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Studies of Chain Conformational Kinetics in Poly(di-*n*-alkylsilanes). 5. The Effect of Side-Chain Structure on Piezochromism

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ABSTRACT: Structural studies of asymmetrically substituted poly(di-*n*-alkylsilanes) as a function of pressure have shown that side-chain architecture is important for the observation of piezochromism. UV–vis, Raman, and FTIR measurements of poly(di-*n*-alkylsilanes) with linear side chains of two different lengths indicate that a piezochromic shift of the UV–vis absorption maximum at 315 nm is observed. However, if instead one or both of the side chains are branched, the Si backbone is prevented from adopting a planar zigzag conformation and hence no large changes in the UV–vis spectrum are observed.

I. Introduction

Although certain of the poly(di-*n*-alkylsilanes) have been known to exhibit thermochromism[1] for more than a decade, only recently has the effect of high pressure on the UV absorption spectrum been investigated. The observation of piezochromism was first made in poly(di-*n*-hexylsilane)[2] (PDHS) and characterized by Raman scattering measurements in a diamond-anvil cell at pressures ranging from 2–44 kbar. Preliminary results indicated that geometrical distortion of the backbone occurred at elevated pressures, perturbing the σ-conjugated backbone and giving rise to a continuous blue shift in the UV absorption maximum at 370 nm. More recently, extensive studies on the nature of this piezochromic effect have been made using X-ray diffraction, solid-state NMR,[3] FTIR, and Raman[4,5] measurements. It has become clear that as pressure is applied, two sequential events occur. In the low-pressure regime (<2.5 kbar) a conversion of disordered PDHS into an ordered phase occurs, giving rise to a decrease in the intensity of the UV band at 315 nm. With a further increase in pressure, conformational distortion results, causing a gradual reversible shift of the 370-nm band to lower wavelengths. This represents the difference between lateral compression at low pressures and chain compression at elevated pressures.

A more marked effect of lateral compression on chain conformation was recently[6] demonstrated in the case of poly(di-*n*-pentylsilane) which undergoes a piezochromic shift of 50 nm in its UV spectrum when subjected to moderate pressures. Similar work[3] on poly(di-*n*-butylsilane) yielded similar results with the exception that a significant amount of hysteresis occurred after the pressure was removed. In both cases[6] the piezochromic shift was attributed to a conformational change from a 7/3 helix to a planar zigzag structure.

Recently a study[7] was undertaken to determine the effect of asymmetric side-chain substitution on thermochromism in the poly(di-*n*-alkylsilanes). It was found that asymmetrically substituted polysilanes (containing one hexyl side chain) exhibit variable degrees of intra- and intermolecular disorder due to the mismatch of side-chain length. This mismatch causes interruption of the trans planar backbone sequence, giving rise to a UV absorption at 350 nm in the solid state instead of the 370-nm band usually observed for the *all-trans*-PDHS. The present study was undertaken to assess the role of asymmetric side-chain substitution on the piezochromic behavior of certain polysilane derivatives. For this purpose a series of materials consisting of poly(*n*-pentyl-*n*-hexylsilane) (PPHS), poly(*n*-hexylisohexylsilane) (PHIS), poly(*n*-hexyl-*n*-heptylsilane) (PHHS), poly(*n*-hexyl-*n*-octylsilane) (PHOS), and poly(diisohexylsilane) (PDIS) were synthesized, and their thermo- and piezochromic behavior was studied and compared to that previously observed in PDHS.

II. Experimental Section

A. High-Pressure Measurements. The synthesis and purification of polysilanes used in this study are identical with those described previously.[8] For the measurements of all high-pressure spectra, a diamond-anvil cell[9] was used with the essential components shown in Figure 1. In addition to the sample to be studied, a small piece of powdered ruby was enclosed within a metal gasket (Inconel X 600) between two opposing diamond anvils in order to calibrate the pressure at the sample. The ruby fragment occupies less than 10% of the volume and does not interfere with spectroscopic measurements. Using the 514.5-nm line of an Ar$^+$ laser, the sharp ruby R$_1$ fluorescence line at 694.2 nm can be excited together with the second weaker component (R$_2$) located at 692.8 nm. The peak positions of both fluorescence lines have been found[9] to exhibit a pressure-dependent shift (-0.753 cm^{-1}/kbar) which is linear to 300 kbar.

