A Detailed UV and Raman Study of Poly(*n*-butyl-*n*-hexylsilylene) Phase Transitions

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ABSTRACT: Poly(*n*-butyl-*n*-hexylsilylene) (PBHS) has been studied by UV and Raman spectroscopy as a function of temperature from 300 to 27 K. At room temperature, PBHS adopts a hexagonal columnar mesophase. Upon cooling to 250 K or below, a complex first-order phase transformation takes place, leading to three other forms: a 7/3 helical form, an all-*trans* form, and an intermediate form with unknown conformation. The amount of each form depends on the thermal history of the sample. The final transformation, from 7/3 helical to the all-*trans* conformation, does not proceed to completion because equilibration ceases at the glass transition temperature, near 210 K.

Introduction

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. According to wide-angle X-ray diffraction measurements, it forms a hexagonal columnar mesophase (hcm). The structure and properties of such mesomorphic states formed by poly(di-*n*-alkylsilanes) are comprehensively described in ref 2. Differential scanning calorimetry and dynamic mechanical analysis showed that PBHS undergoes two phase transitions on lowering the temperature: a first-order transition at 251 K (T_c) and a quasi-second-order discontinuity at ca. 233 K due to a probable glass transition (T_g).

To further elucidate the nature of these transitions, we have investigated in detail the UV and Raman spectra of PBHS. The combination of these two internally related methods has proved very informative in analogous studies.[3−8a] A brief report of the results given below was published recently.[9]

Experimental Section

The PBHS polymer, synthesized as described in ref 1, was monomodal with $M_w = 2 \times 10^6$. UV spectra were obtained using a computerized M-40 Karl Zeiss spectrophotometer. UV band profiles were analyzed using a specially created computer program, in which the bands are analyzed as Gaussian or Lorentzian functions. Two types of samples were studied by the UV method: as-prepared bulk samples and thin films cast from a concentrated solution in hexane.

Raman spectra were recorded for the as-prepared solid bulk polymer samples sealed in glass capillaries in vacuo. A U-1000 Jobin-Yvon Raman laser spectrometer was employed, usually with 514.5 nm excitation, but 488.0, 476.5, and 457.9 nm lines were also used in some studies.

A Displex Air Products DE-202S cryosystem with an automatic temperature APD-F indicator/controller was used to maintain the temperature within ±0.5 K. Various rates of cooling and heating were applied.

Results and Discussion

UV Data. At room temperature, the UV spectrum of a thin film of PBHS cast from solution in hexane consisted of a single broad asymmetrical band with λ_{max} 321 nm (Figure 1) typical of the two-dimensionally ordered hexagonal columnar mesophases (hcm).[10] The process of the spectrum transformation on cooling is rather complicated and it seems best to consider it as consisting of four stages: above T_c; in the vicinity of T_c; between T_c and T_g; below T_g.

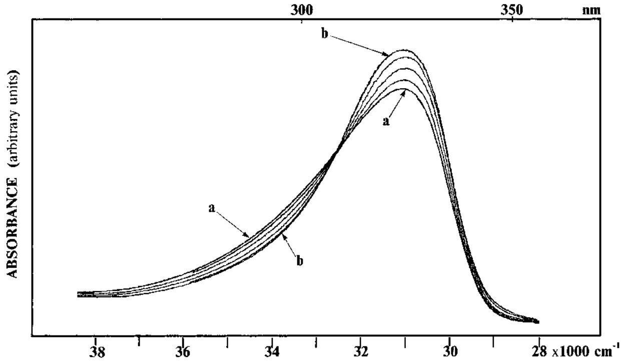

Figure 1. Temperature evolution of the UV spectrum of PBHS film above T_c in the interval 300−250 K: (a) 300 K; (b) 250 K.

Stage I. Above T_c. The temperature evolution of the UV spectrum in the interval from 300 to 250 K is shown in Figure 1. When the sample was cooled, the band maximum moved slightly but continuously to lower energies (from 321 to 323 nm) and its contour changed noticeably. The low-wavelength wing diminished gradually and an isosbestic point was observed. This behavior is characteristic of the UV bands of polysilane phases with disordered backbone conformations and is quite understandable taking into account that this band is a result of superposition of many absorptions corresponding to the Boltzmann equilibrium of different *trans* and *gauche* conformation sequences in the silicon chain.[10] Upon cooling, the number of *gauche* units which partially break the $\sigma-\sigma$ conjugation decreases, shifting the absorption band maximum to lower energy.

