Thermoreversible Gelation in Binary Mixtures of Poly(di-*n*-alkylsilanes) and Aromatic Solvents

There has been much recent interest[1-3] in poly(di-*n*-alkylsilanes), especially poly(di-*n*-butylsilane) (PDBS), poly(di-*n*-pentylsilane) (PDPS), and poly(di-*n*-hexylsilane) (PDHS). These polysilanes have attracted attention because the addition of one or two methylene groups in the side chain has been shown to have a strong effect on the conformation of the polymer backbone. The silicon backbone in PDHS adopts a trans-planar conformation at ambient conditions,[4-6] while both PDBS[7] and PDPS[8] backbones consist primarily of silicon atoms arranged in a 7/3 helix.

Conformational changes in poly(di-*n*-alkylsilanes) have been induced by a variety of methods. Thermochromism was first observed in PDHS, which undergoes a reversible transition from planar zigzag to an extended, but conformationally disordered, state when heated above 42 °C. This transition is reflected by a peak shift from 374 to 317 nm in the UV absorption spectrum.[4] PDBS and PDPS disorder at slightly higher temperatures, but in both cases the UV absorption peak remains at 315 nm while becoming broader as a result of disordering.[9] Several polysilanes are also piezochromic, and spectral changes are induced by the application of pressure. This was first seen in PDHS, where UV and Raman measurements indicate that side-chain compression and backbone distortion away from the trans-planar conformation occur as the pressure is increased.[10] However, the first consequence of applied pressure for polysilanes with helical backbones appears to be a collapse to a trans-planar conformation. Both PDBS and PDPS show features characteristic of trans-planar structure in their Raman spectra under high pressure, and the 315-nm UV peak shifts to near 350 nm.[11] ^{29}Si NMR results are also consistent with the development of trans-planar structure in PDPS with application of pressure.[12] There has also been a report of altered structure in PDBS precipitated from pentane at -78 °C.[13] The low-temperature NMR spectrum is consistent with the presence of some trans-planar structure, and the UV maximum shifts to 358 nm. However, this structure disappears upon warming the materials above 0 °C. In this paper we will describe the formation of thermally reversible gels from PDBS and PDPS in aromatic solvents. These gels are stable at room temperature, and the UV and Raman spectra are indicative of the existence of a trans-planar structure in the polymer backbone.

The polymers used in the current work were synthesized by Wurtz coupling of the respective dichlorosilanes similar to that in previous work.[14] Solutions were prepared by dissolution at elevated temperatures (generally 40-60 °C). Typical concentrations ranged from 1 to 10 wt %. The kinetics of cooling had a distinct effect on the morphology of the product formed in aromatic solvents. For example, quenching a warm solution of high molecular weight PDPS ($M_w = 1.7 \times 10^6$) in ice water resulted in the formation of a translucent gel phase. Letting the solution cool slowly to room temperature yielded a precipitate instead. With low molecular weight PDPS (M_w = 45 000), slow cooling to room temperature resulted in formation of a gel, while rapid cooling in ice water produced a suspension of small particles, which slowly settled out of solution. Both high and low molecular weight polymer gave two phase systems (gel and clear solvent) at low concentrations. No precipitate was observed for poly(*n*-pentyl-*n*-hexylsilane), poly(di-*n*-hexylsilane), or longer chain symmetrical poly(alkylsilanes). Also, neither a gel nor a precipitate formed at 0 °C with PDBS or PDPS in a number of *n*-alkanes, cyclohexane, or decalin.

