Electronic Absorption and Structural Properties of Poly(di-*n*-butylsilylene) Precipitated from Solution at Low Temperature

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ABSTRACT: The Si backbone in crystalline poly(di-*n*-butylsilylene) (PDBS) has been shown to be a 7/3 helix, which is in marked contrast to the trans chain conformation of poly(di-*n*-hexylsilylene) (PDHS). The electronic absorption properties of these two polymers are almost identical in solution but are entirely different in the solid state. In this work, we show that a new, long-wavelength-absorbing solid form of PDBS can be prepared by precipitating the polymer from dilute solution at low temperature. The structure of the new form is investigated using ^{29}Si NMR and X-ray diffraction. On the basis of NMR and UV absorption, we conclude that the new polymorph of PDBS is characterized by a trans conformation, although it contains substantial intra- and intermolecular crystallographic disorder, unlike PDHS.

Introduction

Polysilylenes are a unique class of polymers in which the σ-electrons are delocalized along the entirely sp^3-bonded silicon backbone, causing their electronic absorption properties to be strongly dependent on the conformation of the silicon backbone.[1-4] This property, combined with the synthesis of crystalline symmetrically substituted polysilylenes, has created much interest in the structure of these polymers in the solid state.

Most of the structural studies of these polymers have involved poly(di-*n*-hexylsilylene) (PDHS).[4-7] It has been well established by X-ray[4,6] and electron[6] diffraction and Raman scattering[4] that the silicon backbone in PDHS at room temperature is in a trans planar zigzag conformation and the hexyl side chains are packed in an ordered trans-like array perpendicular to the backbone. As the temperature is raised above 42 °C, conformational defects are introduced into the backbone and the side chains undergo partial disordering. This order–disorder transition gives rise to a very sharp and dramatic thermochromic transition in the solid state.

In direct contrast to the trans conformation of the backbone in PDHS, the backbones in poly(di-*n*-pentylsilylene) (PDPS) and poly(di-*n*-butylsilylene) (PDBS) form 7/3 helices under ambient conditions.[8,9] It is striking that a simple reduction by 1 or 2 carbon atoms in the polymer side chains causes such a major change in the conformation of the polymer. In addition, PDPS and PDBS do not exhibit dramatic thermochromism in the solid state, unlike PDHS. Although thermal and structural analyses of PDPS and PDBS show weak disordering transitions at elevated temperatures,[9] the maxima of their electronic absorption spectra remain essentially unchanged, indicating that the effective conjugation length on the backbone is not substantially affected by the disordering. While the electronic absorption properties of solid PDBS and PDPS are similar, there are large differences compared to solid PDHS; nevertheless, the solution UV absorption properties of all three are remarkably similar.[9,10] They all demonstrate sharp thermochromic behavior, with ~40-nm red-shifts of the absorption maxima below the low-temperature transitions.

The long-wavelength-absorbing form of PDBS, which exists in solution below the thermochromic transition, has now been obtained in the solid state by precipitation from dilute solution at very low temperature. The presence of the new form of the polymer is evident in the UV absorption spectrum and has been structurally analyzed by ^{29}Si solid-state NMR and X-ray diffraction. On the basis of these studies, we conclude that a polymorph of PDBS characterized by trans sequences has been obtained by the procedure presented here; however, this polymorph is crystallographically much more disordered than the all-trans phase of PDHS.

Experimental Section

PDBS was synthesized according to Zeigler.[11] The polymer was purified by precipitation from toluene twice with ethyl acetate and from tetrahydrofuran once with methanol, resulting in a white flocculent powder having a monomodal molecular weight distribution with $M_w = 562\,000$. The molecular weight distribution was determined by size-exclusion chromatography in tetrahydrofuran solution using Ultrastyragel Linear columns calibrated with polystyrene standards.

The low-temperature precipitation of PDBS was carried out by preparing a dilute solution (<0.1% by weight) of PDBS in anhydrous pentane (99+%, Aldrich), quenching this solution to −78 °C, and holding at this temperature for several hours. The solvent was decanted off and the polymer dried at −78 °C with a continuous flow of dry nitrogen. Thin films of the polymer for UV absorption measurements were made by precipitation directly onto a quartz substrate. The sample was then rapidly transferred to the sample chamber of a commercial spectrophotometer, which had been cooled to −80 °C with cold, dry nitrogen gas. Temperatures were varied by changing the flow rate of the cold gas and were measured with a thermocouple placed near the sample.