Stage II. Near T_c. Near T_c, 251 K according to the DSC experiment, the results strongly depend on the conditions of cooling. When the temperature was lowered slowly (during an hour) from 250 to 248 K and

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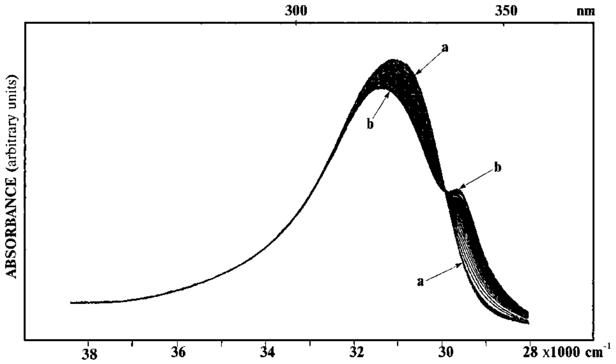

Figure 2. Isothermal transformation of the UV spectrum of PBHS film proceeding in the vicinity of T_c at 248 K (see text): (a) initial curve; (b) after 18 h.

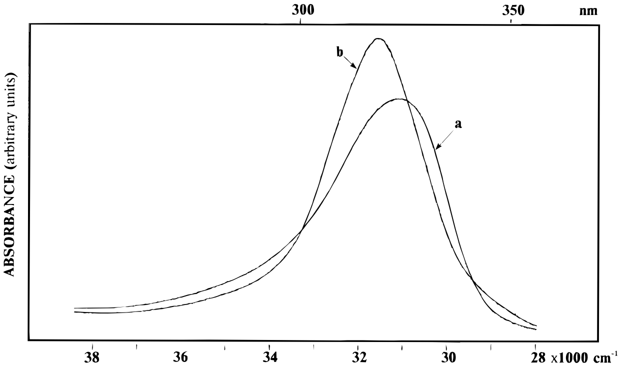

Figure 3. Abrupt transformation of the PBHS film UV band on fast cooling from 250 to 245 K (see text): (a) 250 K; (b) 245 K.

then maintained constant for 18 h, a shoulder on the long-wavelength side at 339 nm became noticeable and gradually grew in intensity. This was accompanied by a slight decrease in intensity and a blue shift (from 323 to 317 nm) of the main band. This isothermal process, occurring at 248 K and exhibiting an isosbestic point, is presented in Figure 2. It is obvious that a new band at 339 nm is formed at the expense of the long-wavelength side of the initial band; that is, a new modification which absorbs at 339 nm is formed at the expense of the longer *trans* sequences in the silicon chain of the hcm. We do not know yet to which conformation of the backbone the band at 339 nm corresponds and will designate it as the "intermediate form". It is notable that an additional polymorphic form intermediate between the columnar mesomorphic and low-temperature ordered phases was suggested for several poly(dialkylsilanes) on the basis of thermochemical data.[2]

If the film was cooled from 250 to 245 K rather rapidly (1 K/min) without a stop at 248 K, then no intermediate form was observed but the main band shape changed dramatically. The peak intensity increased, the band narrowed significantly (half-width decreased from 3100 to 2300 cm^{-1}) and became more symmetrical with disappearance of its short-wavelength wing. The λ_{max} value also shifted slightly to 316 nm (Figure 3). These changes evidently reflect a rather abrupt transformation of the initial hcm into a new form. By analogy with data for the $[n\text{-}Bu_2Si]_n$ phase transition[11] and on the basis of the WAXD results of KariKari and co-workers,[8a] who reported for an oriented film of PBHS at 243 K a pattern similar to that of a 7/3 helical backbone conformation, we assume this new conformation to be a 7/3 helical one.[12] However, it should be noted that a comparison of ref 8a is not conclusive because different samples of a polymer may behave differently (see below), especially if they have different molecular mass distributions. The dependence of a polysilane transition temperature on molecular mass was shown recently.[12]

