Solid-State Structures, Phase Transitions, and Thermochromism in Polysilylene Copolymers

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ABSTRACT: Building upon our previous results on silicon-based homopolymers, we have now synthesized and characterized copolymers of these novel materials. The copolymers poly(di-*n*-butylsilylene-*co*-di-*n*-pentylsilylene) (PB-*co*-PS) and poly(di-*n*-pentylsilylene-*co*-di-*n*-hexylsilylene) (PP-*co*-HS) were synthesized from solutions containing equal molar concentrations of the two respective monomers. The materials were examined by solution- and solid-state NMR, X-ray diffraction, DSC, and UV spectroscopy to obtain a description of the solid-state structures, phase transitions, and thermochromism of these copolymers. The conformational properties, crystal packing, and UV absorption characteristics of PB-*co*-PS are found to be the same as those of the two corresponding homopolymers poly(di-*n*-butylsilylene) (PDBS) and poly(di-*n*-pentylsilylene) (PDPS). In contrast, we find that while the silicon chain conformation of PP-*co*-HS (either a 7/3 or 9/4 helix) appears similar to that of the PDPS homopolymer, the UV absorption characteristics and the crystal packing differ from those of either of the corresponding homopolymers, PDPS and poly(di-*n*-hexylsilylene) (PDHS). The results of this study demonstrate that the properties of the polysilylene copolymers are complex and not directly predictable solely on the basis of the corresponding homopolymers.

Introduction

The very large number of recent publications relating to the polysilylenes (also named polysilanes) demonstrates the growing interest in this class of silicon-backbone polymers. However, only a few of these studies have considered copolymers of the di-*n*-alkylsilylenes.[1-7] We have previously reported the solid-state structures and properties of poly(dimethylsilylene-*co*-di-*n*-hexylsilylene) (PM-*co*-HS).[7] Both comonomers used to form PM-*co*-HS adopt an all-trans silicon bond conformation in their respective homopolymer. However, the electronic properties of these two homopolymers, as reflected in their UV absorption characteristics, differ significantly. We found that at room temperature PM-*co*-HS contains an ordered trans phase (phase I) corresponding to phase I of poly(di-*n*-hexylsilylene) (PDHS), but not one characteristic of that found in poly(dimethylsilylene) (PDMS). The UV absorption characteristics and thermochromic solid-state transition of phase I in PM-*co*-HS also are very similar to those of PDHS. The trans content and three-dimensional order in PM-*co*-HS are increased when the copolymer is cooled below room temperature. In addition, at temperatures of −10 to −40 °C the conformationally disordered phase II crystallizes partly into a new analogue of phase I (phase III) that has a much larger interchain spacing than either PDMS or PDHS.

We now describe two other types of copolymers: (1) poly(di-*n*-butylsilylene-*co*-di-*n*-pentylsilylene) (PB-*co*-PS), a copolymer for which both of the corresponding homopolymers adopt a 7/3 helical arrangement of their silicon backbones, and (2) poly(di-*n*-pentylsilylene-*co*-di-*n*-hexylsilylene) (PP-*co*-HS), a copolymer for which one of the corresponding homopolymers prefers a 7/3 helical conformation while the other adopts an all-trans structure. We have examined these materials by solution- and solid-state NMR, X-ray diffraction, DSC, and UV spectroscopy. We discuss here the solid-state structures, phase transitions, and thermochromism of these copolymers in relation to those of their parent homopolymers. We should note that throughout this discussion the stable, well-ordered structure of each polymer is designated phase I regardless of its specific chain conformation, and the conformationally disordered structure is named phase II.

Experimental Section

Synthesis of PB-*co*-PS and PP-*co*-HS. The poly(di-*n*-butylsilylene-*co*-di-*n*-pentylsilylene) (PB-*co*-PS) and the poly(di-*n*-pentylsilylene-*co*-di-*n*-hexylsilylene) (PP-*co*-HS) were obtained in a similar manner by polymerizing equal molar amounts of the two comonomers, except that the solvent system for polymerization was cyclohexane/xylene and benzene/xylene for PB-*co*-PS and PP-*co*-HS, respectively. The molecular weights, M_n and M_w, were 7×10^5 and 3×10^6, respectively, for PB-*co*-PS and 3.1×10^5 and 1.25×10^6, respectively, for PP-*co*-HS. All molecular weights were determined from size exclusion chromatography in THF flowing at 1 mL/min in an Ultrastyragel linear column and are referenced relative to low-polydispersity polystyrene standards.

Methods. NMR data were recorded on Varian XL-200 and Unity-400 spectrometers operating at carbon frequencies of 50.31 and 100.58 MHz, respectively, and silicon frequencies of 39.75 and 79.46 MHz, respectively. Polymer solutions were prepared at a concentration of 8% in toluene-d_8 with hexamethyldisiloxane (HMDS) as an internal reference. Solution-state spectra were recorded at +20 °C (PB-*co*-PS) and +80 °C (PP-*co*-HS). Solid-state NMR spectra were obtained using variable-temperature Doty Scientific, Inc., magic-angle spinning probes with zirconium rotors fitted with Vespel end caps. To minimize heating of the samples a spin rate of 2.5 kHz was employed. The ^{29}Si NMR spectra are referenced to the TMS scale by comparison to an external sample of PDHS (phase II signal set at −24.98 ppm, +23 °C). Spin–lattice relaxation times were measured with both the inversion–recovery and cross-polarization methods.

X-ray diffraction data were obtained in the reflection mode using Ni-filtered Cu Kα radiation at scanning rates of 0.25–2.0° 2θ/min. The sample materials were pressed into films by application of a spatula blade. The films were placed on an X-ray slide capable of being heated electrically or cooled below room temperature by passage of chilled and dried nitrogen gas. Temperature was measured by means of an attached thermocouple.