Samples for X-ray diffraction were prepared by precipitating the PDBS from dilute solution directly onto a glass X-ray sample holder. This resulted in a much smaller amount of material than normal for the X-ray analysis. The sample holder was rapidly transferred to the X-ray chamber, which had been precooled to −90 °C with a flow of cold, dry nitrogen gas. Temperatures were controlled by varying the gas flow rate and measured with a thermocouple placed directly below the sample holder. Special care was taken to avoid condensation of water

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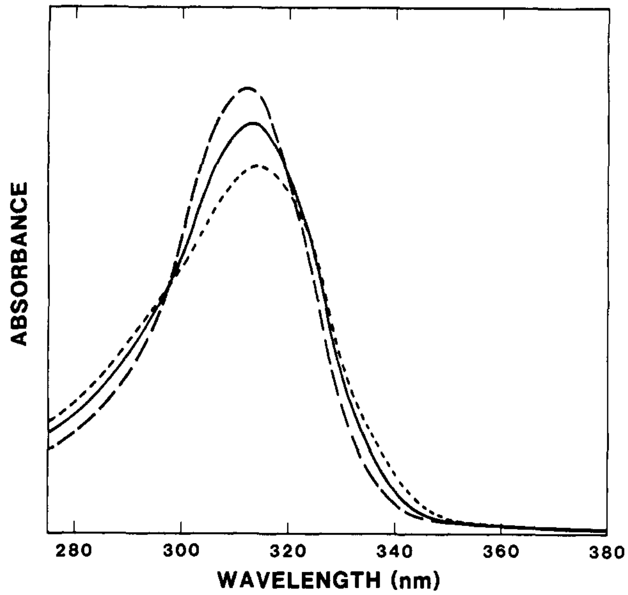

Figure 1. Temperature dependence of the UV absorption spectrum of a film of PDBS: (- -), T = 21 °C; (—), T = 60 °C; (- - -), T = 90 °C.

on the slide. Specimens were scanned at 0.5° 2θ/min under Ni-filtered Cu Kα irradiation.

The NMR spectra were recorded on a Varian XL-200 spectrometer (39.75 MHz for ^{29}Si) employing a Doty Scientific MAS probe with Al_2O_3 rotors and the standard Varian temperature controller. To prepare samples for solid-state magic angle spinning NMR studies, the cold, dried precipitate was placed in a rotor packed in dry ice. The packed rotor was then transferred rapidly to the precooled probe of the instrument, again with care to avoid condensation of water, which would prevent spinning.

Results and Discussion

As mentioned in the introduction, solid films of PDBS made from polymer precipitated from solution at ambient temperature demonstrate no dramatic thermochromic behavior. Thermal analysis indicates a weak endotherm at 87 °C, which has been shown by X-ray diffraction and ^{29}Si NMR to be due to a disordering of the 7/3 helical structure.[9] Comparison of the absorption spectra of a thin film of PDBS taken at 21 °C and at 90 °C shows only a broadening and very slight shift of the absorption maximum at the higher temperature (see Figure 1). Conversely, PDBS in solution exhibits very sharp thermochromic behavior. This is shown in Figure 2a. In hexane, the absorption maximum is red-shifted by 40 nm at -36 °C.[9,10] The transition has been interpreted as a coil-rod transition.[1] However, the nature of this thermochromic transition has generated much discussion.[10,12]

The UV absorption spectrum at -80 °C of a thin film of PDBS prepared in the manner described above is shown in Figure 2b. The polymer exhibits two absorption maxima, one at 316 nm, which could be due to the 7/3 helix or the disordered form, and one that is red-shifted by ca. 40 nm. The absorption maximum of the red-shifted peak is the same as that of PDBS in solution below the thermochromic transition. As shown in Figure 2a, the solution absorption spectrum indicates that only the long-wavelength-absorbing form of PDBS exists at -80 °C. The conformational complexity of the precipitated form, as indicated by the two broadened absorption peaks, may be attributable to conversion of the extended form to the helical or a disordered form as it precipitates or during inadvertent heating of the sample while handling.