Thin films for UV absorption measurements were made by casting a dilute solution of polymer in hexane directly onto a diamond anvil on which a 0.01-in.-thick metal gasket with a 0.03-in. hole at the center was mounted. After drying overnight in a vacuum, a drop of a ethanol/methanol (4:1) mixture was placed in the gasket hole as a pressure-transmitting fluid and then the other diamond anvil was quickly replaced and sealed. For the Raman measurement, the polymer sample was placed directly into the metal gasket on the diamond anvil. The diamond-anvil cell was then placed into the Raman spectrometer using a 180° back-scattering geometry. IR samples were prepared by dispersing the polymer into KBr powder and enclosing the mixture within the diamond-anvil cell.

B. Characterization. UV spectra were recorded on a Hewlett-Packard photodiode array spectrometer fitted with a neutral density and a cutoff filter to eliminate photodegradation of the polysilanes during the measurement. IR measurements were made with an evacuable IBM/Bruker IR 98 instrument equipped with a room-temperature deuterated triglycine sulfate detector. The spectra were recorded at 4-cm^{-1} resolution with the coaddition of 2000 scans.

Raman experiments were recorded using a Jobin-Yvon HG-2S double monochromator equipped with holographic gratings and a spatial filter to enhance stray light rejection. Laser excitation was provided by the 514.5-nm line of a Spectra-Physics 2020 argon ion laser. Generally, the spectra were recorded at

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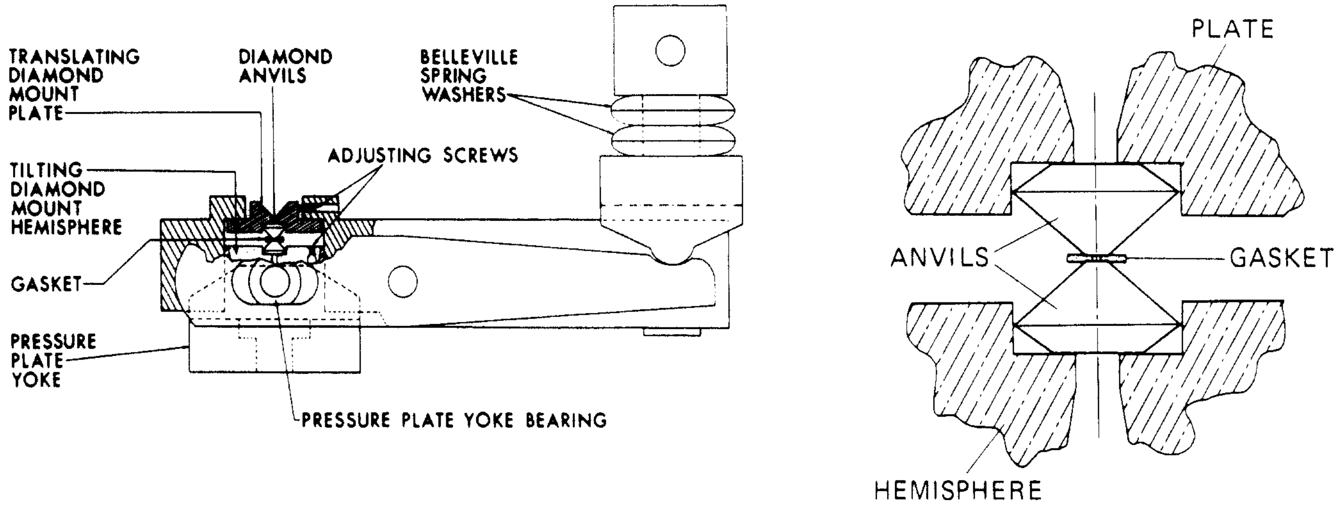

Figure 1. Schematic diagram of a diamond-anvil cell (DAC) used for Raman studies at high pressures.