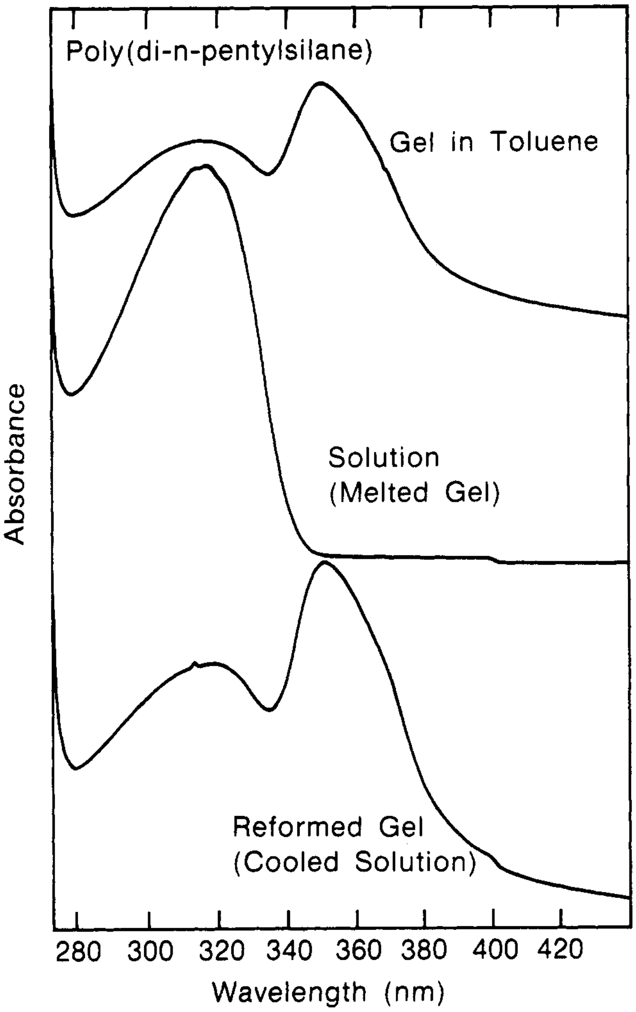

Figure 1. Effect of heating and cooling a 2 wt % solution of PDPS in toluene on the UV/visible spectrum. The spectra shown are the fifth, sixth, and seventh steps of four complete cycles of heating and cooling. The observed spectral changes are completely reversible.

A crude UV cell was made by sealing a drop of a 2 wt % solution of PDPS in toluene between two quartz plates. The cell was then cooled in ice water to form a gel. The UV spectrum, as shown in Figure 1, contained peaks at both 315 and 350 nm, rather than the single peak at 315 nm, which is characteristic of PDPS in the solid state or in solution. The long-wavelength peak disappeared upon melting but returned again when the solution was cooled to re-form a gel. The cycle was repeated many times, and the process appears to be completely reversible. The new structure, which is present only in the gel and not in true solution, has a UV peak at the same wavelength (350 nm) as that observed for PDPS under high pressure.

The Raman spectrum of the gel also shows features similar to those observed for PDPS under pressure. A particularly distinctive vibrational band is the intense Si-C symmetric stretch at 689 cm^{-1}. Previous Raman and X-ray diffraction studies on PDHS have shown that this band is correlated with the presence of trans-planar conformation in the polysilane backbone.[5] The scattering cross section of the 689-cm^{-1} band is greatly enhanced due to resonance interactions when 4880-Å laser excitation is used, making it a convenient marker for the detection of trans-planar structure. No band is seen at this position in either

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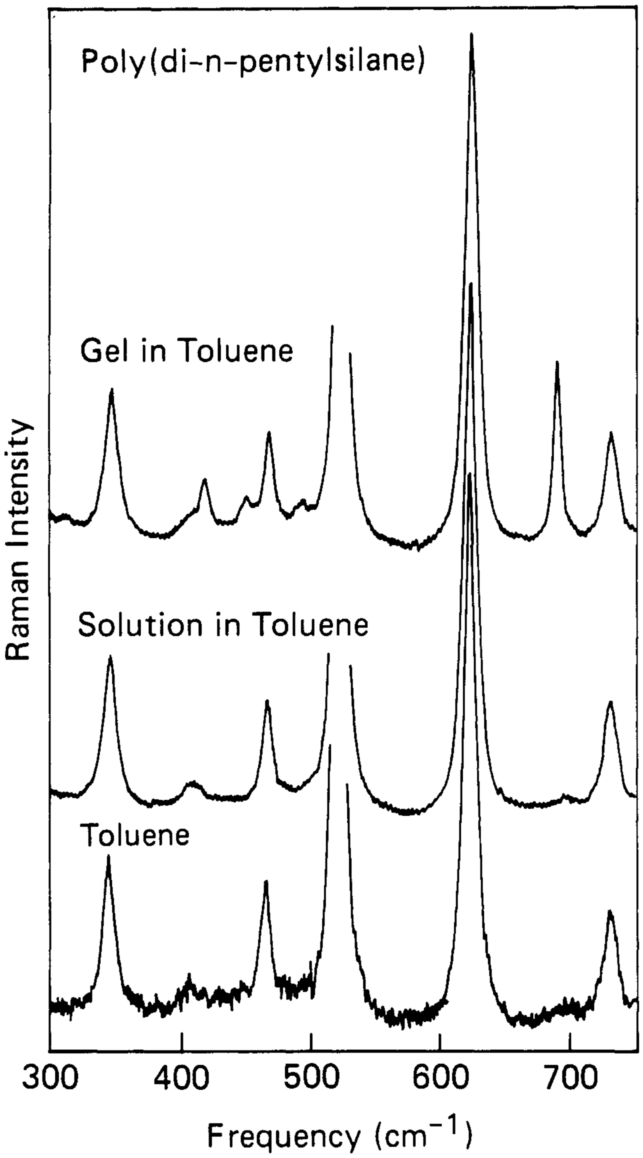