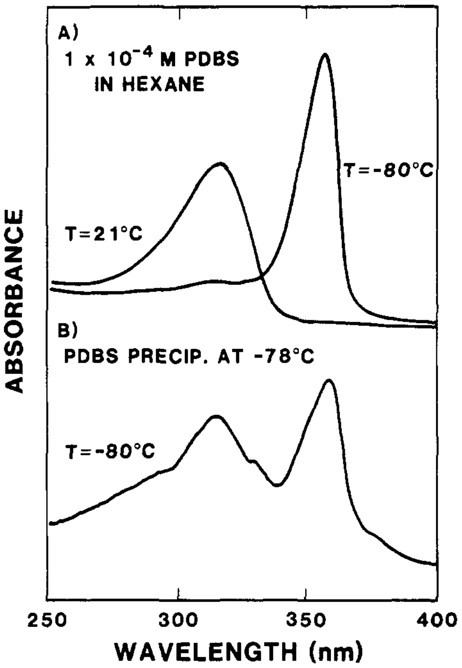

Figure 2. (a) UV absorption spectrum of PDBS in solution, above and below the thermochromic transition. The thermochromic transition temperature for PDBS in hexane is -36 °C.[10] (b) UV absorption spectrum of a film of PDBS precipitated from dilute pentane solution at -78 °C. The spectrum was recorded at -80 °C, and the polymer had never been warmed above -78 °C.

A structural probe that is particularly useful for polysilylenes is ^{29}Si NMR, since the silicon chemical shift is extremely sensitive to the conformation of the Si backbone.[9] The ^{29}Si solid-state NMR spectrum of PDBS precipitated from solution at -78 °C is compared with that of the normal 7/3 helical form of PDBS and that of the *all-trans*-PDHS in Figure 3. (All three spectra were recorded at -40 °C.) The spectrum is quite broad, indicating a distribution of chain conformations. It can be interpreted as consisting of three components: the downfield portion of the band is an overlap of several resonances, and this band includes the shift position for long sequences (>5) of the trans backbone conformation; the upfield shoulder is attributable to polymer in the 7/3 helical conformation; and the center peak can be associated with the disordered conformational component of the polymer. The broad nature of the silicon resonance suggests a distribution in the length of the trans sequences, resulting from a random placement of other bond conformations along the polymer chain. This type of conformational disorder has also been suggested by Hallmark et al. in describing the conformation of the unsymmetrically substituted poly(di-*n*-alkylsilylenes).[13] This interpretation of the NMR data is consistent with the UV absorption data (Figure 2b) in which the broad peak at 316 nm and shoulder near 332 nm are due to the 7/3 helix and the disordered components, respectively, while the peak at 358 nm is attributed to PDBS with a sequence of trans conformations along the Si backbone.

Although these results show that it is possible to prepare PDBS containing trans sequences by the method described here, this conformation of the polymer is not thermally stable. All experiments discussed so far have been carried out on precipitated polymer never warmed above -40 °C. The effect of further heating on these samples is shown by UV absorption in Figure 4 and by ^{29}Si NMR in Figure 5. If the polymer is warmed above 0 °C, it irreversibly converts to a somewhat disordered ana-

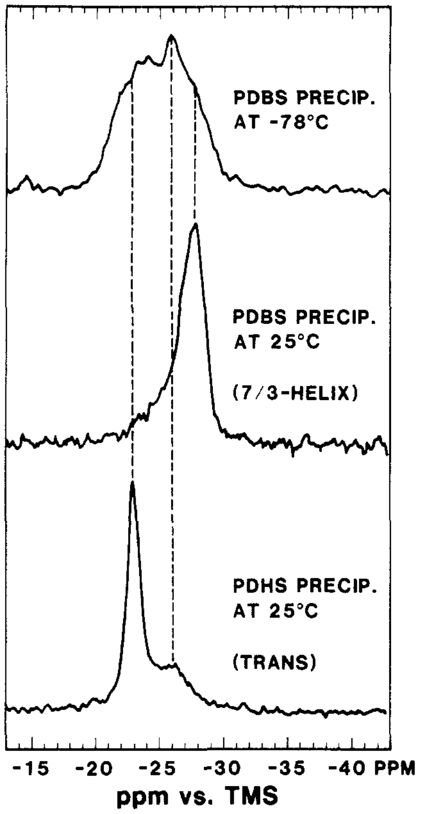

Figure 3. ^{29}Si NMR spectrum of solid PDBS, which has been precipitated from dilute pentane solution at −78 °C, compared with that of solid PDBS and PDHS precipitated at 25 °C. All spectra were recorded at −40 °C using cross polarization, magic angle spinning, and dipolar decoupling (CPMAS/DD).

