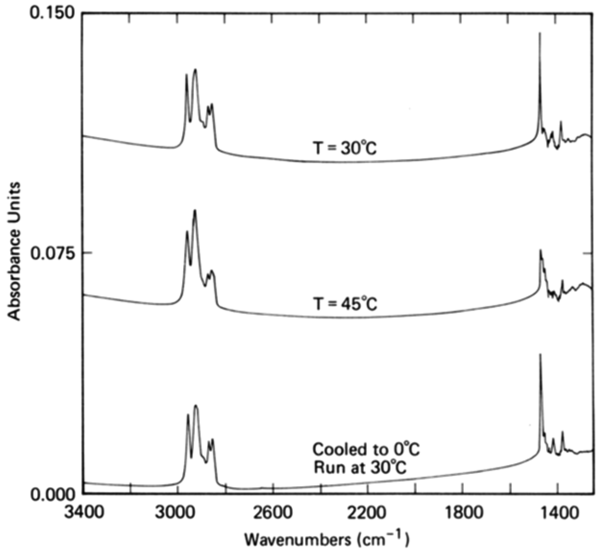

Figure 7. The effect of quenching a heated sample of PDHexS into ice water is shown in its IR spectrum obtained immediately.

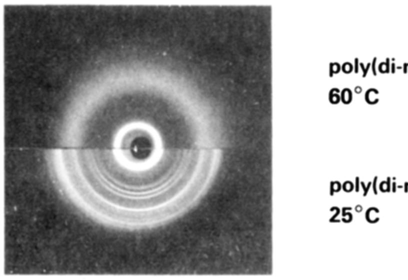

Figure 8. Wide-angle X-ray diffraction pattern of PDHexS obtained at a sample to film distance of 50 mm. Lower half of PDHexS at 25 °C compared to upper half taken at 60 °C.

of bands characteristic of the Si–C bond. Tentative band assignments are indicated in Figure 4.

A dramatic change occurs when the PDHexS is heated to 46 °C as is shown in the upper trace of Figure 4. The noise level on this spectrum and its counterpart at 15 °C have been kept constant, thus illustrating the dramatic disappearance of all the sharp features assigned to the silicon vibrations.

The kinetics of the backbone conformational changes were followed by first recording the Raman spectrum at 46 °C and then scanning the spectrometer to the position of the most intense silicon vibration at 689 cm^{-1} and allowing the temperature to return to ambient. By monitoring the band intensity as a function of time, the return of the backbone to its ordered conformation was observed. This is shown in Figure 5. It took approximately 10 min for the sample to return to room temperature and then 60 min for the initial intensity of the 689-cm^{-1} band to be restored. Hence, this is in agreement with the time required for the reestablishment of order in the side chains as indicated by the IR measurements. In addition, it also correlates well with the return of the 374-nm absorption peak in the UV spectrum indicating that its origin is attributable to a recrystallization or reordering of the main and side chains of PDHexS.

Further insight into the mechanism of this transition was provided by DSC measurements. A typical trace is shown in Figure 6, where a sample of PDHexS has been heated and cooled at a rate of 1 °C/min. Although the minimum of the endotherm occurs at 38 °C, it is clear that there is gradual disorder occurring that begins some 10–12 °C earlier and is indicated by the deviation of the DSC trace from the base line. This can be associated with a gradual introduction of conformational defects into the n-alkyl side chains prior to the total disorder introduced at the melting point. Another interesting aspect of the thermal behavior is that PDHexS recrystallizes at 27–28 °C, some 11 °C lower than its melting point. This supercooling phenomena is commonly found[34] in long-chain polymers and is usually a sensitive function of cooling rate. The interesting observation that recrystallization occurs in the vicinity of 27 °C, very close to the ambient temperature at which the UV and IR measurements were made, suggests an explanation for the temporal component of this transition. The recovery period observed for the transition can be attributed to the fact that crystal nucleation and growth occur slowly when the observation temperature is near the recrystallization temperature. Thus, it takes ~60 min for the side and main chains of PDHexS to reorder. However, the nucleation and growth rates would be larger if the observation temperature was much lower. The IR measurements shown in Figure 7 lend credence to this argument. As shown, when a heated sample was quenched into ice water (0 °C) and then warmed to room temperature and reexamined, its spectrum immediately returns to that of the ordered solid. This confirms that the observation of a 60-min recovery period was fortuitous and occurred only because the PDHexS recrystallized close to the temperature at which the IR and UV measurements were made. In another sample of low molecular weight PDHexS, the degree of supercooling was much less, persumably due to the enhanced mobility of the chain.