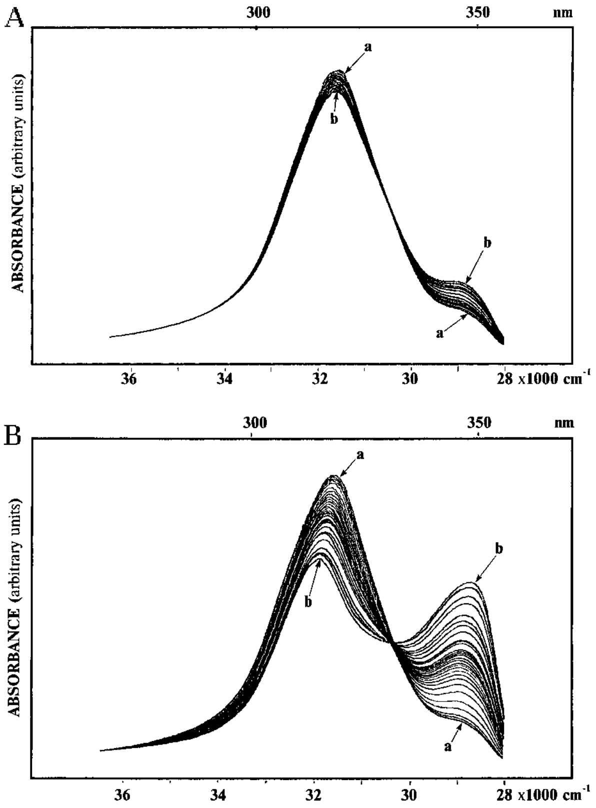

Figure 4. A prolonged kinetically controlled phase transition proceeding in the PBHS film in the temperature interval between T_c and T_g, from a helical to an all-*trans* modification, reflected by the UV spectrum. (A) Isothermal process of the all-*trans* form nucleation at 240 K over 2 h: (a) initial curve; (b) after 2 h. (B) Equilibrium coexistence of the two modifications in the temperature interval 240−225 K: (a) 240 K; (b) 225 K.

Further slight cooling of the same sample from 245 to 243 K led to the appearance of a shoulder at 346 nm which grew into a band at 349 nm (Figure 4a). When the temperature was lowered to 240 K and then held at this point, a slow isothermal process with an isosbestic point was observed, the intensity of the band at 349 nm increasing at the expense of the 316 nm band. This spontaneous process of polymer relaxation required several hours to reach equilibrium.

The value of 349 nm is very close to that observed for crystalline all-*trans* polysilanes (other than poly(dihexylsilane), which absorbs at about 370 nm).[3−6] The all-*trans* conformation of the silicon chain favors maximal $\sigma - \sigma$ conjugation[10,13] and thus exhibits the most red-shifted UV band. The assignment of the PBHS band at 349 nm to a form with an all-*trans* backbone conformation agrees well with the Raman data (see below).

Stage III. Between T_c and T_g. Further cooling of PBHS to 210 K was carried out in the same manner: the temperature was decreased by several degrees and then held constant for several hours, allowing successive isothermal relaxation to take place. This resulted in further redistribution of the intensity between the two bands, that is, in an increase in the fraction of the all-*trans* form and a decrease in the amount of the helical form (Figure 4B). Our assignment of these two bands