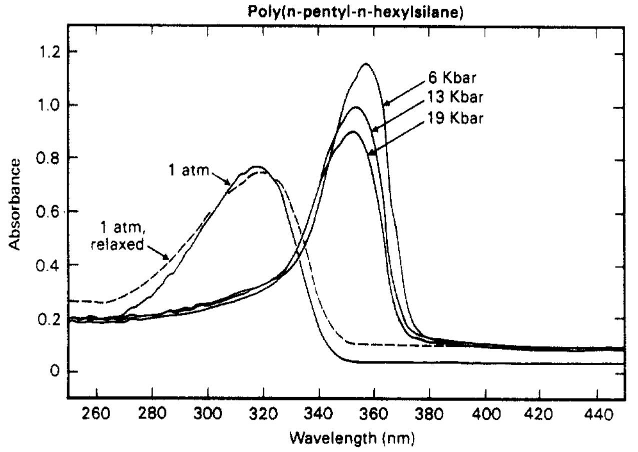

Figure 2. UV–vis spectra of PPHS as a function of pressure.

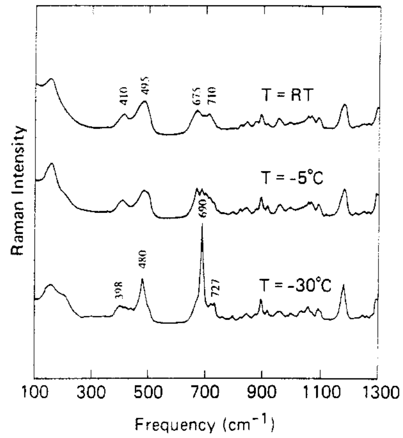

Figure 3. Raman spectra of PPHS at ambient and low temperatures.

Table I
Thermo- and Piezochromic Properties of Poly(R_1,R_2-silanes)

R_1, R_2	thermochromic shift in UV spectrum (nm)	transition temp (°C)	piezochromic shift in UV spectrum (nm)
hexyl, hexyl	370 → 315	42	370 → 350
hexyl, pentyl	350 → 315	−20	315 → 355
hexyl, heptyl	350 → 315	−5	315 → 360
hexyl, octyl	350 → 320	−5	320 → 350
hexyl, isohexyl			315 → 330, 365 (weak)
isohexyl, isohexyl			315 → 320

400-mW power with a resolution of 6 cm^{-1}. The scattered light was detected by a cooled RCA 31034A-02 photomultiplier tube using standard photon-counting electronics. All data were collected and processed digitally by the Nicolet 1180 Data System. Low-temperature measurements were made in a vertical Harney-Miller cell[10] by blowing cooled nitrogen gas across the sample. The temperature was varied by gas flux and measured by mounting a thermistor adjacent to the sample position.

III. Results and Discussion

A. Poly(*n*-pentyl-*n*-hexylsilane) (PPHS). The effect of pressure on PPHS is somewhat different from that of PDHS[3,4] as shown by its UV–vis spectra in Figure 2. At ambient temperature and atmospheric pressure PPHS has a broad UV absorption at 315 nm characteristic of the disordered helical structure found for PDHS at elevated temperature.[7] At relatively low pressure (<4 kbar) this broad absorption disappears and is replaced by a more intense, sharper absorption band at 355 nm. As the pressure is further increased, the 355-nm band undergoes a continuous blue shift similar to that found[5] for PDHS at elevated pressures.

