Intramolecular Ordering Stopped by Glassification. A UV and Raman Study of Poly[*n*-butyl-*n*-hexylsilylene] Phase Transitions

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UV and Raman data show that a prolonged first-order phase transition of PBHS which begins at *ca.* –25 °C consists of a gradual transformation on cooling of a disordered macromolecule main chain into more ordered, probably helical conformation and then into an all-*trans* conformation with accompanying crystallization. The polarizability-driven transition from the helical to the all-*trans* conformation does not proceed to completion, but ceases at *ca.* –60 °C due to a quasi-second-order phase transition of a glassification type which "freezes out" some thermal molecular motions necessary for this transformation to occur. Even at –240 °C the polymer exists as a mixture of two forms.

Recently, two of us reported the synthesis and some of the properties of poly[*n*-butyl-*n*-hexylsilylene] (PBHS).[1] This polymer is a rubbery solid at room temperature, forming a hexagonal columnar liquid-crystalline (hclq) mesophase according to wide-angle X-ray diffraction measurements. Differential scanning calorimetry and dynamic mechanical analysis showed that this polymer undergoes two phase transitions on lowering the temperature: a first-order transition at −22 °C and a quasi-second-order discontinuity at *ca.* −40 °C due to a probable glass transition.

In this paper we briefly report a detailed study of the Raman and UV spectra of PBHS to further elucidate the nature of these transitions.[†] Such a combination of methods has proved very informative in analogous investigations.[2–10]

The UV spectrum of a thin film of PBHS at room temperature exhibits a single broad band at 321 nm (Fig. 1, 1) typical of disordered hclq phases. When the temperature is lowered to −25 °C, a shoulder on the long wavelength side becomes noticeable, its intensity increasing with further cooling. At −30 °C the shoulder becomes a clear new band with λ_{max} = 345 nm. This value is very close to that observed for crystalline all-*trans* polysilylenes [other than $(n\text{-Hex}_2\text{Si})_n$ which absorbs at 370 nm].[6–9] In the same narrow temperature interval −25 to −30 °C the initial band shifts from 321 to 316 nm, with a dramatic change in its contour (an increase in the peak intensity and significant band narrowing, see Fig. 1). We believe the latter changes reflect an abrupt transformation of the initial disordered hclq phase into a new one with a probable helical conformation of the silicon backbone. This assumption is based on analogy with the UV data for $(n\text{-Bu}_2\text{Si})_n$ phase transitions[11] and is to some extent confirmed by the WAXD data of KariKari and co-workers,[10] who reported for an oriented film of PBHS at −30 °C a pattern similar to that of a 7/3 helical backbone conformation. However, we realize that the latter is not strong evidence because different samples of a polymer may behave differently (see below), especially if they have different molecular mass distribution. Our PBHS sample was monomodal with $M_W = 2 \times 10^6$; its preparation is described in ref. 1. The dependence of the polymer crystal structure on the molecular weight has been demonstrated by the authors[10] for $(n\text{-Oct}_2\text{Si})_n$.

Further cooling of PBHS to −60 °C leads to an increase in intensity of the 345 nm band and a decrease in intensity of the band at 316 nm. The entire process is reversible. However, it is important to note that the intensity ratio of the two bands is not a single-valued function of temperature but strongly depends on the sample prehistory and on the rate of cooling, which seems to be typical of polymers in accordance with the review data.[12,13]

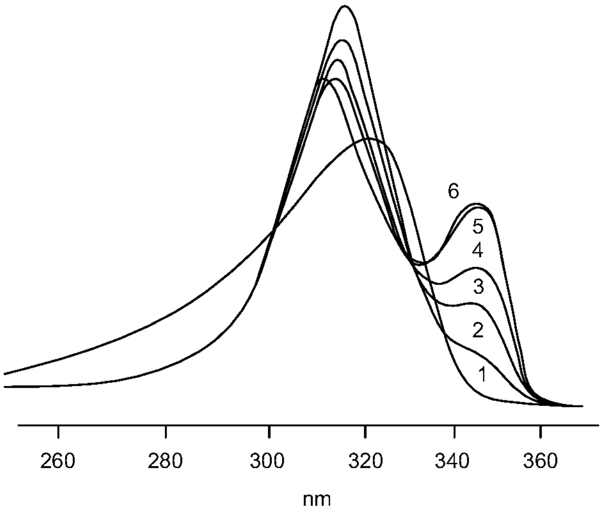

Fig. 1 UV spectrum of a PBHS film at different temperatures: 1, 25 °C; 2, −28 °C; 3, −30 °C; 4, −45 °C; 5, −60 °C; 6, −240 °C.

Thus, UV data allow us to conclude that at −25 °C the process of ordering of the hclq phase begins. In the temperature interval −25 to −30 °C most of the hclq substance first transforms into a new, perhaps helical form with a simultaneous nucleation of a phase with the all-*trans* backbone conformation. The latter conformation favours maximal σ-σ-conjugation[14] and hence maximal polarizability of the macromolecules.[15] In the temperature interval from −30 to −60 °C the amount of the all-*trans* form gradually increases.

However, when the PBHS sample is cooled further (down to −240 °C), no further change in band intensities is observed in the UV spectrum. This implies that at −60 °C a glass transition takes place in accordance with the DSC data[1] which detected this quasi-second-order phase transition at *ca.* −40 °C. We believe the difference in the temperatures found is due again to different sample prehistories and cooling rates.