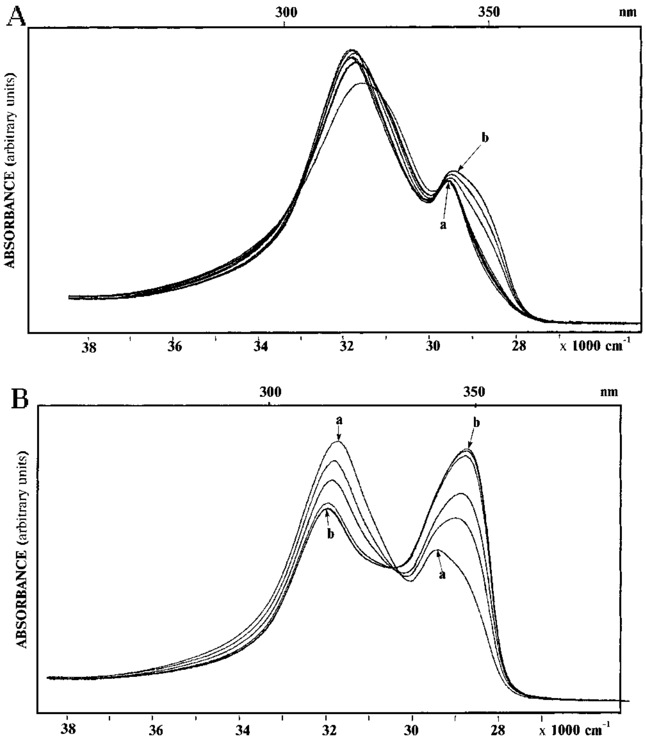

Figure 5. The same processes as in Figure 4 but occurring in the presence of the intermediate form absorbing at 339 nm (see text). (A): (a) 248 K; (b) 240 K. (B): (a) 240 K; (b) 200 K.

is strongly supported by the recent observations of KariKari et al.,[8b] who reported an analogous coexistence of the helical and the all-*trans* modifications for $[n\text{-Pent}_2\text{-Si}]_n$ polymer. These authors also noted that the transformation of the helical into the planar zigzag form is a kinetically limited process.

When the sample, which was treated so as to exhibit a UV spectrum with the 339 nm intermediate band (Figure 2), was further cooled slowly (2 K/h) to 243 K, the same transformations took place as in Figures 3 and 4; that is, the hcm transformed over a short temperature interval to a helical modification followed by appearance of the all-*trans* form. However, the intermediate form did not disappear during this process. This was evidenced by a more complicated spectral pattern without an isosbestic point (Figure 5A,B). On subsequent cooling, the intensity of the 349 nm band grew rapidly so that this band obscured the intermediate 339 nm band, but the presence of the latter was still evident from a slight $\lambda_{\max}$ shift of the lower energy band to 347 nm and from its asymmetry.

The process of transformation of the helical form into the all-*trans* form on cooling was reversible. However, it is necessary to emphasize here that the intensity ratio of the two bands at equilibrium was not a single-valued function of temperature. This is illustrated by Figure 6, where two spectra recorded at 200 K but using different cooling rates are presented. The intensity ratio, that is the fraction of each form in the process of the phase transformation, strongly depends on the sample thermal and mechanical prehistory, which can be important for the properties of many polymers.[14,15] It is especially noteworthy that if the rates of cooling were comparable with those usually applied in DSC measurements, the fraction of the all-*trans* form obtained prior to the glassification temperature was much less than with slow cooling (Figure 7). Such rates of temperature decrease are too rapid for the polymer to follow the temperature gradients adiabatically and to reach an equilibrium state.

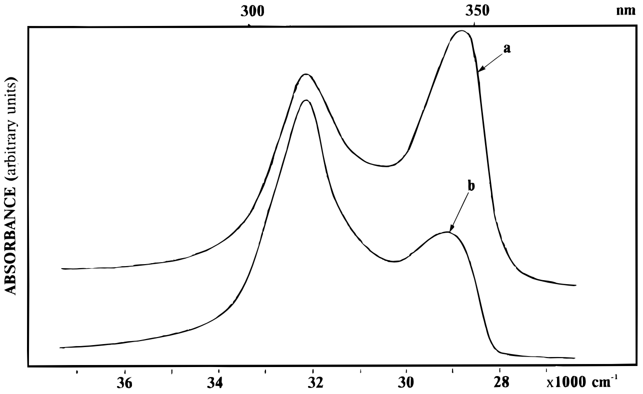

Figure 6. Two UV spectra of the PBHS film, both recorded below T_g at 200 K but for different cooling rates: (a) slow equilibrium cooling; (b) faster nonequilibrium cooling.