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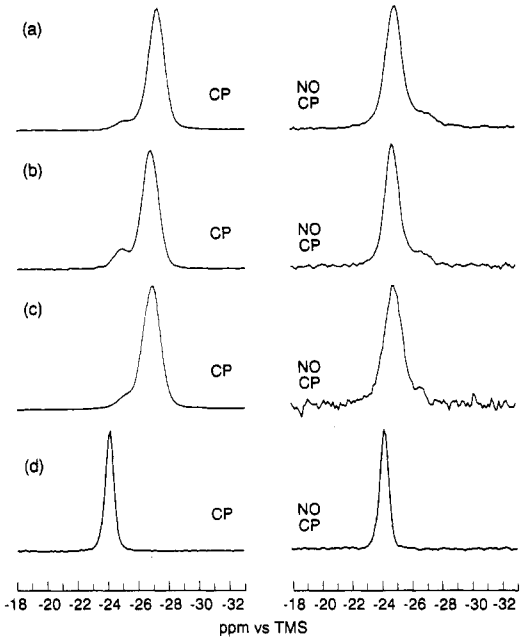

Figure 1. 39.75-MHz solid-state ^{29}Si NMR spectra recorded with and without cross-polarization (CP) at +22 °C for (a) PDPS, (b) PB-*co*-PS, and (c) PDBS and at +70 °C for (d) PB-*co*-PS.

UV absorption spectra were recorded on a Hewlett-Packard 8452 diode array UV–vis spectrophotometer. Variable-temperature spectra were obtained from thin films on quartz substrates by heating or cooling with dry nitrogen gas at the required temperature (the sample temperature was monitored by a thermocouple near the irradiated region). Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-4 at a heating rate of 10 °C/min under a dry helium atmosphere.

Results and Discussion

PB-*co*-PS. An analysis of the ^{13}C NMR spectrum of PB-*co*-PS in toluene solution indicates a di-*n*-butyl:di-*n*-pentyl comonomer ratio of 0.9:1.0. Because of the similarity of the alkyl side chains, the solution-state spectra do not provide information on the distribution of the two comonomer units along the polymer chain. However, since the reactivities of such similar monomers are not expected to differ significantly, it is expected that the comonomer sequencing will be random.

The room-temperature, solid-state ^{29}Si NMR spectra for the PB-*co*-PS copolymer and the poly(di-*n*-butylsilylene) (PDBS) and poly(di-*n*-pentylsilylene) (PDPS) homopolymers are shown in Figure 1a–c. The spin–lattice relaxation times for silicon nuclei in the highly ordered phases of the polysilylenes are very long (240–11400 s) compared to the much shorter relaxation times of nuclei in the disordered phases (5–10 s).[8] Recording spectra without cross-polarization (CP) permits us to selectively probe the motionally labile, conformationally disordered phase of each material by taking advantage of this difference in relaxation times. In contrast, the data obtained with CP represent the silicon nuclei in the well-ordered, near-static phase of each polymer. The silicon resonances at −27.0 ppm for PDBS and −27.3 ppm for PDPS (Figure 1, CP) are representative of the 7/3 helical structure.[8] The observation of a resonance at −26.9 ppm in the copolymer indicates that PB-*co*-PS has an ordered phase I structure in which the polymer chain adopts the same 7/3 helical arrangement as in the two homopolymers. Likewise the similarity in chemical shift (−25 ppm) for the resonances observed without CP demonstrates the same average bond conformation in the disordered phases of the three materials. These resonances also appear in the spectra recorded with CP but with much reduced intensity.

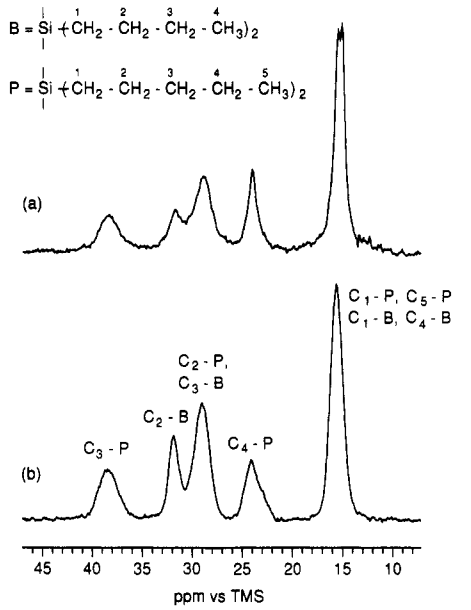

Figure 2. 50.31-MHz solid-state ^{13}C NMR spectra of PB-*co*-PS recorded at +24 °C (a) without CP and (b) with CP.

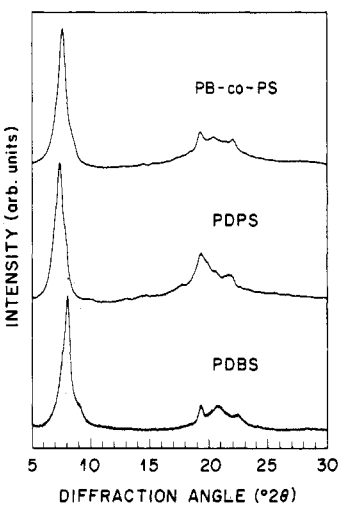

Figure 3. X-ray diffractograms of PB-*co*-PS, PDPS, and PDBS recorded at ambient temperature.

In the spectra of PB-*co*-PS recorded with and without CP at +70 °C (Figure 1d) only the resonance representative of the disordered phase is observed. This suggests a solid-state phase transition in which the ordered phase I structure is converted to the conformationally disordered phase II structure. Such a transition is known for both of the corresponding homopolymers.[8,9]

The solid-state ^{13}C NMR spectra of PB-*co*-PS at +24 °C are shown in Figure 2. The data recorded with and without CP exhibit resonances of the *n*-butyl and *n*-pentyl side chains that are broad and without resolved fine structure, similar to the data we have reported for PDBS and PDPS.[8] The side chains appear to have significant conformational disorder and local motion in all three polymers.

