Poly(*n*-butyl-*n*-hexylsilylene), a Liquid-Crystalline Polysilane

Of the polysilane polymers,[1] probably the best characterized are poly(di-*n*-butylsilylene) (PDBS)[2] and poly(di-*n*-hexylsilylene) (PDHS).[3] The latter polymer exists in a fully extended trans zigzag conformation below its transition temperature of 42 °C[4] and in a hexagonal mesomorphic phase above this temperature,[5] whereas PDBS adopts a 7/3 helical arrangement below its transition temperature of ~86 °C.[6] Here we report the polymer with one *n*-butyl and one *n*-hexyl group on each silicon, poly(*n*-butyl-*n*-hexylsilylene) (PBHS), which has properties quite different from those of either PDBS or PDHS.

PBHS was prepared from *n*-butyl-*n*-hexyldichlorosilane by condensation with sodium metal in toluene at 110 °C, in the usual manner.[7] It is a rubbery solid at room temperature. At 25 °C and above, a thin (10-μm) film of PBHS showed a broad UV absorption band at 320 nm. When the sample was cooled, λ_{max} shifted hypsochromically to 312 nm at about −25 °C; at still lower temperatures (ca. −40 °C) a new band grew in at 345 nm. These results suggest that two different phase transitions occur for PBHS below 0 °C.

This interpretation was confirmed by differential scanning calorimetry (DSC) and dynamic-mechanical measurements. The DSC for PBHS shows a second-order discontinuity due to a probable glass transition at −40 °C and an endotherm with Δ = 4.6 cal/g from a first-order melting-type transition at −22 °C. The dynamic-mechanical measurements are apparently the first to be reported for a polysilane polymer. As shown in Figure 1, a weak tan Δ peak accompanied by a sharp decrease in loss modulus is observed near −45 °C, and a rapid increase in tan Δ and further decrease in modulus are found near −20 °C, at the first-order transition. The phase transition at −20 °C appears to represent a partial crystallization, perhaps due to locking-in of motion of the side chains, as has been observed for PDHS.[8] The second-order transition at −45 °C may be associated with loss of motion of the main chain.[9]

Photomicrographs of PBHS films, prepared by evaporation from ether solution, between crossed polarizers are shown in Figure 2. PBHS polymer is strongly birefringent in the partially crystalline states at both −50 and −30 °C. When the polymer is heated above the −20 °C transition, the birefringence decreases somewhat but does not vanish completely until a very high temperature ~220 °C. Above 220 °C the polymer melts completely, becoming freely flowing and isotropic at 230 °C.

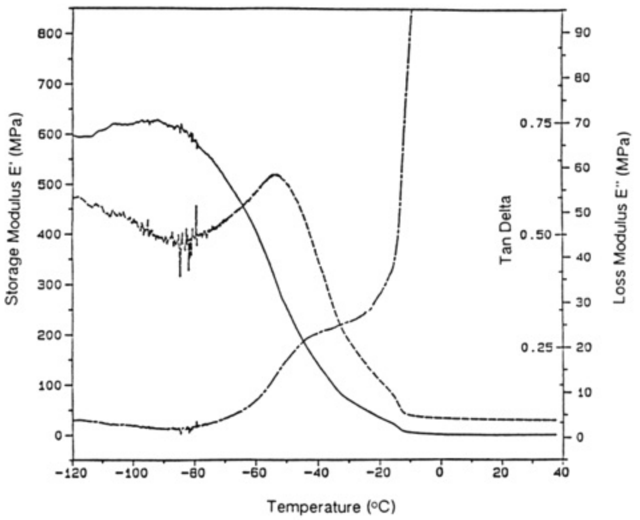
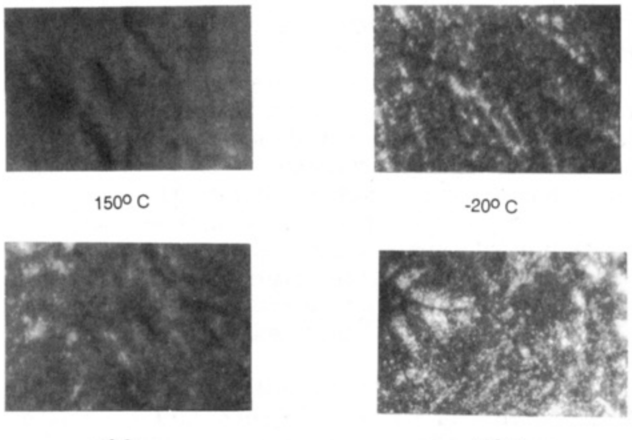


Figure 1. Results of dynamic-mechanical measurements on a film of PBHS: (—) storage modulus, *E'* (MPa); (- - -) loss modulus *E''* (MPa); (– • –) tan Δ.