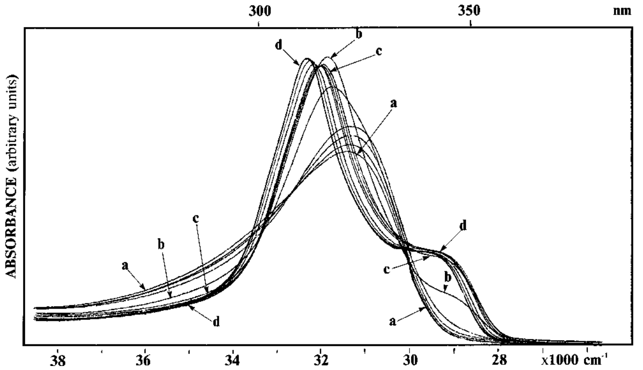

Figure 7. Temperature evolution of the PBHS film UV spectrum when using a high cooling rate comparable to that used in the DSC experiments: (a) initial spectrum of the hcm at 300 K; (b) the helical modification with a simultaneous nucleation of the all-*trans* form at 240 K; (c) the helical and all-*trans* forms at the glass point 210 K (note a small fraction of the all-*trans* form!); (d) a frozen mixture at 27 K.

Thus the conclusion can be drawn that the quantitative results obtained even for one and the same sample of a polymer by different methods may not be comparable.

Differently prepared samples of a polymer are likely to show even greater variation. The UV results obtained for a solution-grown film as described above were quite different from those obtained by us for a PBHS sample prepared from a three-dimensional chunk of this polymer by simply pressing it between quartz plates without dissolving. The fraction of the all-*trans* form obtained at a given temperature was much less for the three-dimensional sample (Figure 8). Analogous differences in the degree of crystallinity between a “bulk” polymer sample and a “solution-grown” polymer film are emphasized in a review.[15] Techniques such as DSC, NMR, WAXD, and Raman spectroscopy are often carried out on “bulk” samples, that is, polymer chunks, while UV and IR spectra are mostly determined on solution-grown polymer films. Thus, different results obtained by different methods are quite understandable. The same was inferred by Harada and Furukawa[16] for π-conjugated polymers.

Stage IV. Below T_g. After the temperature was lowered to ca. 210 K, no further change in band intensity ratio was observed in the UV spectrum on cooling (down to 27 K; see corresponding curves in Figures 7–9). This implies that at ca. 210 K a glass

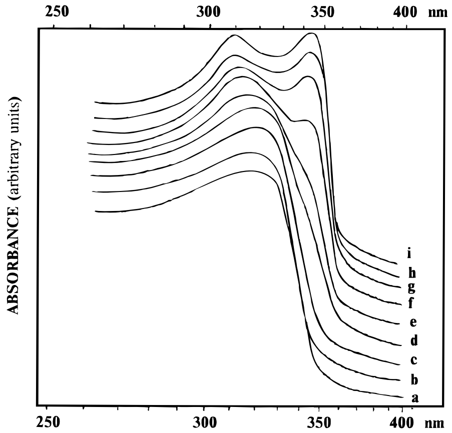

Figure 8. Temperature evolution of the UV spectrum of a bulk PBHS sample: (a) 293 K; (b) 273 K; (c) 263 K; (d) 258 K; (e) 248 K; (f) 243 K; (g) 228 K; (h) 223 K; (i) 153 K.

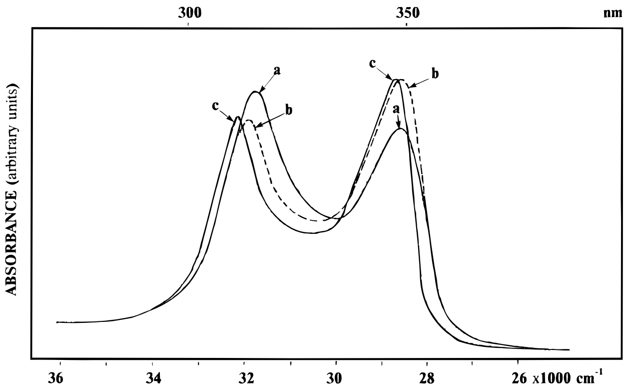

Figure 9. Temperature evolution of the PBHS film UV spectrum below T_g: (a) 240 K; (b) 210 K; (c) 27 K.

transition does take place, in accordance with the DSC data[1] which detected this quasi-second-order phase transition at ca. 233 K. We believe the difference in the T_g temperatures reported in this paper and in ref 1 is due again to different sample prehistories and different cooling rates.