The X-ray diffraction patterns for PB-*co*-PS, PDPS, and PDBS are shown in Figure 3. The data for the two homopolymers have been interpreted as representing three-dimensionally ordered structures in which the silicon backbones adopt a 7/3 helical arrangement.[8,9] The major peaks at 7.4 and 8.0° 2θ in PDPS and PDBS, respectively, represent the interchain spacing (1.20 and 1.11 nm, respectively) of the helical chains in the ordered structure, while the peaks in the 19–23° 2θ region have strong intramolecular components. As seen in Figure 3, the diffraction pattern of the copolymer is nearly identical to

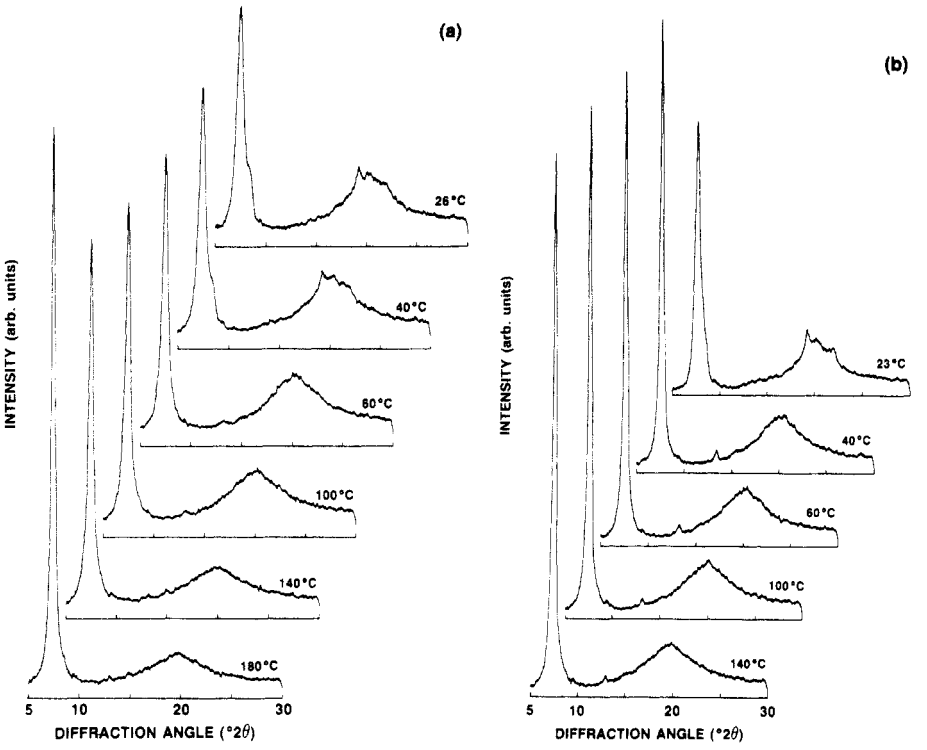

Figure 4. X-ray diffractograms of PB-*co*-PS recorded with a scanning rate of 2° 2θ/min upon (a) heating from +26 to +180 °C and (b) cooling back to +23 °C.

that of the homopolymers, demonstrating again that the copolymer contains the same ordered phase at room temperature as do the two parent homopolymers. The strong similarity in the patterns at 19–23 °C 2θ suggests closely analogous molecular conformations. Likewise, the peak position and line shape at 7.4–8.0° 2θ indicate that the interchain packing of the copolymer is very similar to that of the two homopolymers and that its spacing is intermediate, albeit closer to that of the bulkier constituent (PDPS).

The diffractograms obtained upon heating the sample of PB-*co*-PS to 180 °C are shown in Figure 4a. The data indicate a solid-state phase transition in PB-*co*-PS at ca. +60 °C, consistent with the ^{29}Si NMR data (Figure 1). Above this temperature the peaks in the 19–23° 2θ region are replaced with a broad background signal indicating randomization of the side chains and a change from the regular 7/3 helical conformation along the silicon backbone to a disordered conformational arrangement. However, even at +180 °C the intermolecular packing of the polymer chains is not randomized, as we previously have reported for PDBS at elevated temperatures.[8] As seen in Figure 4a, the interchain peak at 7.4 °C 2θ sharpens significantly, indicating that the silicon backbones are arranged on a hexagonal lattice similar to that of a columnar mesophase. The small peak observed at 13.1° 2θ is related to the major hexagonal peak by $\sqrt{3}$ and confirms the hexagonal packing. Upon cooling from +180 °C (Figure 4b) the diffractograms demonstrate that this solid-state phase transition in PB-*co*-PS is reversible. The conformationally disordered, hexagonally packed phase II structure survives cooling to ca. +40 °C, below which the 7/3 helical phase I is re-formed.

The solid-state UV absorption spectra of PB-*co*-PS are presented in Figure 5. A single band, similar in breadth and position (λ_{max} = 320 nm) to that of the PDBS homopolymer,[8] is observed at +23 °C. Upon heating to +180 °C the absorption band of the copolymer broadens and a slight red shift to 325 nm is observed, again similar to the absorption characteristics of PDBS. As in PDBS and PDPS there appears to be little correlation between

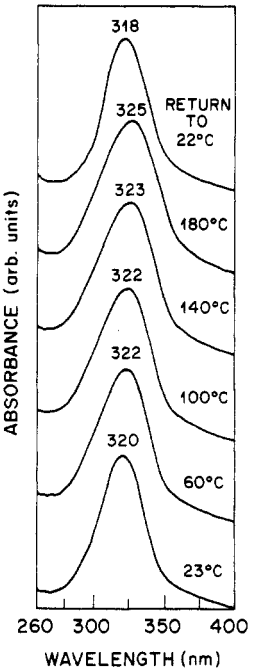

Figure 5. Solid-state UV absorption spectra of PB-*co*-PS on heating from +23 to +180 °C and after return to +22 °C.

the small changes in the absorption characteristics and the solid-state phase transition.

