Solid-State Piezochromism in Poly(di-*n*-hexylgermane)

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Since the discovery that σ-conjugated polymers undergo order–disorder transitions when subjected to either temperature or pressure variations, there have been numerous investigations[1-8] using X-ray, NMR, IR, Raman, and thermal measurements in an attempt to characterize the conformational structure in the ordered and disordered states. Most of the emphasis has been on the symmetric poly(di-*n*-alkylsilanes) which exhibit at least three regimes of crystallization having either a planar zigzag, 7/3 helix, or TGTG′ conformation depending on the length of the *n*-alkyl side chain. More recently the poly(di-*n*-alkylgermanes) have become the subject of a number[9,10] of studies which have shown that those too exhibit thermochromic behavior. In the case of poly(di-*n*-hexylgermane) (PDHG)[9] this thermochromic transition was observed below room temperature (12 °C) compared to above room temperature (42 °C) for its silane analogue, poly(di-*n*-hexylsilane) (PDHS).[1] In the ordered state, both PDHS[4,5] and PDHG[9,10] have been shown to adopt a planar zigzag conformation with the latter having a slightly larger X-ray repeat distance, reflecting the slightly larger Ge-Ge bond distance (2.41 Å compared to 2.35 Å for Si–Si).

The purpose of this work was to explore the effect of elevated pressure on PDHG since earlier studies had shown that the poly(di-*n*-alkylsilanes) underwent significant shifts (50 nm) in the UV spectra when placed under hydrostatic pressure.

As shown in Figure 1, the UV–visible spectrum of PDHG at room temperature and atmospheric pressure differs somewhat from that of its silane analogue. Above its thermochromic transition point PDHG absorbs at 332 nm compared to 316 nm for PDHS, although in the ordered state both absorb at 370 nm. The former observation has been attributed to less disorder in the organization of the Ge backbone. The bandwidths of the UV–visible absorptions in PDHG at 332 nm and 370 nm (at elevated pressures) were observed to be intrinsically larger than those observed in PDHS under identical conditions. Although the exact cause is unclear, it is believed to be related to the larger range of conformations available to the germanium backbone resulting from the larger Ge–Ge bond distance. This increased flexibility would contribute to a broadening of the UV–visible bands both at ambient and elevated pressures.

As soon as the pressure is raised 4 kbar, the UV absorption band at 332 nm in PDHG shifts to 370 nm, the precise location[9] found when the temperature of PDHG was lowered below 12 °C. This would suggest that the application of pressure has transformed the Ge backbone from a disordered conformation to one that is planar zigzag. This is further supported by a comparison of the Raman spectra obtained as a function of temperature (Figure 2) and pressure (Figure 3). One can easily see that the sharpening and splitting of bands attributable to Ge–Ge stretching and torsional vibrations of the PDHG backbone found below 300 cm^{-1} as a function of lowering the temperature (Figure 2) below the order–disorder transition is clearly mimicked by applying pressure (Figure 3). In fact, as shown in Figure 3, the Raman spectrum of PDHG at 9 kbar is very similar to that obtained at −50 °C with the exception of the observed vibrational bandwidths which are considerably broader due to lower instrumental resolution.

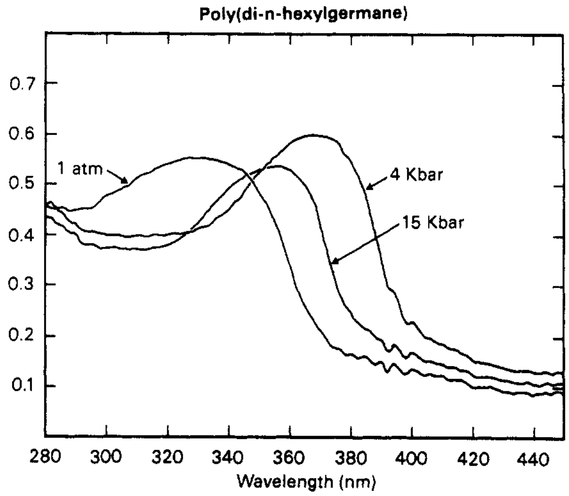

Figure 1. UV–vis spectra of poly(di-*n*-hexylgermane) in a diamond anvil cell at atmospheric and elevated pressures.