Wide-Angle X-ray Diffraction (WAXD). A further confirmation of the proposed side-chain melting transition was provided by WAXD measurements taken at 25 and

Table II
Observed *d* Spacings for PDHexS at Ambient and Elevated Temperatures[a]

20 °C		60 °C	
d spacing	intensity	*d* spacing	intensity
13.5	m	13.5	vs
12.0	s		
9.1	vw		
8.9	vs		
6.55	m	7.6	w
5.96	m–s		
5.47	m		
4.99	w	4.7	smear
5.54	s		
4.26	vw		
3.86	m		
3.74	m		

[a] w, weak; s, strong; m, medium; vs, very strong.

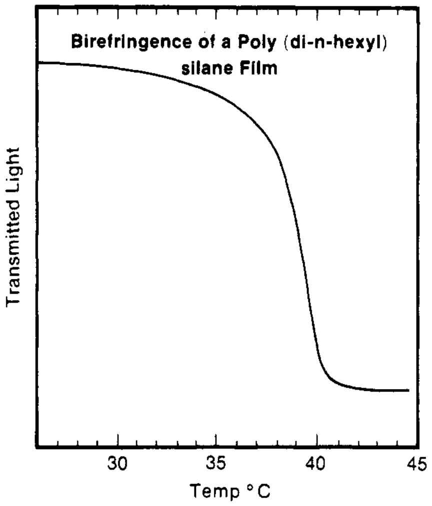

Figure 9. Optical birefringence of PDHexS film as a function of temperature.

60 °C. As seen in Figure 8, the set of sharp *d* spacings present at 25 °C disappear when the temperature is heated above 41 °C.

Table II contains a list of the observed *d* spacings and their intensity at both ambient and elevated temperatures. As can be seen, a number of strong spacings are observed. Previous work on side-chain crystallization[5,6] suggests that the 4.54-Å *d* spacing is characteristic of the packing of trans planar alkyl side chains into a triclinic unit cell. The observation of a single CH_2 rocking vibration at 727 cm^{-1} in the IR spectrum of PDHexS strongly supports this finding. Interestingly enough, the triclinic subcell structure has also been observed[32] for *n*-hexane, *n*-heptane, and *n*-octane. It is clear from Figure 8 that most of the strong–weak spacings disappear when the temperature is raised above the DSC transition point, with the exception of the 13.5-Å line, which persists. This spacing may be attributable to overall short-range order that may persist in the amorphous phase. Further WAXD studies of a whole series of symmetrically substituted poly(di-*n*-alkylsilanes) are presently in progress.

Birefringence. Consistent with the suggestion of order in the polymer was the observation that films of PDHexS were strongly birefringent. The birefringence decreased markedly above the transition temperature for side-chain melting ($T_m \sim 40$ °C) but did not disappear completely until the polymer began to decompose above 250 °C (see Figure 9). This behavior should be compared with atatic poly(methylhexylsilane), which exhibits no birefringence at or above room temperature. It is postulated that rapid relaxation of the aligned chains above 40 °C is responsible for the critical drop in the birefringence, but in spite of this disorder, which is also reflected by the IR, Raman and UV spectra, the chains remain partially oriented in the polymer films.

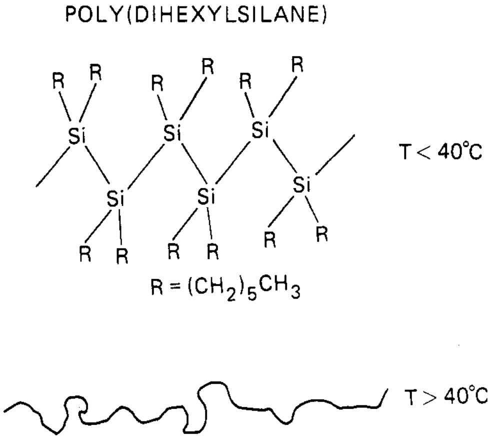

Figure 10. Schematic illustration of side chain crystallized PDHexS with ordered backbone ($T < 40$ °C) compared to disorder introduced upon heating ($T > 40$ °C).