PP-*co*-HS. NMR. The ^{13}C NMR data for our sample of PP-*co*-HS in toluene indicate a 1:1 comonomer ratio. As was the case with PB-*co*-PS, the solution-state NMR data do not provide information on the comonomer sequencing because of the very close similarities of the two comonomer units. The variable-temperature, solid-state ^{29}Si NMR spectra recorded with CP for PP-*co*-HS are shown in Figure 6 (cooling–heating cycle, bottom to top). At +20 °C (bottom spectrum) only a single resonance at −25.0 ppm is observed. A similar spectrum is obtained when recording the data without CP. The resonance position observed is exactly that of the conformationally disordered phase II in PDPS[8] and PDHS[10] and remains

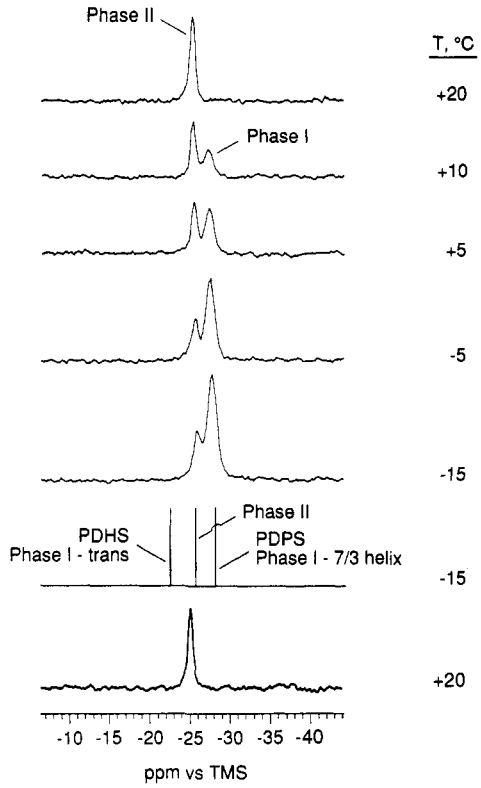

Figure 6. 79.46-MHz solid-state ^{29}Si NMR spectra of PP-*co*-HS recorded with cross-polarization on cooling from +20 °C (bottom spectrum) to −15 °C, followed by heating back to +20 °C (top spectrum).

unchanged during heating to +70 °C (not shown). However, as seen in Figure 6, after cooling the copolymer to −15 °C the resonance at −25 ppm in PP-*co*-HS is weakened in intensity and a new resonance appears at −27.7 ppm. The new peak cannot be observed in data accumulated without CP, demonstrating that the resonance represents silicon nuclei in a more motionally restricted environment than that of the nuclei in phase II. These spectra indicate a solid-state transition in which the phase II material is converted to an ordered structure that we shall call phase I of this copolymer.

In Figure 6 a stick spectrum is shown that illustrates the chemical shift positions at −15 °C for the silicon resonances in the all-trans arrangement of phase I in PDHS, in the 7/3 helical structure of phase I in PDPS, and in the conformationally disordered phase II of both homopolymers. Comparison of these data to that of PP-*co*-HS at −15 °C demonstrates that the resonance at −27.7 ppm in the copolymer is very close to the resonance of the 7/3 helix (−28.1 ppm) in PDPS at this temperature, the smaller resonance at −25.8 ppm in the copolymer spectrum is at the same chemical shift position as the phase II signal in the two homopolymers, and the copolymer data show no signal in the position of the resonance representing the trans structure of PDHS. These results strongly suggest that at low temperature PP-*co*-HS undergoes a phase transition that converts the conformationally disordered phase II to an ordered helical structure (phase I) similar in conformation to that of PDPS. A similar conclusion was previously reported for PP-*co*-HS synthesized under different conditions.[3,4] Due to the difference in the rate of CP for silicon nuclei in the two motionally dissimilar phases of PP-*co*-HS, it is not possible to determine the relative amounts of each phase from these solid-state NMR data. The data in Figure 6 demonstrate that the phase II → phase I solid-state transition is reversible upon heating from −15 °C back to +20 °C, where again only the resonance of phase II is observed. As the NMR data indicate, this

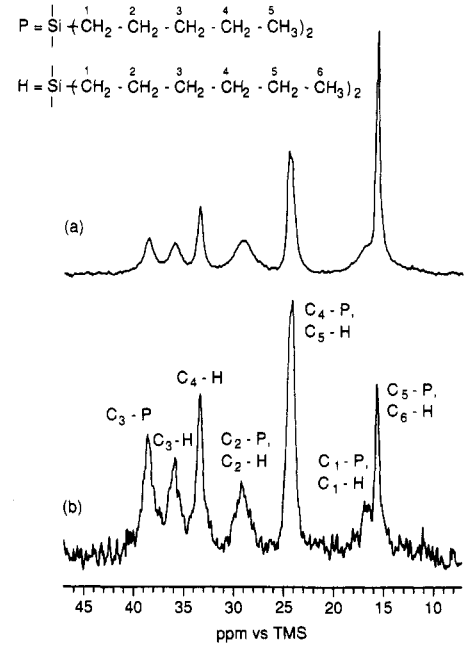

Figure 7. 50.31-MHz solid-state ^{13}C NMR spectra of PP-*co*-HS recorded at +24 °C (a) without CP and (b) with CP.

order–disorder transition occurs over a temperature range of at least 15 °C, significantly broader than the 2 °C range observed for PDHS[10] and the 9–10 °C range observed for PDBS and PDPS.[8]

The ^{29}Si NMR spin–lattice relaxation times, T_1, for the solid sample of PP-*co*-HS provide insight into the motional character of the phase I and phase II structures. At +20 °C we find the T_1 of the silicon nuclei in phase II to be 12.7 s, close to the value of 7.8 s for the phase II nuclei in PDPS.[8] In contrast, the value of T_1 for silicon nuclei in phase I of the copolymer at −40 °C is 112 s, indicating a significant decrease in local chain motion in phase I compared to phase II (T_1 of phase II = ca. 15–20 s at −40 °C). This reduction in the silicon relaxation time for phase I results from the higher degree of order in the conformationally fixed helical structure. However, while certainly more rigid than phase II, the phase I structure of the copolymer is more flexible than the phase I structures of either PDPS or PDHS as indicated by their silicon T_1 values of 240 and 11 400 s, respectively.[8] The increased mobility in phase I of the copolymer most likely results from the mismatch in the packing of the *n*-alkyl side chains that differ in length and perhaps also from a less rigid conformational structure. In addition, the suggestion of local order based upon the NMR data does not necessarily indicate a system with substantial three-dimensional order. NMR is essentially a probe of local motions and of order with a length scale of about 1–10 bonds.