The broad UV absorption at 315 nm in PPHS has been attributed to a disordered helical conformation similar to that found for PDHS above 42 °C. A previous study[7] has concluded that this transition in PDHS from a planar zigzag conformation to a disordered helix is suppressed (see Table I) due to the disorder introduced by appending both a pentyl and a hexyl group to the same Si backbone atom. Since the di-*n*-pentyl derivative is known to be a 7/3 helix while the di-*n*-hexyl derivative attains a planar zigzag conformation, the side-chain length mismatch of a pentylhexyl derivative introduces significant disorder in the lattice. Hence, at room temperature the PPHS backbone exists as a disordered helix. This is in contrast to PDPS which also absorbs at 315 nm at room temperature but which adopts an ordered 7/3 helical conformation at room temperature. Interestingly enough the effect of pressure[6] on both polymers is quite similar; i.e., the 315-nm band shifts to 355 nm at relatively low pressures.

Some insight into the mechanism responsible for this shift in the absorption maximum can be obtained by investigating conformational changes in the PPHS backbone with temperature and pressure using Raman spectroscopy. As shown in Figure 3, the Raman spectra are particularly sensitive to temperature-induced conformational changes. It is apparent from Figure 3 that as the temperature of PPHS is lowered below the transition at −20 °C (see Table I) sharp bands at 727, 690, 480, and 398 cm^{-1} characteristic of the planar zigzag structure become

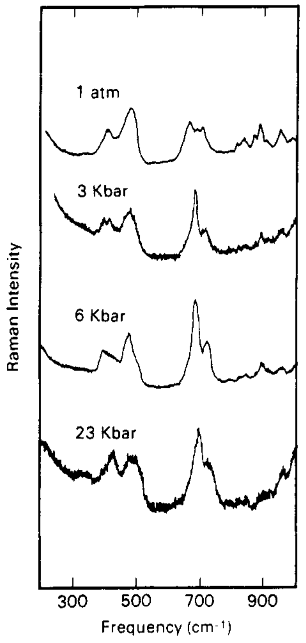

Figure 4. Raman spectra of PPHS as a function of pressure.

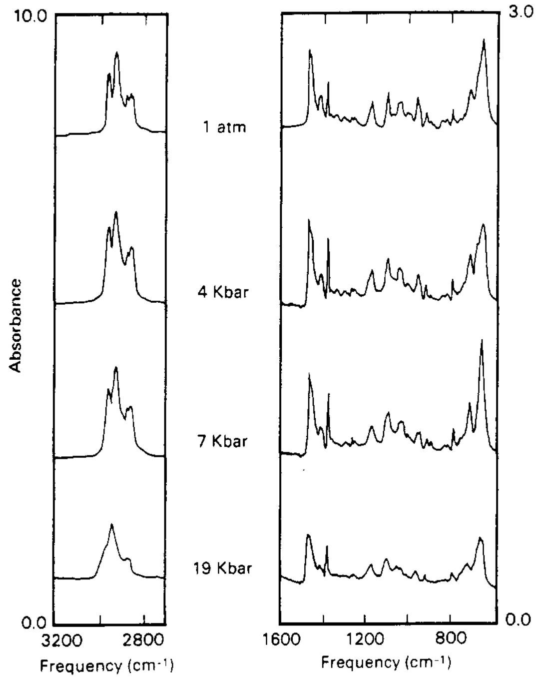

Figure 5. Infrared spectra of PPHS as a function of pressure.

visible. The former (727 and 690 cm^{-1}) have been assigned[11] to Si–C stretches, while the latter have been attributed to Si–Si vibrations. At room temperature (RT) the spectrum contains broad, weak features at 710, 675, 495, and 410 cm^{-1} characteristic of the disordered helical form.[6,11] When this latter form is subjected to an increase in pressure at room temperature as shown in Figure 4, new bands at 727, 690, 480, and 398 cm^{-1} again appear analogous to the low-temperature results shown in Figure 3. This then indicates that applying moderate pressure to PPHS brings about a conformational transition from a disordered helix to a structure that is predominantly planar zigzag and which absorbs at 355 nm.