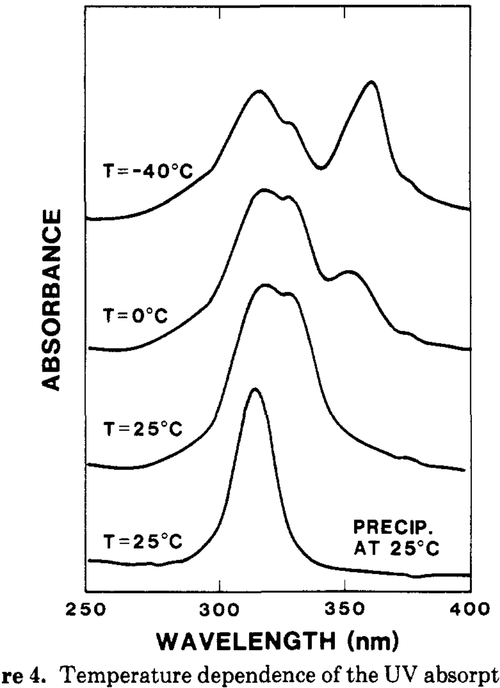

Figure 4. Temperature dependence of the UV absorption spectrum of PDBS, which had been precipitated from solution at −78 °C. The data show the complete disappearance of the band at 358 nm as the polymer is warmed. Even when the polymer has been warmed to 25 °C, the spectrum remains quite broad and has a shoulder around 332 nm, indicating residual disorder. The spectrum of PDBS precipitated at room temperature is shown as the bottom curve for comparison.

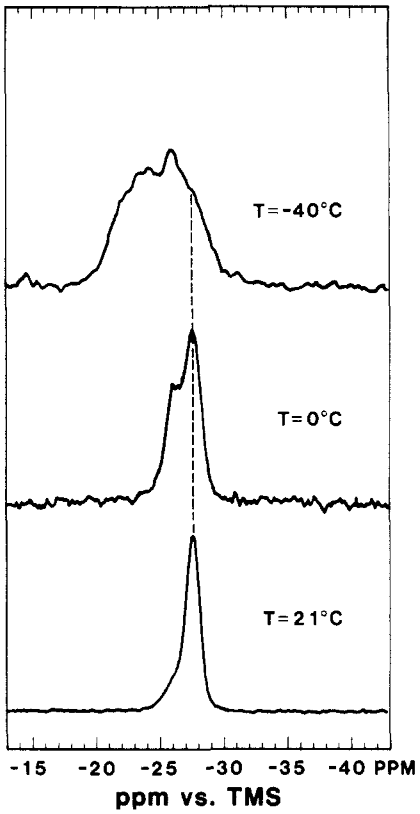

Figure 5. Temperature dependence of the CPMAS/DD ^{29}Si NMR spectrum of PDBS precipitated at −78 °C. As the polymer is heated, the downfield shoulder completely disappears, indicating the diappearance of the trans form of the polymer. (It should be noted that the chemical shifts in polysilylenes are extremely temperature dependent.[9] The reason for this effect is not clear; yet, the effect is completely reproducible. To illustrate best the relevant point of the disappearance of the downfield shoulder, we have compensated for the temperature effect in this figure.)

logue of the 7/3 helix, as indicated by the complete disappearance of the 358-nm band in the absorption spectrum and of the downfield shoulder in the ^{29}Si NMR spectrum. The disorder is evident in the broadening of the absorption spectrum and persistence of the shoulder near 332 nm even as the polymer is warmed to 25 °C. The absorption spectrum of PDBS precipitated at room temperature is shown as the bottom curve in Figure 4 for comparison.

Figure 6 shows temperature-dependent X-ray diffraction patterns of PDBS precipitated from solution at −78 °C. The data at −90 °C show that the major reflection at ~8° 2θ, which corresponds to the interchain spacing of the backbones,[9] is broadened substantially but not shifted. This implies that the interchain lattice is much more disordered but that the average intermolecular packing distances have not changed significantly. *Intra*molecular peaks for both the trans and the 7/3 helical conformations are expected at larger angles.[6,9] However, even though we examined the diffractograms at angles extending to 50° 2θ, there were no discernible peaks. This implies that the polymer obtained by this method is crystallographically very poorly ordered, so that although it must contain significant trans segments to cause the red shift in the absorption spectrum and the change in NMR chemical shift, these segments must be short and separated by disordered sequences. Moreover, these trans runs must not be effectively packed in registry, since no coherently diffracted X-ray intensity appears at the characteristic angles. The X-ray diffraction patterns also show the polymer converting to a *disordered* analogue of the 7/3 helix as the temperature is raised above 0 °C (see Figure 6). The conversion is indicated by the gradual sharpening