The solid-state ^{13}C NMR spectra of the copolymer recorded at +24 °C (Figure 7) display well-resolved, symmetrical resonances for the carbon nuclei in the side chains. The resonances in the spectrum recorded under conditions of cross polarization (CP) are very weak compared to those observed in the data recorded without CP. This reflects the significant local motions present in the side chains of phase II. At −40 °C (data not shown) the data with CP are much enhanced in intensity compared to the data at +24 °C. Some of the signals broaden and overlap at the lower temperature but show no indication of side chain order such as that exhibited by the carbon resonances of the ordered side chains in PDHS.[10] The value of T_1 has also been measured for the carbon nuclei in the side chains of the PP-*co*-HS. We find the values to range from 0.4 to 1.7 s at +20 °C where only the phase

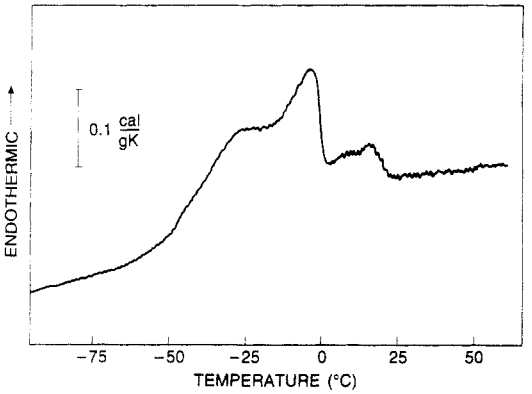

Figure 8. DSC thermogram of PP-*co*-HS.

II structure exists. At −40 °C the values range from 0.4 to 0.7 s, indicating considerable local chain motion in the side chains of both the disordered phase II and the ordered helical structure of phase I in PP-*co*-HS. Similar results were found for PDPS where significant local motions occur in the carbon side chains of both phase I and phase II. The values of the ^{13}C T_1's in PDPS range from 0.2 to 3.5 s in the pure phase II (+61 °C) and from 0.7 to 3.5 s when the sample is predominantly the 7/3 helical phase I (+23 °C).[8]

Thermal Properties. The thermal data for PP-*co*-HS as obtained by DSC are shown in Figure 8. A weak, composite endotherm is observed with a maximum at −3.5 °C and with a ΔH of 4.00 cal/g. We ascribe the composite endothermic process extending from ca. −40 to ca. +24 °C to the solid-state transition reflected in the ^{29}Si NMR data presented above. Unfortunately, the presence of multiple transitions complicates the thermal analysis. The endothermic process is clearly a composite of a number of weaker peaks, and all of these endotherms are reproducible both among different samples and in subsequent scans. They may represent different stages of the transition or transformation of different blocks in the copolymer. The total enthalpy of the composite endotherm is nearly twice that found for PDPS (2.6 cal/g)[8] but only about one-fourth that reported for PDHS (20.0 cal/g).[11] The lower value of ΔH reflects a lesser degree of order in the packing of the side chains in the copolymer and a less rigid conformational structure as compared to the PDHS homopolymer sample, consistent with our NMR and X-ray diffraction results (the latter described immediately below).

X-ray Diffraction. The X-ray diffraction pattern of PP-*co*-HS at room temperature is presented in Figure 9 together with the diffraction data for the following: (1) the conformationally disordered phase II of PDHS (recorded at +60 °C), (2) the all-trans phase I of PDHS formed by cooling from +200 °C after annealing at that temperature for 10 min, and (3) the 7/3 helical phase I of PDPS. A comparison of the diffraction patterns demonstrates that at room temperature the copolymer does not contain a three-dimensionally ordered phase as do the PDPS or PDHS homopolymers. The strong similarity between the data from the copolymer and from phase II of PDHS confirms that the chains are conformationally disordered but with significant intermolecular order. As we described previously,[12] the disordered chains are packed on a hexagonal lattice (with a for the copolymer = 1.50 nm) in a manner similar to that of a columnar mesophase. This is consistent with the NMR data presented above.

The X-ray diffractograms recorded upon heating of the PP-*co*-HS sample from +26 to 180 °C (Figure 10) exhibit no change in the broad, amorphous-like background signal in the 19–22° 2θ region. However, the peak at 6.8° 2θ does narrow very substantially, indicating an increase in the columnar intermolecular order. A similar change in the

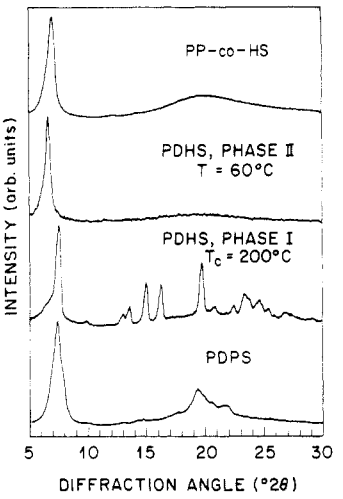

Figure 9. X-ray diffractograms of PP-*co*-HS; PDHS, phase II; PDHS, phase I; and PDPS recorded at room temperature unless otherwise indicated; T_c indicates crystallization by cooling from +200 °C.