Figure 2. Raman spectra of toluene, a 2 wt % solution of PDPS in toluene, and the same solution as a gel. All three spectra were collected at 4-cm^{-1} resolution using 200 mW of laser power at 4880 Å. Because the trans-planar structure is resonance enhanced, the sharp peaks in the gel spectrum corresponding to the trans-planar structure are readily apparent. These bands are absent in the solution spectrum, indicating that the structure forms upon gelation.

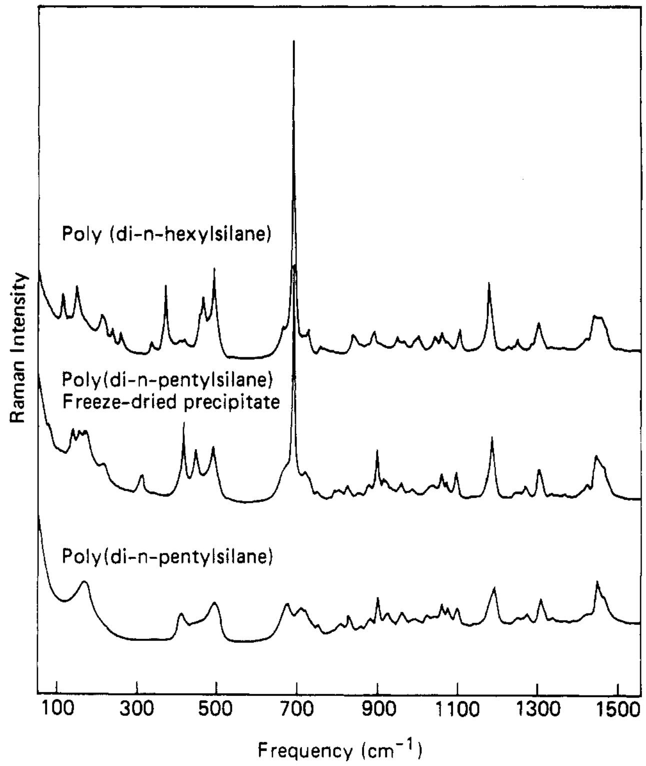

Figure 3. Raman spectra of solid PDHS, a freeze-dried gel of PDPS, and solid PDPS. All three spectra were collected at 4-cm^{-1} resolution using 200 mW of laser power at 4880 Å. The retention of some trans-planar structure in the freeze-dried PDPS is illustrated by the presence of the intense peak at 689 cm^{-1}.

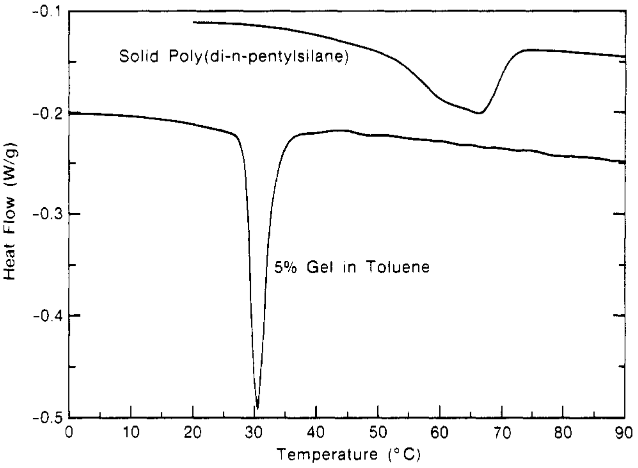

Figure 4. DSC traces of pristine PDPS solid and a 5 wt % solution of PDPS in toluene. The gel transition is much sharper and occurs at a much lower temperature than that of the solid. Both runs used a heating rate of 10 °C/min.

