methanol content exceeded about 50%. The anisotropic behavior suggests that the shrinkage occurs by the solvent exclusion from the intervening regions between helical polypeptide chains.

The anisotropic change of dimensions presented in this paper was reversible when the solvent composition was changed alternatively.

In conclusion, PBLG gels having nematic liquid-crystalline order were prepared. The NLC gel showed reversible anisotropic swelling and shrinking by a change of solvent compositions. This is the first observation of anisotropic dimensional change in polymer gels.

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Spectroscopic Characterization of Piezochromism in Poly(alkylsilanes): Poly(di-*n*-hexylsilane)

Although the conformational and crystal structures of poly(di-*n*-hexylsilane) (PDHS) have been well-known for some time,[1-3] a complete understanding of its thermochromic behavior has not yet been obtained. Initial results[1] indicate that, at the transition temperature, gauche bonds are introduced into the *n*-hexyl side chains, thus relieving the steric constraints that had locked the silicon (Si) backbone into a planar zigzag conformation. This disordering of the backbone results in a change in the overlap of the electronic wave functions, giving rise to the change in UV absorption from 370 to 315 nm. Information about the exact structure of the *n*-hexyl side chain is as yet unknown, but conformational energy calculations[4] have revealed that some rotations about the C-Si bond to alleviate the interaction of side chains along the main chain are likely. Furthermore, little is known about the intermolecular packing of the *n*-hexyl side chains on adjacent Si backbones, but band splittings observed in the Raman spectra of PDHS suggest that the side chains organize into an orthorhombic subcell arrangement similar to that of the odd *n*-alkanes.

It is the purpose of this paper to report the effect of elevated pressure on the spectroscopic properties of PDHS. This work is a continuation of that reported[5] earlier in which piezochromism was first observed in PDHS by Raman scattering. In this case Raman measurements were made on PDHS as it underwent a transition from an ordered state to a disordered state when submitted to elevated pressures (1-44 kbar) in a diamond anvil cell.[6] Recently, Schilling et al.[7] have used pressure (<2.5 kbar) and temperature to explore the nature of the piezochromic effect in poly(di-*n*-alkysilanes) in the low-pressure regime. In this case X-ray diffraction, solid-state NMR, and UV spectroscopy were used to characterize structural changes with pressure and temperature.

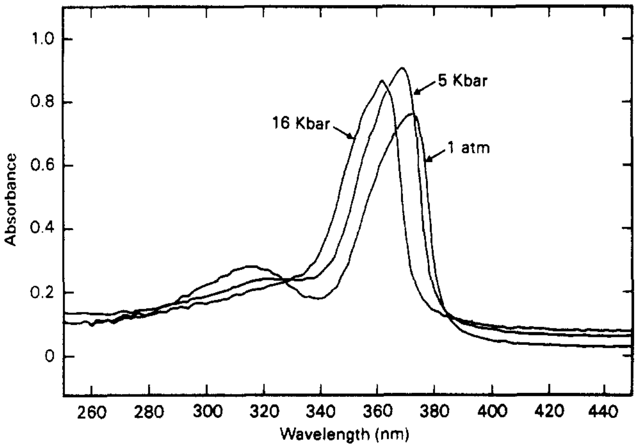

Figure 1. UV-vis spectrum of poly(di-*n*-hexylsilane) as a function of pressure.

As shown in Figure 1 the UV absorption spectra of PDHS change as a function of pressure. At 1 atm two bands are observed at 370 nm (ordered phase) and 315 nm (disordered phase). However, as the pressure is increased there is a shift of the 370-nm peak to lower wavelength while that at 315 nm appears to decrease in intensity, possibly shifting slightly to higher wavelength. This latter observation was also observed by Schilling et al.[7] and may reflect the conversion of disordered PDHS to the trans planar structure at low pressure. Interestingly, changes in the Raman spectra shown in Figure 2 are minimal until the pressure exceeds 12 kbar with the exception of a continuous shift of most of the bands to higher frequency with pressure and small changes of the Si-Si stretching bands found in the 400-500-cm^{-1} region. As the pressure increases further, however, the decrease of scattering

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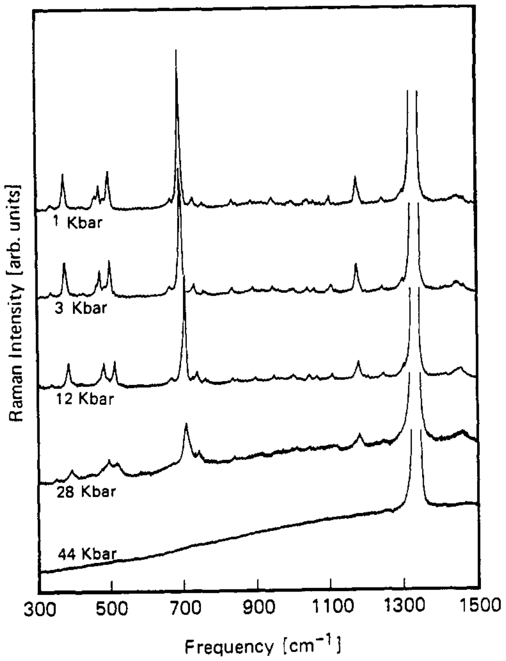

Figure 2. Raman spectrum of poly(di-*n*-hexylsilane) as a function of pressure in a diamond cell. Strong band at 1330 cm^{-1} is due to Raman scattering of diamond.