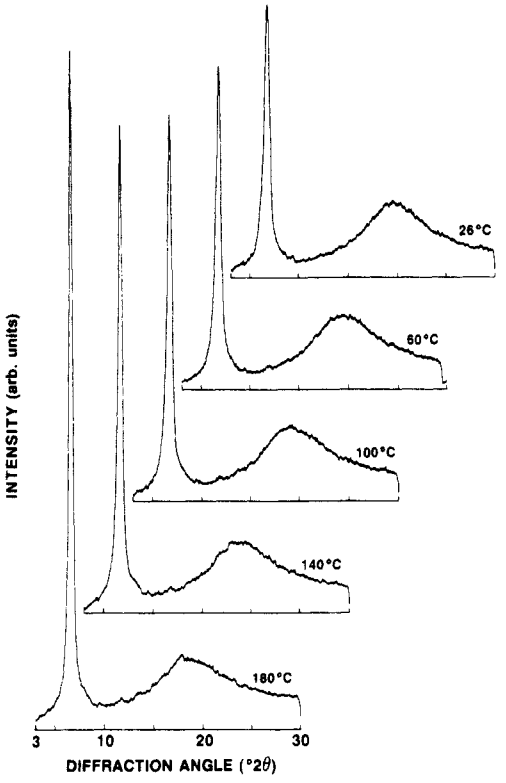

Figure 10. X-ray diffractograms of PP-*co*-HS recorded on heating from +26 to +180 °C.

phase II structure at high temperatures was observed in PDHS[12] and to a lesser extent in PDBS.[8] Upon cooling back to room temperature the recorded diffraction patterns change little with only a slight broadening of the peak at 6.8° 2θ.

More important changes in the X-ray data are observed upon cooling the PP-*co*-HS sample from +25 to −41 °C as shown in Figure 11. Below ca. −5 °C two shoulders appear on the large intermolecular peak at 6.8° 2θ (specifically these are at 6.6 and 7.4° 2θ at −22 °C). The appearance of two additional peaks (on the low- and high-angle sides of the main interchain peak) is exactly analogous to what we reported earlier for PDBS and PDPS (see Figures 6 and 8 of ref 8), has not been seen in the other polysilylenes examined, and may therefore be taken as a characteristic indication of the packing of helices similar to the 7/3 in these polysilylene molecules. In addition, as the temperature is lowered, a large number of extremely weak

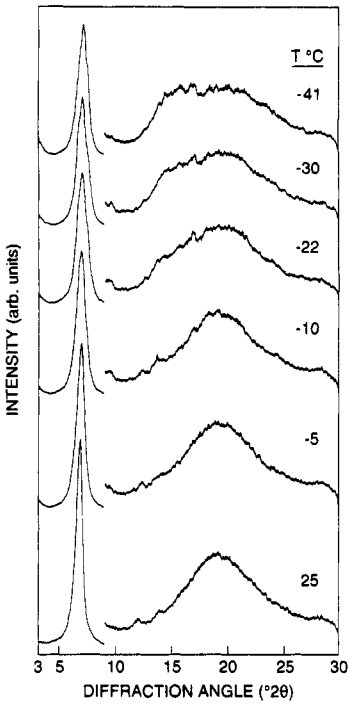

Figure 11. X-ray diffractograms of PP-*co*-HS recorded on cooling from +25 to −41 °C.

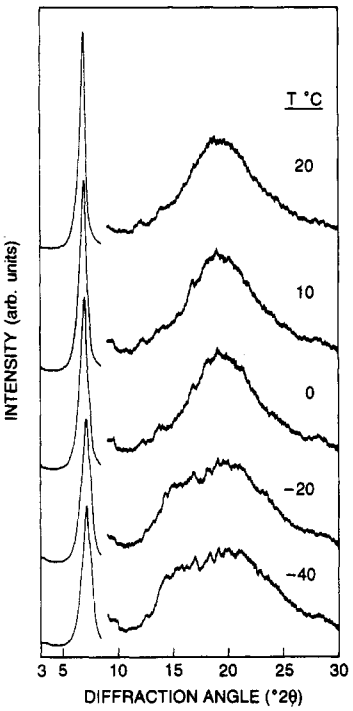

Figure 12. X-ray diffractograms of PP-*co*-HS recorded on heating from −40 to +20 °C.

peaks appear in the region of 9–24° 2θ. We have observed[13] the same peaks much more clearly resolved in a sample from a different source (that used for refs 3 and 4). Upon heating back to +25 °C, the diffractograms, as shown in Figure 12, indicate a transition occurring between ca. −20 and +20 °C in which the helical structure reverts back to the conformationally disordered state. These indications of a reversible, low-temperature transition in the copolymer structure are consistent with the NMR and thermal data described above. The very weak intensity of the new peaks that appear in the diffraction pattern of PP-*co*-HS below −5 °C suggests that this sample contains only limited three-dimensional order. The position of the major intermolecular reflection of PP-*co*-HS (at ca. 7.2° 2θ at −41 °C) demonstrates that the *d*-spacing between silicon chains is

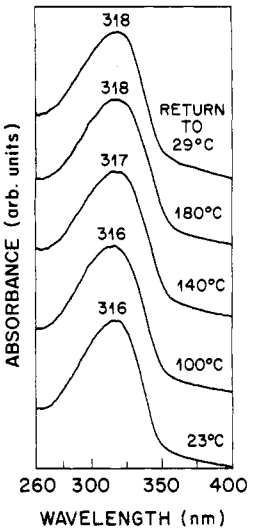

Figure 13. Solid-state UV absorption spectra of PP-*co*-HS recorded on heating from +23 to +180 °C and after return to +29 °C.