Further support for this premise comes from the IR spectra shown in Figure 5. Bands characteristic of the CH_2 stretching vibrations (3000 cm^{-1}) show subtle changes in the relative intensity with increasing pressure. As shown in the second panel of Figure 5, as the pressure is raised to 4 kbar the asymmetric CH_2 stretching vibration at 2854 cm^{-1} undergoes a slight shift to lower frequency and an increase in intensity relative to the symmetric CH_3 stretching band at 2871 cm^{-1}. In fact the band intensity pattern in PPHS in this region at 4 kbar is identical to that found[5,11] for planar zigzag PDHS at room temperature and ambient pressure, suggesting that it too has undergone a conformational change to a trans planar structure. In addition, bands attributable to Si–C stretching at 668 and 717 cm^{-1} show measurable changes in band intensity and position with pressure. As seen in the 7-kbar spectrum, the intensity of the 668-cm^{-1} band has increased dramatically and shifted slightly to higher frequency while that at 717 cm^{-1} has shifted to 727 cm^{-1}. This is also consistent with the fact that the PPHS backbone transforms to a planar zigzag structure in the low-pressure regime, with the side-chain conformation becoming similar to that found for PDHS.

As mentioned previously, with a continued increase in pressure there is a blue shift in the UV band of PPHS at 355 nm. As seen in Figure 4, the Raman spectrum obtained at 23 kbar contains bands characteristic of the planar structure but the Si–Si stretching vibrations (495 and 410 cm^{-1}) corresponding to the disordered helix reappear but are considerably diminished. This then suggests that the application of high pressure causes a compression along the chain axis, resulting in distortions of the trans planar backbone. This geometrical distortion is also evident in the IR spectrum shown in the bottom panel of Figure 5. It is most apparent in the CH_2 stretching region (2800–3000 cm^{-1}) where the bands are considerably broader at elevated pressures. This and the characteristic broadening of the intensity of the 1460-cm^{-1} CH_2 bending mode have also been observed[11] in PDHS and attributed to the introduction of gauche bonds in the *n*-hexyl side chains similar to that observed[12] in solid *n*-alkanes in the high-pressure regime (>10 kbar). The introduction of disorder into both the side chains and main chain at high pressure results in a change in the nature of the overlap of σ bonds, leading to a reversible shift in UV absorption to lower wavelength.

B. Poly(*n*-hexyl-*n*-heptylsilane) (PHHS) and Poly(*n*-hexyl-*n*-octylsilane) (PHOS). Studies of PHHS and PHOS under pressure yielded results similar to that of PPHS where all polymers exhibit a piezochromic shift in their UV absorption spectrum (see Table I). One slight difference was the pressure at which the transition was observed to occur. The red shift of the UV absorption at 315 nm (or 320 nm for PHOS) is observed at 3.5 kbar for PPHS, at 5 kbar for PHHS, and at 9 kbar for PHOS. This is understandable since the mismatch of side-chain length in PHOS is larger than those in PPHS and PHHS which results in a difference in the amount of disorder present in the polymers at ambient pressure.

It is worth mentioning that although the change in the UV absorption spectrum of PHOS is the same both for temperature and pressure effects, the Raman spectrum shows a difference in the relative intensity between some of the bands characteristic of the planar structure. The 690-cm^{-1} Raman band (Si–C symmetric stretch) is much sharper and stronger than the 727-cm^{-1} (Si–C asymmetric stretch) band in the low-temperature spectrum, while in the high-pressure spectrum the 690-cm^{-1} band shows a broad and reduced intensity. This might be due, in part, to the fact that the symmetric Si–C stretching mode involves larger atomic displacements during vibrations than the asymmetric Si–C stretching mode, therefore making it more sensitive to the volume constraints which occur at elevated pressures.