Thus all the experimental data collectively suggest that the change in electronic structure is directly associated with the change in molecular conformation of the backbone and side chains. As illustrated schematically in Figure 10, when the side-chain lattice is thermally disordered, there is a relaxation of the silicon backbone into a more random conformation. Realistically, it is not totally random since the transition must be reversible. In all probability, there is some local order giving rise to the 13.5-Å spacing.

Conclusion

Spectroscopic studies of PDHexS, PDHepS, and PDOctS revealed that they behave similarly at elevated temperatures. Whereas UV measurements indicated that the polysilane backbone existed in a predominantly extended form at room temperature, IR and Raman studies have shown that both the side and main chain disorder at elevated temperatures. Thermal measurements (DSC) indicate the presence of a phase transition in the 40–50 °C range for all of the polymers studied, which can be attributed to a melting of the side chains followed by a relaxation of the ordered polymer backbone. WAXD supports this finding for PDHexS since the diffraction maxima are observed to disappear when the transition point is exceeded. This appears to represent a case of a conformationally driven change in electronic structure observed in a polymer and raises the spectre of controlling the speed and temperature of such a transition through variations in molecular weight and side-chain length, respectively.

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Registry No. PDHepS (homopolymer), 100044-91-5; PDHepS (SRU), 100044-92-6; PDOctS (homopolymer), 97036-68-5; PDOctS (SRU), 98865-30-6; Dichlorodihexylsilane (homopolymer), 97036-67-5; poly(dihexylsilane) (SRU), 94904-85-5.

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Spectroscopic Characterization of the Microstructures in Disklike Liquid Crystalline Molecules: Model Compound for Polymers

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ABSTRACT: Vibrational spectroscopy has been used to analyze the microstructures of disklike crystalline macromolecules. These analyses suggest that the structure of the polymethylene sequences are correlated to the phase behavior of the three molecules studied. Spectroscopic analysis also suggests that two distinct conformations are associated with the ester groups attached to the "core" rings. The relative intensities of the two components correlate well with the phase transitions observed.

Introduction

Even though disklike liquid crystalline macromolecules have been recognized for only a relatively short time,[1] a considerable amount of interest exists in better characterizing their mesophases and associated properties.[1-6] The main purpose of our study is to analyze the microstructures in several of the phases found and to define those structural units necessary to achieve the liquid crystalline state.

The structures of these disklike or platelike molecules are fairly unique. In the present study, the compounds we are studying are benzenehexa-*n*-alkanoates, as shown schematically in Figure 1, although samples with considerably different cores have also been prepared. The "branches" attached to the benzene rings may vary in length and seem to influence their phase behavior.[1] Three homologues with $n = 6$–8, where n is the number of carbons in the branch, (denoted as BH6, BH7, and BH8, respectively) are the main subjects of our study. Several transitions associated with these macromolecules have been determined by thermal studies and optical microscopy.[1] Primarily on the basis of X-ray diffraction studies,[2] structures associated with some of the various phases have been proposed. The most interesting finding is that the homologue with $n = 6$ does not exhibit the intermediate liquid crystalline phase between the crystalline and isotropic phases found at extreme temperatures. For homologues with $n = 7$ or 8, these molecules do possess an intermediate state. The proposed structure for this intermediate state contains lamellar order with hexagonal symmetry in two dimensions and liquid like disorder in the third.[2] In fact, this intermediate phase is referred to as discotic or columnar, with the disks stacked on top of each other, forming columns. However, the spacing along the column axis is irregular. There is some uncertainty associated with the interpretation of the phase transitions found for the $n = 6$ molecule. In the initial study, it was proposed that this molecule also contained this intermediate phase, a conclusion that was subsequently modified.[2] Instead, a solid-solid transition was proposed.

Even though the existence of various phases and their transition temperatures have been previously established, experimental evidence suitable for microstructural analysis is rare. Most of the studies, including thermal measurements or optical microscopy, are not actually directed at