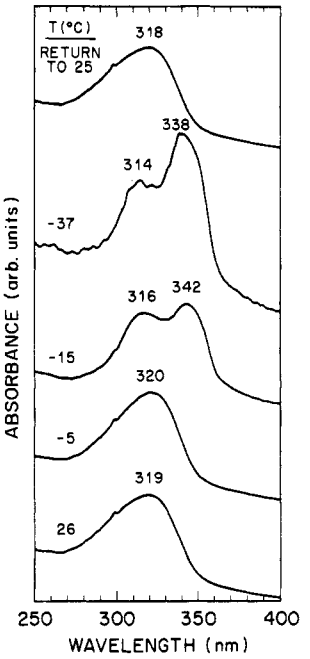

Figure 14. Solid-state UV absorption spectra of PP-*co*-HS recorded on cooling from +26 to −37 °C and after return to +25 °C (small glitch at ca. 300 nm is an instrumental artifact).

similar to that of the PDPS homopolymer at room temperature (Figure 9). However, the new peaks at larger angles (9.5, 14, and 17° 2θ) are not congruent with the peaks in the diffraction pattern of either the trans structure of PDHS or the 7/3 helical structure of PDPS (Figure 9). These weak reflections indicate an intermolecular packing arrangement in the copolymer different from that of PDPS despite the apparent similarity in the chain conformation. Because of the weakness of the reflections and the inability to obtain macroscopic orientation of the material (and fiber-pattern analysis), we are not yet able to describe fully the three-dimensional structure of PP-*co*-HS.

UV Absorption Characteristics. We have recorded the variable-temperature UV absorption spectra for PP-*co*-HS, which are shown in Figures 13 and 14. At room temperature a broad band with λ_{max} at 316 nm is observed (Figure 13). Upon heating to +180 °C, the spectra remain virtually unchanged. However, as seen in Figure 14, significant changes do occur upon cooling. At temperatures below −5 °C a blue shift of several nanometers is observed for the main absorption band and a new band

with a λ_{max} of ca. 342 nm appears and intensifies with decreasing temperature, consistent with the changes observed in the X-ray diffraction data. The reversibility of this transition is demonstrated in the UV spectrum recorded after returning to +25 °C. Such a thermochromic shift in the UV absorption is also observed in PDHS but the transition is more dramatic (λ_{max} change from 317 to 374 nm).[14]

The most intriguing aspect of the UV data for PP-*co*-HS is that the absorption band associated with the formation of the helical structure at low temperature (λ_{max} = 340 nm) differs substantially from the absorption band found for the helical structure in PDPS homopolymer (λ_{max} = 313 nm).[8] To date, PP-*co*-HS is the only material in which a silicon backbone structure in a presumed helical arrangement shows an absorption peak beyond 320 nm. In fact, the only nontrans structure reported to have an absorption peak beyond 320 nm is the tgtg′ conformation found in poly(di-*n*-tetradecylsilylene) (PDTDS).[15,16] The ^{29}Si chemical shift for this material[17] is −21.7 ppm at −13 °C compared to the chemical shift of −27.7 ppm for PP-*co*-HS (see Figure 6). Therefore a tgtg′ conformation for the PP-*co*-HS polymer would not be consistent with the NMR evidence.

The association of the 340-nm absorption band with a helical structure is so unexpected that we have decided to consider any other conceivable interpretation of our results. The available X-ray diffraction data do not provide an unambiguous assignment of chain conformation but do indicate that the intermolecular packing of PP-*co*-HS is similar to that of the 7/3 helical chains of PDPS. The assignment of a helical conformation to the copolymer is based primarily on the NMR results. It is important to remember that the silicon NMR chemical shift does not in itself provide a specific identification of the silicon bond conformation. The association of a specific silicon chemical shift with a specific chain conformation is made on the basis of comparisons of systems with known conformational structures. For example, at room temperature the chain conformation of PDHS was identified by X-ray and electron diffraction techniques to be all-trans.[12] Therefore the chemical shift at −21.5 ppm for the silicon nuclei in the trans phase of PDHS is taken as a marker of the trans conformation.[10] Similarly, at room temperature the chemical shift at −27 ppm observed for the silicon nuclei in PDBS and PDPS is associated with the 7/3 helical structure identified for these materials.[8] The chemical shift difference of 5.5 ppm for the nuclei in the trans and 7.3 helical arrangements reflects the conformational differences as indicated in the Newman projections of Figure 15a. This sensitivity of the chemical shift to chain conformation is well-known.[18] Differences in the chemical shift reflect changes in the conformational arrangement between a silicon nucleus and its γ-substituent three bonds removed.

As stated above, the similarity in chemical shifts for the PDPS homopolymer and the PP-*co*-HS copolymer is interpreted as an indication of a similarity in chain conformation. However, there are two other possible chain conformations that would be expected to produce a silicon chemical shift similar to that of the 7/3 helix. We can understand how different conformations can result in the same chemical shift by examining the trans and gauche main-chain conformations. As indicated in the Newman projections of Figure 15b, both the trans and the gauche conformations are staggered. The observed silicon (marked with an asterisk) is γ-gauche to two carbons three bonds removed in the trans structure and gauche to one carbon and one silicon in the gauche arrangement. Considering both directions in an all-trans chain, the silicon nucleus

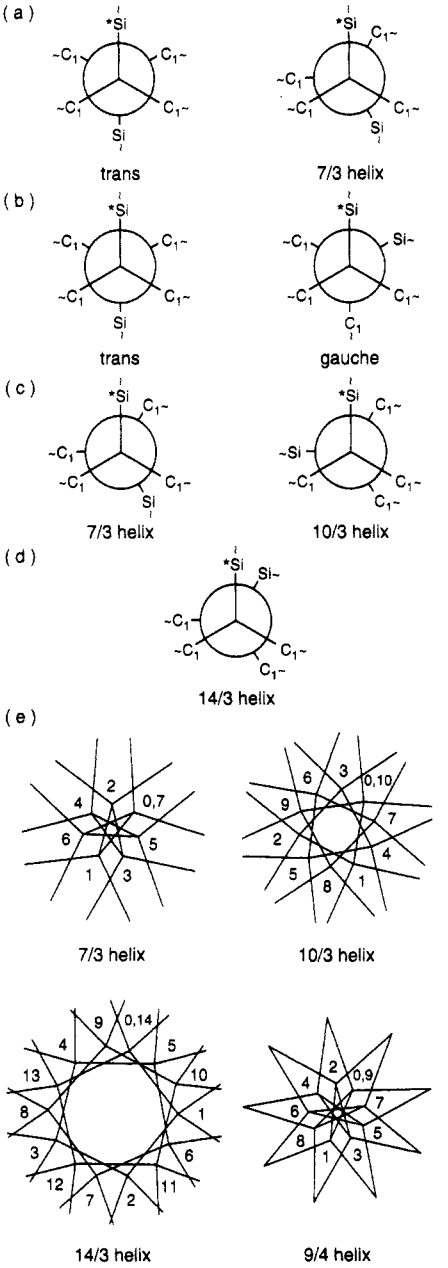

Figure 15. Newman projections of silicon chain conformations (a–d) and projections along the chain axis (e) for some possible helical structures in PP-*co*-HS.