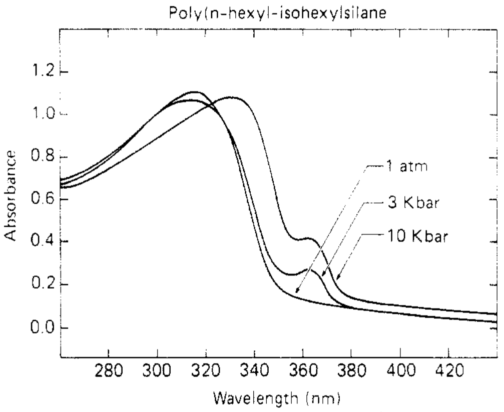

Figure 6. UV–vis spectra of PHIS as a function of pressure.

C. Poly(*n*-hexylisohexylsilane) (PHIS). In the continuing study of the effect of side-chain structure on piezochromism, a polysilane derivative, PHIS, containing a branched side chain was also investigated. As shown in Table I, PHIS is not thermochromic, but as seen in Figure 6 its UV spectrum does change as a function of pressure. At 3 kbar the UV absorption band at 315 nm shifts slightly, but more significantly a weak band appears at 365 nm. With increased pressure this weak band does not appear to change in intensity but the 315-nm band has shifted to 330 nm at 10 kbar. This shift is accompanied by a slight change in the band intensities in the Si–Si stretching region (400–500 cm^{-1}) of the Raman spectrum presumably due to a minimal increase in order signified by the 15-nm red shift.

Interestingly enough, there were no bands observed in the Raman spectrum at elevated pressure which could be attributed to the presence of any planar zigzag structure in the backbone. This is surprising in light of the presence of the weak band at 365 nm since the presence of a band in this region has always been correlated with the existence of a planar zigzag backbone in poly(alkylsilanes).[11,13]

D. Poly(diisohexylsilane) (PDIS). The final polymer studied, PDIS, contains two branched side chains and did not exhibit thermochromism. A slight red shift (5 nm) in its UV band at 315 nm was observed with pressure, but no evidence of any conformational change was found spectroscopically. Presumably this can be understood by considering that the pressure-induced lateral compression thought to be responsible (in the low-pressure regime) for transforming a helical structure into a planar one is unable to do so in PDIS due to the bulkiness of the branched isohexyl side chains.

IV. Conclusions

The effect of the side-chain structure on piezochromism in poly(alkylsilanes) has been investigated by UV–vis, FTIR, and Raman spectroscopy. It was found that in polysilanes containing linear side chains of two different lengths, there is an increase in the disordered helical backbone content at room temperature which is then reversibly transformed into a planar zigzag backbone at low pressures. At high pressures, chain axis compression occurs, leading to a geometrical distortion of the backbone causing a continuous blue shift in the 355-nm absorption to lower wavelength. The introduction of branched side chains interferes with the ability of the Si backbone to adopt a planar zigzag conformation even at relatively high pressures, and hence no large shifts in their UV absorption band at 315 nm occur.

An intermediate case exists when both a branched and a linear side chain are attached to the polysilane backbone. Subjecting PHIS to high pressure causes a 15-nm red shift of its broad 315-nm UV band and the appearance of a weak feature at 365 nm presumably due to the presence of small amount of trans planar structure. Raman and FTIR studies under pressure could not verify the presence of a planar zigzag structure in PHIS.

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Registry No. PDHS (homopolymer), 97036-67-4; PDHS (SRU), 94904-85-5; PPHS (homopolymer), 125121-05-3; PPHS (SRU), 120517-00-2; PHHS (homopolymer), 125121-09-7; PHHS (SRU), 120534-41-0; PHOS (homopolymer), 125121-11-1; PHOS (SRU), 120517-01-3; PHIS (homopolymer), 125121-07-5; PHIS (SRU), 125121-33-7; PDIS (homopolymer), 117652-54-7; PDIS (SRU), 117652-58-1.