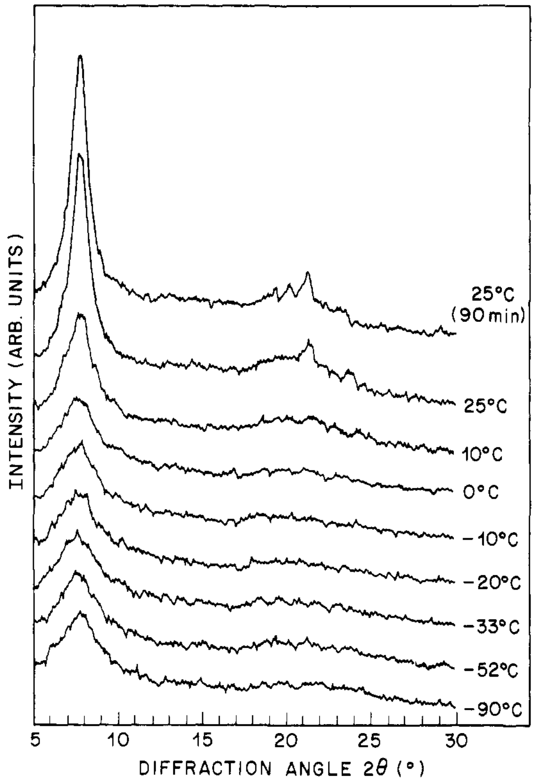

Figure 6. Temperature dependence of the X-ray diffraction pattern of PDBS, which has been precipitated from solution at −78 °C. All spectra recorded at temperatures ranging from −90 to 0 °C show a broadening of the major peak at 8° 2θ and no coherently diffracted intensity at larger angles (which would have been indicative of intramolecular order).

of the major peak at 8° 2θ and the appearance of peaks in the region of 19–22° 2θ, which are characteristic of the 7/3 helix.

Our demonstrated irreversible conversion of *trans*-PDBS to the 7/3 helical polymorph raises the question of the possible conformational motions involved. The exact structure of the PDBS chains in the 7/3 helical conformation is not known. However, a molecular axis projection of the 7/3 helix observed for PDPS [poly(di-*n*-pentylsilylene)] and calculated to be the lowest energy conformation for PDHS is given by Farmer et al.;[14] such a helix is reproduced in Figure 7a for PDBS. An alternative model that may be considered is drawn schematically in Figure 7b. Both models have the same central-core structure (i.e., Si backbones and Si–C_1 bonds); both also have their side chains in an extended (trans) conformation. Their difference lies simply in the relative dispositions of their side chains as determined solely by rotation about their Si–C_1 bonds.

This difference becomes apparent in parts a and b of Figure 8, which show a single Si–Si bond (with its attached side chains) for each of the two models. In both of these, exact trans arrangement of the side chains would lead to steric conflicts among (different) pairs of C_2 methylene groups, so that small rotations away from such a strictly trans arrangement are anticipated. Nevertheless, the similarity of the structure in Figure 8b to that of the all-trans backbone conformation (Figure 8a), as observed in PDHS, is evident. Therefore, conversion of trans sequences to a 7/3 helical conformation such as that of Figure 8b should require only small rotational movements. On the other hand, conversion to a structure such as that seen in Figure 8a would require (in addition to these motions) an approximately 180° rotation of each side chain about its Si–C_1 anchor to the backbone. Even though this appears much less favorable than the alternative of Figure 8b, no conclusions can be drawn about the true structure without full potential energy calculations for both conformations (which ideally should include interchain packing effects, as well). Farmer et al.[14] have reported energy calculations that find conformations similar to that of Figure 8b and several other arrangements to be about 4 kcal/mol higher in energy than the conformational arrangement shown in Figure 8a.