At the glassification point, the process of transformation of the polymer main chain conformation ceases, because below this temperature some molecular translational and rotational motions which enable this transformation are frozen out. Below 210 K, the polymer exists as a frozen composite mixture of at least two forms with different backbone conformations.

However, on cooling from T_g down to 27 K, some changes in the UV spectrum are nevertheless observed (Figure 9). Both bands become narrower, and their λ_{max} move noticeably to shorter wavelength, reaching at 27 K the values of 310 and 342 nm for the helical and the all-*trans* bands, respectively (in the experiments where the intermediate form 339 nm was not present).

It is evident from computer analysis that a good fit to the experimentally observed spectral pattern at 27 K presented in Figure 9 cannot be achieved by deconvolution of overlapping bands into only two symmetrical bands with λ_{max} 310 and 342 nm; contributions from other species are probably present. Analogous complicated band contours were observed by us for the UV band of $[n\text{-Hex}_2\text{Si}]_n$ film at low temperature.[7] This phenomenon calls for further investigation.

Thus, the UV data allow us to conclude that at 250 K a complicated process of phase transformation of the hcm of PBHS into more ordered phases begins and continues down to 210 K, at which point it is stopped by glassification. Overall this process can involve at least four forms, each being characterized by its own separate UV absorption band. These are initial hcm with its broad band near 320 nm, a probable helical form presenting a 316 nm band of a specific shape, an all-*trans* form with a 349 nm band, and sometimes an intermediate form exhibiting a 339 nm band.

Close λ_{max} values of the first two bands indicate similar conditions for $\sigma-\sigma$ conjugation in the silicon chain of the hcm state and of the helical structure. The λ_{max} 339 nm value of the intermediate form is closer to the value of the ordered all-*trans* form, and one can assume that it corresponds to a rather ordered but "imperfect" *trans* form. It is pertinent to mention here that recently a new model for conformational thermochromic transitions involving four levels and proceeding via hypothetical intermediate conformations was proposed for polysilanes.[17]

It is notable that the λ_{max} values of all the bands are slightly temperature dependent, but in different manner. The band of the hcm moves on cooling to the red while the bands corresponding to the helical and all-*trans* forms shift to the blue. This enables one to easily distinguish between the hexagonal columnar mesophase and the helical form, even though both absorb in the same region, 310−320 nm.

Thermochromic first-order phase transitions in the solid state are well-known for other poly(dialkylsilanes) (see recent papers[6,8,12,18] and references therein). In the early papers reviewed in ref 10, these transitions were considered as involving only two phases: a high-temperature disordered (amorphous) or partially ordered one (hcm), on the one hand, and an ordered crystalline all-*trans* or helical one, on the other. These phase transitions can be understood in terms of a model suggested by Schweitzer.[19] According to this theory, the thermochromic transition arises from dispersion interactions between the delocalized electrons along the polysilane chain and the surrounding medium, in solids the pendent side chains. This dispersion interaction is strongest in the all-*trans* polysilane conformation.

Later, attention was paid to the fact that such transformations could occur relatively abruptly or may proceed over a considerable temperature range, depending on the temperature of the transition onset and on the prehistory of the polymer sample.[6,7] A good example of an abrupt transition from the crystalline all-*trans* phase to the hcm is that of a homopolymer $(n\text{-Pr}_2\text{Si})_n$ on heating to ca. 230 °C.[6] According to the UV data, this transition is completed within 10 °C. However, its copolymer $[\text{Et}_2\text{Si}]_n[n\text{-Pr}_2\text{Si}]_m$ exhibits an analogous phase transition but over a greater temperature range, from 80 to 120 °C.[6] Later, we have found that thermochromic transitions occurring *on cooling* proceed more slowly, and if they do not reach completion prior to glassification, they are frozen at this point. On further cooling, such polymers exist as a frozen composite mixture.[7,9] It was also shown that a thermochromic phase transition can involve more than two phases.[7,8b,18] In unsymmetrical poly(di-*n*-alkylsilanes), crystallinity is reduced and thermochromic transitions can take place between liquid crystalline or amorphous phases.[12,18]