the solid or solution spectrum of PDPS. Figure 2 shows Raman spectra of toluene, a 2% solution of PDPS in toluene, and a gel formed by cooling this solution. It is clear that in solution PDPS has no strong scattering maximum in the region of interest. The Si–C stretching region around 700 cm^{-1} is barely detectable in the solution spectrum due to the low concentration of polysilane. However, the gel formed from this solution shows sharp, intense bands at 419, 449, 491, and 689 cm^{-1} due to resonance enhancement. The association of the 689-cm^{-1} peak with trans-planar conformation coupled with the correspondence between the other resonance enhanced peaks in the gel and in PDPS under high pressure,[11] where the existence of trans-planar segments is also supported by NMR and X-ray results,[12] leads to the conclusion that gel formation is accompanied by formation of trans-planar structure. All observed spectral changes are reversible upon melting and re-formation of the gel or precipitate. Similar spectral features were seen for the PDPS precipitate in the presence of solvent, as well as for both the gel and precipitate of PDBS in either benzene or toluene. No attempt to quantify the extent of structural change for any particular set of processing conditions has yet been made.

The trans-planar structure present in the gels and solvent-containing precipitates appears to be lost upon drying at room temperature. Raman spectra of the dried materials resemble those of the original solids, and no evidence of the existence of trans-planar structure is seen. However, preliminary experiments indicate that solid PDPS, which retains some of the induced trans-planar structure, can be obtained by freeze-drying gels produced in benzene. The Raman spectrum of a freeze-dried PDPS gel is compared to that of solid PDPS and PDHS in Figure 3. The 689-cm^{-1} band is a very clear feature of the spectrum of freeze-dried PDPS gel, indicating the presence of a trans-planar conformation similar to that in PDHS. However, the shoulder at 670 cm^{-1} (this band is not resonance enhanced) suggests that a helical structure is present as well. A shoulder of this magnitude is not observed for the solvated gel. The sharp bands at 372 and 458 cm^{-1} in the spectrum of PDHS were previously assigned to Si–Si vibrations associated with the trans-planar conformation.[5] The reasons for the difference between the frequencies of these bands and those observed for the freeze-dried PDPS gel are not yet understood.

DSC measurements (Figure 4) show that the loss of the gel structure is associated with a distinct thermal transition. The onset of gel melting occurs at 29 °C, while the transition of the solid from a 7/3 helix to a conformationally disordered state begins around 52 °C. The enthalpy of disordering in solid PDPS is 207 cal/mol of repeat unit ($C_5H_{11}SiC_5H_{11}$). However, the enthalpy of melting for a 6.8 wt % gel in toluene is 4.0 J/(g of gel) or 2400 cal/mol of PDPS repeat units present. This value includes both the enthalpy of disordering and the enthalpy of dissolution. For comparison, the enthalpy change for the PDHS transition from trans-planar to disordered structure is about 1650 cal/mol of repeat units. The sharpness of the gel transition seems to imply a more uniform structure than is suggested by the UV spectrum. The magnitude of the enthalpy change on gel melting also indicates that there are strong forces favoring the formation of trans-planar structure for PDPS in toluene.

In summary, we have demonstrated the formation of thermally reversible polysilane gels in benzene and toluene. UV and Raman measurements indicate that both gel and precipitate formation appear to be accompanied by the formation of trans-planar structure in the polymer backbone. Similar results have been observed for PDBS. This is the first time such a structure has been observed for PDBS or PDPS without resorting to extremes of high pressure or low temperature. It is not clear why the thermodynamic forces driving microphase separation in this system should lead to the adoption of a trans-planar conformation. It is tempting to try to assign a direct role to the aromatic solvent, but the previously reported results for PDBS precipitated from pentane at low temperature[13] suggest that adoption of a trans-planar structure during phase separation may be a more general phenomenon. Further characterization of the gel phase and freeze-dried material is underway, and the results will be reported in a future article.

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