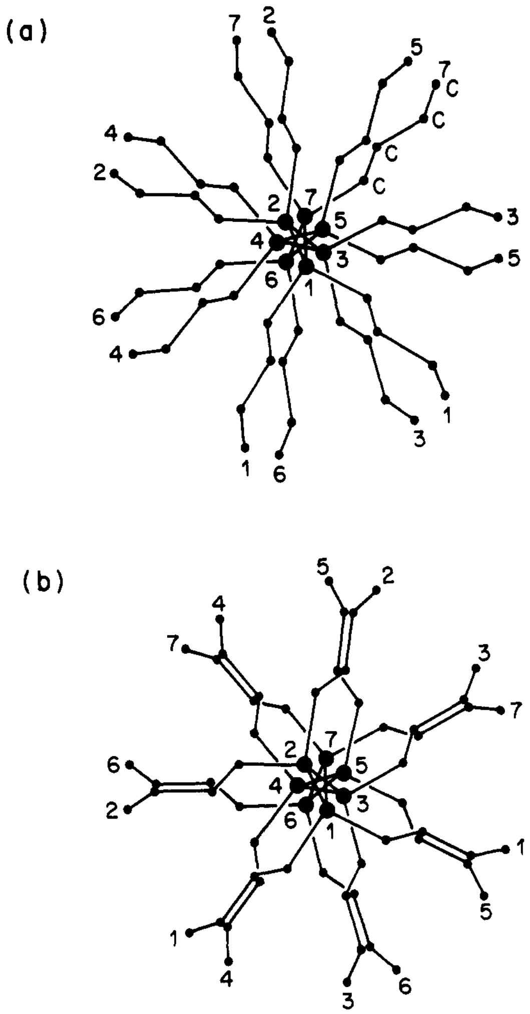

Figure 7. (a) Molecular axis projection for PDBS analogous to that proposed by Farmer et al.[14] to describe the 7/3 helical conformation observed for PDPS and calculated to be the lowest energy conformation for PDHS. (b) Alternative molecular axis projection for PDBS.

We have recently shown that a long-wavelength-absorbing (350-nm) conformation of PDBS can be made with the application of pressure.[15] X-ray diffraction patterns indicate that this form does possess highly increased crystallographic order.[15] In addition, it is more thermally stable than the low-temperature precipitated PDBS, which is probably due to the more highly ordered lattice present in the pressure-transformed PDBS. Further studies are in progress.

Conclusion

We have demonstrated here that a long-wavelength-absorbing form of PDBS in the solid state can be prepared by cooling a dilute solution of the polymer well below its thermochromic solution transition temperature and then holding the resulting precipitate at a temperature below −30 °C. By ^{29}Si NMR we have established that the polymer obtained by this method con-

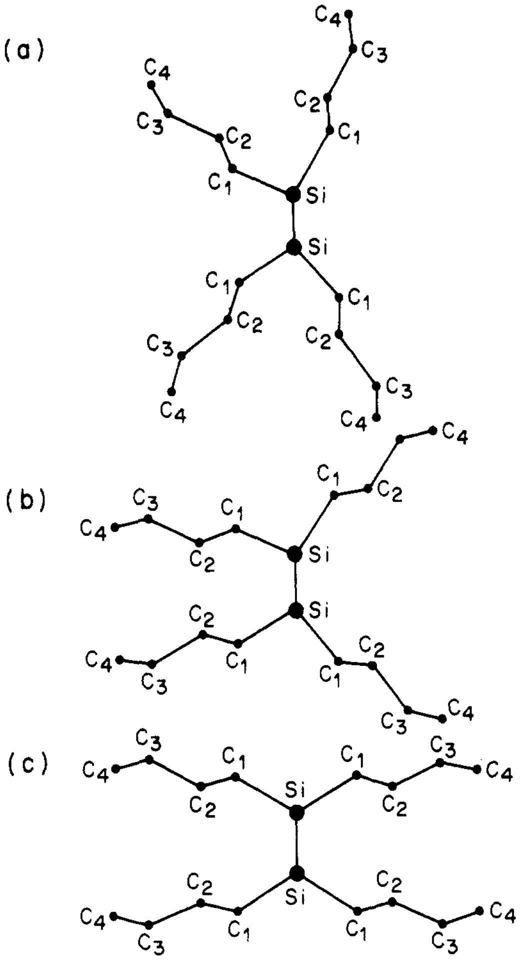

Figure 8. (a and b) A single Si–Si bond with attached side chains for the models of PDBS shown in parts a and b of Figure 7, respectively. (c) A single Si–Si bond for the all-trans backbone conformation of PDHS.

sists of a fairly broad distribution of chain conformations including trans, 7/3 helix, and disordered. On the basis of these data, we conclude that the chain conformation responsible for the new absorption band at 358 nm is substantially trans. X-ray diffraction of the polymer precipitated from cold solution shows that it is not packed in any crystallographically ordered manner. The trans conformation is not thermally stable, as UV absorption, NMR, and X-ray all show the polymer irreversibly converting to a disordered analogue of the 7/3 helix when the temperature is raised above 0 °C. The experiments presented here demonstrate that the chain conformation in polysilylenes is a complex function of its thermal history and the interactions between chains.

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