150° C
-20° C
0° C
-50° C

Figure 2. Photomicrographs of PBHS film under crossed polarizers at +150, 0, −20, and −50 °C, showing birefringence.

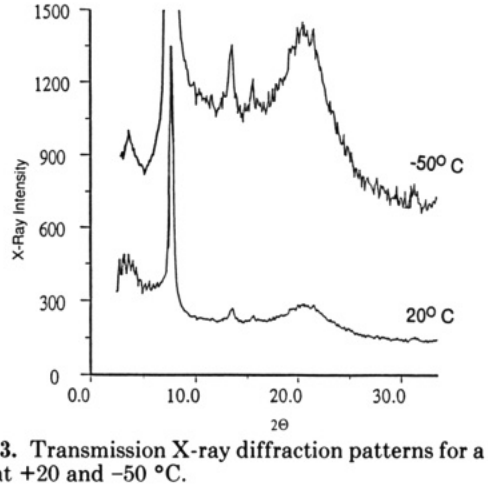


Figure 3. Transmission X-ray diffraction patterns for a film of PBHS at +20 and −50 °C.

The persistent birefringence of PBHS suggests that the polymer exists in a liquid-crystalline mesophase above the −20 °C transition. X-ray diffraction measurements on films of PBHS permit elucidation of the nature of the mesophase. At all temperatures from −50 to +220 °C, PBHS is mainly amorphous, with only two-dimensional order evident from the X-ray patterns. As seen in Figure 3, at −50 °C PBHS shows a strong sharp peak at 2θ = 7.31°, corresponding to a long-range spacing of 12.09 Å. Weak Bragg reflections at 2θ = 12.72 and 14.69°, corresponding to $d/\sqrt{3}$ and $d/2$, indicate that PBHS crystallizes in a hexagonal lattice.[10] The patterns at +20 (Figure 3), +75, and +150 °C are very similar to that at −50 °C. All show a moderately strong peak at $2\theta \sim$ 7.8°, accompanied by weak $d/\sqrt{3}$ and $d/2$ reflections. Thus *the hexagonal lattice of partially crystalline PBHS persists in the mesophase,* up to the eventual isotropic melting temperature. As shown in Table I, as the temperature increases the intensity of the main peak decreases and there are slight changes in the lattice distance.

Recent studies have shown that PDHS also exists in a hexagonal lattice above its 42 °C transition.[5] The mesophases of PDHS and PBHS are similar and can be regarded as columnar liquid-crystalline phases. The units are probably columns of disordered, perhaps coiled, polymer molecules, with the column axis lying along the

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Table I
X-ray Diffraction Data for PBHS at Various Temperatures

temp, °C	lattice distance, Å	peak intensity counts
-50	12.09	3900
+20	11.34	650
+75	11.29	520
+150	11.54	490

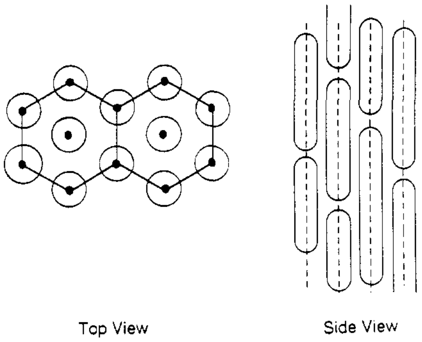

Figure 4. Pictorial representation of the structure proposed for PBHS.

hexagonal lattice axis (Figure 4). The liquid-crystalline phase of PBHS is stable over a very large temperature range, from -20 to +220 °C.

The hexagonal lattice structure of PBHS can also be regarded as an example of a conformationally disordered (condis) crystal lattice.[11] Columnar liquid-crystalline phases occur for many lyotropic liquid crystals[12] but do not seem to be common for polymers. The high-temperature phases of poly(diethylsiloxane)[13] and poly(di-*n*-propylsiloxane)[14] are, however, liquid crystalline[15] and probably columnar in nature. We have observed columnar liquid-crystalline properties for several other polysilanes and will report on these later.

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Tetsuya Asuke and Robert West*
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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