Vibrational Data. We have also obtained vibrational spectra (IR and Raman) of bulk samples of PBHS at room temperature. Comparison of the Raman and IR spectra in the regions 350−500 and 600−750 cm^{-1}, where the stretching vibrations of the Si−Si and Si−C bonds, respectively, are situated (Table 1), reveals a

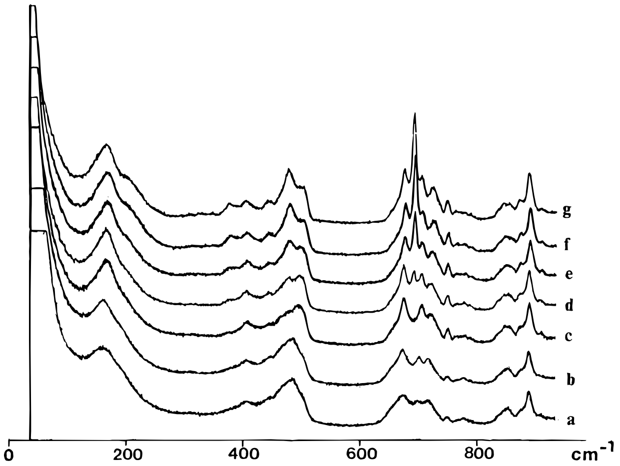

Figure 10. Temperature evolution of the PBHS Raman spectrum (see text) (514.5 nm excitation; bulk sample sealed in vacuo in a glass capillary): (a) 293 K; (b) 253 K; (c) 248 K; (d) 240 K; (e) 237 K; (f) 220 K; (g) 200 K.

Table 1. Raman and IR Spectra of PBHS in the Solid State in the Regions of the Skeleton Vibrations

Raman	IR	assignment
167 s		Si−Si
316 w		
373 vw		
407 m	409 w	
	438 w	
445 w	450 w	
	463 w	
478 s	480 w	
489 vs		
	505 w	
	661 vs	Si−C
674 vs	670 vs	
	680 sh	
701 s		
719 s	719 m	
748 m	745 w	
762 w	762 w	
774 w	775 m	

complicated pattern in both regions, with Raman lines having their IR counterparts and vice versa. This points to a disordered structure of the $[-SiC_2-SiC_2-]_n$ skeleton at room temperature with several conformers about the Si−Si and Si−C bonds being present.[3−8]

The results of the Raman experiments for PBHS are in good qualitative accord with the UV data. It is obvious that comparison is not strict because it is practically impossible to obtain the UV and Raman spectra under exactly identical conditions. The temperature evolution of the Raman spectrum of solid PBHS (a bulk, three-dimensional sample as-prepared from the synthesis) is given in Figure 10.

On going from room temperature to ca. 253 K, no change in the Raman spectrum was observed. Between 253 and 248 K the pattern in both the ν_{Si-C} (600−750 cm^{-1}) and ν_{Si-Si} (350−500 cm^{-1}) regions changed slightly but distinctly. Band narrowing was observed in the ν_{Si-C} region, and a new component at 498 cm^{-1} in the broad ν_{Si-Si} multiplet appeared. These changes seem to correspond to the analogous changes in the UV spectrum, both reflecting a transition from the hcm to a state with a helical backbone conformation. Below 248 K spectacular changes are observed in the Raman spectrum. In the ν_{Si-C} region a new sharp line at 692 cm^{-1} emerges and grows in intensity. Analogous sharp intense ν_{Si-C} lines in the region 640−690 cm^{-1} were reported previously in the Raman spectra of other poly(dialkylsilanes) having a planar zigzag all-*trans* backbone conformation.[3−8] The Raman line at 690 cm^{-1} has been considered by Rabolt, Miller, et al.[3,8] as diagnostic of the all-*trans* modification in their Raman studies of poly(dialkylsilanes) with *n*-alkyl groups *n*-Bu and longer.