At the glass point the process of transformation of the polymer main chain conformation ceases because below this temperature some thermal molecular motions which enable this transformation are frozen out. Below −60 °C the polymer exists as a "frozen" mixture of at least two forms, differing in their UV absorption bands.

Thermochromic first-order phase transitions in the solid state are well-known for other polydialkylsilylenes (see a recent paper[10] and refs. therein). The former are mostly transformations from crystalline to amorphous or hclq

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[†] *Experimental.* UV spectra were obtained for polymer films cast from a concentrated solution in hexane using a M-40 Karl Zeiss spectrophotometer. Raman spectra were obtained using a U-1000 Jobin-Ivon Raman laser spectrometer with 514.5 nm excitation for a solid sample sealed *in vacuo*. For temperature measurements a Displex Air Products model DE-202S cryogenic system with automatic temperature indicator/controller APD-F was used. Various methods of sample preparation and various rates of cooling were applied.

phases, occuring above room temperature. These transformations may be relatively abrupt or may occur over a certain temperature range, depending on the temperature of the transition and on the prehistory of the polymer sample.[9] A good example of an abrupt transition is that of a homopolymer $(n\text{-Pr}_2\text{Si})_n$ at *ca.* 230 °C.[8] According to the UV data, this transition from an all-*trans* to a disordered form is completed within 20 °C. However, the copolymer $(\text{Et}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ exhibits an analogous but prolonged phase transition on heating over the temperature interval from 80 up to 120 °C.[8]

In the case of PBHS we come up against a complex prolonged polarizability-driven first-order phase transition occuring on cooling. This transformation cannot proceed to completion because it is stopped at the glassification point.

The results of the Raman experiments for PBHS are in good accord with the UV data. The temperature evolution of the Raman spectrum of solid PBHS is given in Fig. 2. At room temperature a complicated pattern is observed in the regions where the stretching vibrations $\nu_{\text{Si–Si}}$ and $\nu_{\text{Si–C}}$ are situated (350–500 and 600–750 cm^{-1}, respectively). This is indicative of a disordered polysilylene structure.[4–8] At *ca.* −25 °C a new sharp line in the $\nu_{\text{Si–C}}$ region at 692 cm^{-1} emerged. An analogous sharp $\nu_{\text{Si–C}}$ line was observed previously in the Raman spectra of other $(\text{Alk}_2\text{Si})_n$ moieties and was shown to be diagnostic of an ordered crystalline all-*trans* phase.[2,3]

The intensity of this line in the spectrum of PBHS increased on lowering the temperature in the interval from −25 °C to *ca.* −55 °C. Subsequent cooling did not lead to any further intensity increase, the Raman pattern becoming constant. Analogous but not so spectacular changes are observed in the $\nu_{\text{Si–Si}}$ region. Thus, the Raman method allows detection of a highly ordered all-*trans* form but cannot detect the transformation of the initial hclq phase into a helical one. This fact can be understood in terms of the pre-resonance character of polysilylene Raman spectra.[2,14]

From Raman studies on other polysilylene polymers[2–10,14] it is known that the $\nu^{s}_{\text{Si–C}}$ line in the spectrum of the ordered all-*trans* phase is enhanced by resonance and is therefore much more intense than in the spectrum of the less ordered phases. With this in mind, we are able to infer on the basis of the intensity of the $\nu_{\text{Si–C}}$ Raman lines that the amount of the all-*trans* phase in the PBHS sample studied is still small even near −60 °C. The same is evidenced by the intensity ratio in the UV spectrum. Thus, the phase transition into the all-*trans* conformation for this polymer is interrupted by glassification quite early in the process. That is why, in all probability, the all-*trans* phase was not evident at low temperature in the X-ray diffraction pattern.[1,10]

In summary, the data obtained by UV and Raman methods refine the DSC, WAXD and DMA results[1] and show that PBHS, like other polysilylene polymers, exists at higher temperatures as a columnar liquid-crystalline mesophase and undergoes a prolonged first-order phase transition of the ordering type on cooling. This phase transition involves first an abrupt transformation of the hclq phase into a probable helical form, and simultaneously the nuclei of an all-*trans* phase appear, whose concentration increases on further cooling. However, the latter transformation does not proceed to completion, but ceases due to a quasi-second-order phase transition of a glassification type which "freezes out" some thermal molecular motions necessary for this intramolecular event to occur. Even at −240 °C the polymer exists as a mixture of two forms.

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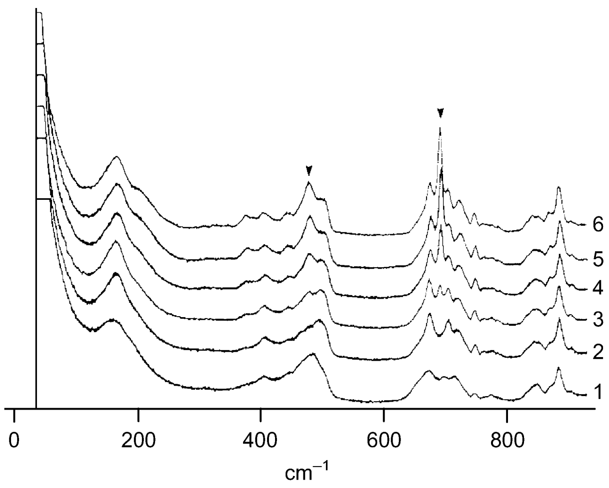

Fig. 2 Raman spectrum of PBHS at different temperatures 1, 20 °C; 2, −20 °C; 3, −30 °C; 4, −35 °C; 5, −55 °C; 6, −70 °C.

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