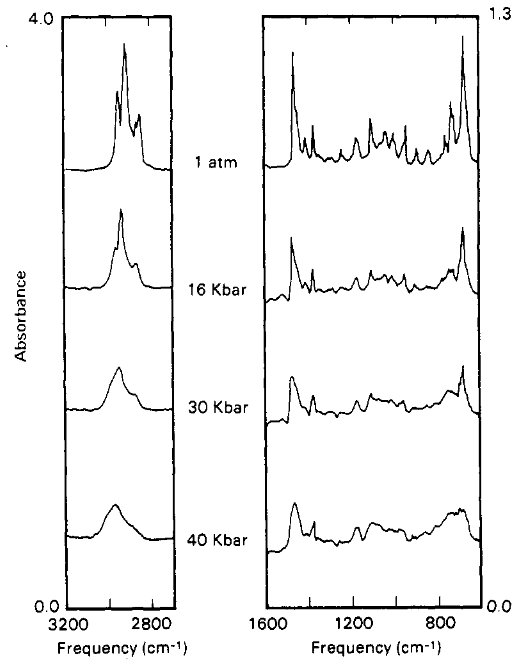

Figure 3. FTIR spectrum of poly(di-*n*-hexylsilane) as a function of pressure.

intensities is observed. This dramatic decrease in Raman intensity can be attributed to a preresonance scattering process, which was also observed[2] when PDHS was heated into the disordered phase. These observations, which are completely reversible, indicate that the Si backbone is undergoing geometrical distortions from the all-trans conformation due to the application of hydrostatic pressure. This distortion will also bring about a change in the nature of the σ conjugation along the backbone, hence causing a shift in UV absorption to lower wavelength away from any resonance interaction with the laser excitation. It is thus interesting that the volume of the sample is initially reduced through the lateral compression, which results in a full extension of the Si backbone chains. At high pressure, however, the lateral compression has reached its maximum, and further reduction in the sample volume can be achieved by compression along the chain axis resulting in distortions of trans planar backbone chains.

Surprisingly, large changes in the structure of the *n*-hexyl side chains occur with pressure as indicated by the infrared spectra shown in Figure 3. In addition to the fingerprint region, the CH stretching region (3200–2700 cm^{-1}) is also shown. It is clear that the sharp bands (characteristic of the CH_2 groups)[1] present in the spectrum at 1 atm are considerably broadened at 16 kbar. The application of pressure, for example, causes the intense band at 1471 cm^{-1} characteristic of a CH_2 scissors vibration to undergo a $2^1/_2$ time increase in bandwidth at 40 kbar, similar to that observed[1] in the IR spectrum when PDHS was heated above 42 °C into the disordered phase.

By inspection of the CH stretching region in Figure 3, it becomes apparent that by 16 kbar a considerable change in *n*-hexyl side chains has occurred. As the pressure is further increased, the broadening of the CH stretching bands is more evident. This is mainly due to the static factor arising from the different conformational environment of the methylene groups. The presence of conformational disorder at high pressure brings about a series of CH_2 stretching bands because each methylene group experiences a different magnitude of intermolecular interactions, which result in slightly different shifts of the CH_2 stretching band for each methylene group. At high pressure, thus, the overlapping of these shifted CH_2 stretching bands gives rise to an overall broad CH_2 stretching band. Such conformational disorder at high pressure is a result of the generation of gauche bonds.[8] Since the volume of a gauche bond is known[9,10] to be smaller than that of a trans bond in short hydrocarbon chains, the volume decrease in the sample due to pressure is attained by the generation of a gauche bond. This tendency of liquid *n*-alkanes to become more globular with increased pressure through the introduction of gauche bonds was first observed by Schoen et al.[9] By monitoring the gauche vs trans content as a function of pressure in short chain *n*-alkanes, they found that the concentration of gauche bonds did in fact increase. In solid-state *n*-alkanes, the generation of gauche bonds with pressure has also been observed[8] in the high-pressure regime (>10 kbar) where compression along the chain axis becomes appreciable. It is this kind of mechanism that can account for the structural disorder introduced into the PDHS side chains at elevated pressure. Subsequently, distortion of the Si backbone occurs with traversals away from the planar zigzag conformation, leading to a reversible shift in UV absorption to shorter wavelength. This is but one type of piezochromism; other mechanisms for piezochromism in the poly(di-*n*-alkylsilanes) will be the subject of a future publication.[11]

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