Thus, Raman data indicate that formation of the all-*trans* form in the PBHS bulk sample takes place below 248 K. The growth of the Raman line at 692 cm^{-1} is accompanied by analogous but not so dramatic changes in other spectral regions. New sharp peaks appear at 375 at 478 cm^{-1}, typical of the ν_{Si-Si} of A_g and B_{2g} species in the all-*trans* polysilane skeleton.[3,4,7]

The intensity of the 692 cm^{-1} line and of other new features gradually increases on lowering the temperature in the interval from 245 to 213 K, that is, to T_g. Subsequent cooling below T_g did not lead to any further intensity alteration, the Raman pattern becoming constant (Figure 10f,g).

From the Raman studies of other polysilane polymers,[3−8,13] it is known that the $\nu^s{}_{Si-C}$ line corresponding to the ordered all-*trans* modification is the most strongly enhanced by resonance and is therefore much more intense than that in the spectra of less $\sigma-\sigma$ conjugated modifications. We have demonstrated this phenomenon for the case of PBHS by studying the dependence of the PBHS Raman spectrum on the wavelength of the exciting laser line at two temperatures, above T_c and below T_c, namely, at 293 and 238 K, using 5145, 4880, 4765, and 4579 Å excitation. The conditions of registration were chosen as to equalize the intensity of the Raman bands in the region 1450 cm^{-1}, corresponding to the deformation modes in CH_2 and CH_3 groups remote from the silicon chain and thus being insensitive to conjugation and resonance.

No resonance enhancement was found for the ambient temperature spectrum, which corresponds to the columnar hexagonal mesomorphic state with the disordered silicon backbone. However, the spectrum at 238 K, which corresponds to a mixture of the helical and the all-*trans* modifications, exhibits noticeable enhancement, but mostly of the 692 cm^{-1} line. On the basis of the intensity ratio observed in the ν_{Si-C} Raman region, we are able to infer that the amount of the all-*trans* modification in the PBHS bulk sample studied is still small even near 213 K (T_g). The same is evidenced by the intensity ratio in the UV spectrum of the bulk samples. Thus, the transformation of the silicon chain into the all-*trans* conformation for the bulk polymer sample is interrupted by glassification quite early in the process. That is why, in all probability, the all-*trans* modification was not evident at low temperature in the X-ray diffraction patterns of refs 1 and 8a.

PBHS is an atactic polymer, and these are known to crystallize with difficulty.[14,15] However, the difference in size between its two alkyl groups is not large, so this polymer can crystallize, as shown by the WAXD data for an oriented film of PBHS at −30 °C which pointed to a crystalline phase with the 7/3 helical backbone conformation.[8a] Our Raman data on the emergence in the PBHS Raman spectrum of the sharp $\nu^s{}_{Si-C}$ 692 cm^{-1} line which corresponds to the all-*trans* form are quite similar to those obtained for $[n\text{-Hex}_2\text{Si}]_n$ polymer,[7] for which the all-*trans* form was shown to be highly crystalline.[20] By analogy, we could assume that the all-*trans* modification of PBHS also forms a crystalline phase, but this point calls for further investigation.

Conclusions

The data obtained by UV and Raman methods refine the DSC, WAXD, and DNA results and show that PBHS, like many other polysilane polymers, exists at high temperature as a hexagonal columnar mesophase and undergoes a complicated first-order phase transition of the ordering type on cooling. The process of the phase transformation begins at ca. 250 K (T_c) and continues down to ca. 210 K (T_g).

Depending on the mode of cooling in the temperature interval near T_c (250−240 K), this transformation can proceed differently, but it necessarily involves a transformation of the hcm into a helical form with a simultaneous appearance of a phase with the planar zigzag all-*trans* backbone conformation. The latter conformation favors maximal $\sigma-\sigma$ conjugation and thus exhibits the most red-shifted UV band. An intermediate form can also emerge within the hcm, but only in the case when the process is stopped at 248 K, the temperature being held there for several hours. If it emerges, the intermediate form seems not to disappear on subsequent cooling.

The all-*trans* form does not appear directly from the hcm. The process of nucleation and growth of the all-*trans* form within the helical form (between T_c and T_g) is kinetically limited and does not take place to completion but ceases at the point of a quasi-second-order phase transition of a glassification type (T_g). The latter "freezes out" some thermal molecular motions necessary for this intramolecular event to occur. Even at 27 K, the polymer exists as a frozen mixture of at least two forms.

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