sees a total of four γ–gauche interactions with carbon nuclei. The silicon nucleus in a tgtg′ chain sees a trans arrangement in one direction along the chain and a gauche arrangement in the opposite direction (g and g′ are equivalent) for a total of three carbon and one silicon γ-gauche interactions. At room temperature the silicon chemical shifts[10,17] of the trans structure of PDHS and the tgtg′ structure of PDTDS are −21.5 and −21.4 ppm, respectively. The nearly identical chemical shift data for the two chain conformations indicate that there is little or no difference in the γ–gauche interaction between two silicon nuclei and the interaction between a silicon nucleus and a carbon nucleus.

This leads us to consider conformations other than the 7/3 helix that could yield the same chemical shift as the 7/3 helical structure. Newman projections for these helices are presented in Figure 15c,d. Because of the similarity of the carbon and silicon γ-gauche effects as described above, the three-bond interactions for the observed silicon (*Si) are identical in the 7/3, 10/3, and 14/3 helices. Therefore, considering only conformational effects, we

should expect identical chemical shifts for these three structures.

Are any of these proposed helices reasonable structures for the polysilylene materials? Energy calculations reported for the polysilylenes have not indicated the 90° torsion angle (10/3 helix) or the 30° torsion angle (14/3 helix) as low-energy arrangements.[19-22] The drawings in Figure 15e show the positions of the silicon backbone and of the first side chain carbon for each helical structure projected along the chain axis. Since the 14/3 helix is only 30° from eclipsing of the backbone silicon atoms, the resultant structure is a highly strained arrangement not far from a closed pentagon that dramatically collapses the helix along its chain axis. Both the 10/3 and the 14/3 helices contain voids in the center of the structure greater than that found in the 7/3 helix, making it unlikely that the polysilylenes would adopt such a structure. Furthermore, the diameters of the 10/3 and of the 14/3 helices are larger than that of the 7/3 helix by 5 and 23%, respectively. Unless the side chains were to adopt some entirely unexpected compensatory packing arrangements, this would result in a larger spacing between the silicon backbones compared to the 7/3 helix. Therefore, while we cannot entirely rule out the possibility of the 10/3 or 14/3 helical structures on the basis of the NMR data, we find that these are not consistent with our X-ray results and published energy calculations.

The most recent energy calculations[22] for isolated chains of PDHS demonstrate that the global energy minimum is at a backbone torsion angle of 162 ± 10°. In addition, a relatively small local maximum separates the global minimum from a local energy minimum that exists in the torsion angle region of 180 ± 30 °. This region of low energy is then bounded by two high-energy barriers. Thus, a region of low-energy torsion angles exists that includes the all-trans structure, the 7/3 helix, and a 9/4 helix. The torsion angle of the 9/4 helix is 155°, close to the 149° angle of the 7/3 helix, and thus it may be difficult to differentiate between these two helices by NMR. As seen in Figure 15e, the diameter and the center void of the 9/4 and 7/3 helices are nearly identical and should produce similar X-ray diffraction powder patterns. The fiber-pattern analysis of an oriented sample of the copolymer would provide an unambiguous identification of the helix. Unfortunately, the copolymer is very soft and does not orient macroscopically. Even in attempts to orient ultrathin films of the copolymer on flexible substrates for electron diffraction, we found the material fractures easily.

Since the torsion angle of the 9/4 helix is closer to trans than is the torsion angle of the 7/3 helix (155 vs 149°), the UV absorption of the 9/4 helix should be shifted slightly from that of the 7/3 helix in the direction of the absorption observed for the all-trans structure. As stated above, the value of λ_{max} for the PDPS-*co*-PDHS material (340 nm) lies between the values of λ_{max} for the 7/3 helix of the PDPS homopolymer (313 nm) and the all-trans structure of the PDHS homopolymer (374 nm). This leads us to conclude that of the known structures adopted by the polysilylenes and those proposed above only the 7/3 helix and the 9/4 helix are consistent with our NMR and X-ray data and published energy calculations. The difference in absorption peaks between the helical structures of PDPS and PP-*co*-HS suggests that additional factors (e.g., bond-angle distortions, packing effects, or other absorbing species) may play an important role in establishing the electronic properties of this material.

Conclusions

The conformational properties and absorption characteristics of PB-*co*-PS are found to be the same as those reported for the two corresponding homopolymers, PDBS and PDPS. Upon heating, the copolymer undergoes a solid-state disordering transition at ca. +60 °C, slightly below the temperature at which similar transitions are observed in PDPS (+70 °C) and PDBS (+87 °C).[8] In contrast, the conformational properties and absorption characteristics of the 1:1 copolymer PP-*co*-HS do not parallel those of either the PDPS or PDHS homopolymers. At room temperature PP-*co*-HS contains only a conformationally disordered phase II molecular structure that is arranged hexagonally in a columnar-like manner. Upon cooling below ca. −5 °C, ^{29}Si NMR and X-ray data show that an ordered phase develops in which the chains apparently adopt a 7/3 or 9/4 helical conformation (based primarily upon ^{29}Si NMR evidence). However, the crystal packing in this phase I structure is more complex than that of PDPS. In addition, the UV absorption characteristics (λ_{max} = 340 nm) of the ordered phase in the copolymer differ significantly from those of PDPS (λ_{max} = 313 nm), which suggests that there is not a 1:1 correlation between the backbone conformation and the electronic properties as may have been assumed for these polysilylenes.

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