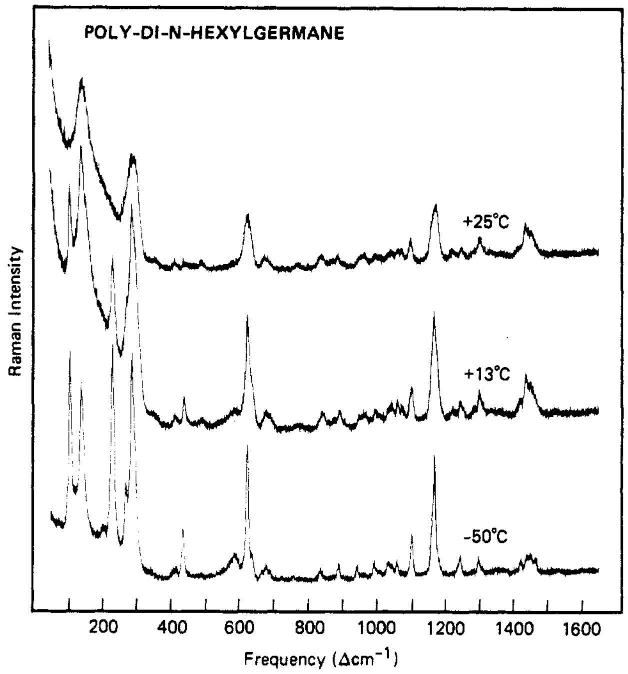

Figure 2. Conventional Raman spectra of poly(di-*n*-hexylgermane) (PDHG) obtained at 514.5-nm excitation (4-cm^{-1} resolution) as a function of temperature.

Another manifestation of the planar zigzag structure of the Ge backbone is shown in the 400–700-cm^{-1} region of Figures 2 and 3. At both low temperature and elevated pressure a band at 435 cm^{-1} characteristic of a transplanar backbone appears. In addition, a definite sharpening of the 633-cm^{-1} Ge–C stretching vibration is also observed. This change in peak intensity with a concomitant decrease in the bandwidth at half peak height has been previously noted[9] to occur when PDHG adopts a planar zigzag conformation. It should be kept in mind that the widths of the bands shown in Figure 3 are somewhat larger at elevated pressure than those in Figure 2 simply due to the lower instrumental resolution used to record Raman spectra in a diamond anvil cell.

Recent X-ray diffraction studies of oriented PDHG below the thermochromic transition[10] have concluded that

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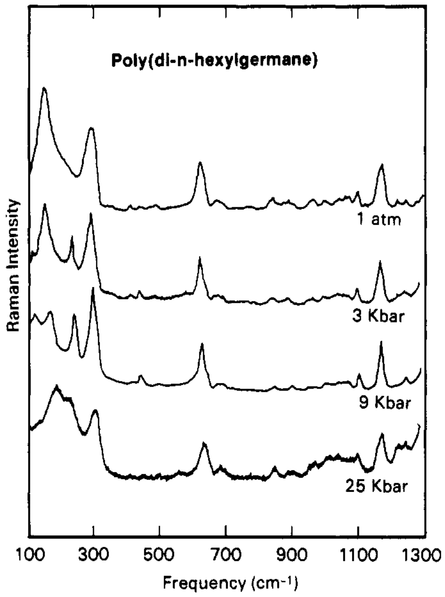

Figure 3. Conventional Raman spectra of PDHG obtained at 514.5 nm (6-cm^{-1} resolution) in a diamond anvil cell as a function of pressure.

the backbone conformation is planar zigzag with the molecules arranged in an orthorhombic unit cell. The similarity of the Raman spectra at both low temperature and elevated pressure taken in conjunction with the low temperature X-ray diffraction data allow us to conclude that PDHG adopts a planar zigzag conformation at pressures exceeding 3 kbar.

Interestingly enough, at higher pressures, 15–25 kbar, both the UV and Raman spectra of PDHG continue to change. The UV band undergoes a blue shift, while the Raman spectrum becomes similar to that found for a partially disordered chain at atmospheric pressure. This would suggest a mechanism similar to that proposed[11,12] for the poly(di-*n*-alkylsilanes) at high pressures; i.e., axial compression occurs which leads to the introduction of backbone defects. This results because at intermediate pressure the intermolecular chain–chain distances are minimized, causing the collapse of a disordered helix into a planar zigzag structure. Further increases in pressure cannot cause any further reduction in lateral distances, and hence axial compression becomes the dominant deformation mechanism.

In conclusion, PDHG does exhibit piezochromic behavior when subjected to elevated pressures. At intermediate pressures, a red shift of 40 nm in the UV absorption band occurs due to a conversion of the backbone from a disordered helix to a planar zigzag structure. Above 9–10 kbar, axial compression results in geometrical distortion of the backbone with a concomitant blue shift of the 370-nm band. This behavior is similar to that observed for certain of the poly(di-*n*-alkylsilane) series.[11,12]

References and Notes

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