Characterization of the Structures and Properties of Poly(dimethylsilylene-*co*-di-*n*-hexylsilylene)

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ABSTRACT: In this report we describe the structures and properties of poly(dimethylsilylene-*co*-di-*n*-hexylsilylene) (PM-*co*-HS), as determined by solution- and solid-state NMR, X-ray diffraction, DSC, and UV spectroscopy. A comparison is made between the structures and properties of the copolymer and those of the homopolymers, poly(dimethylsilylene) (PDMS) and poly(di-*n*-hexylsilylene) (PDHS), formed from each of the comonomers. While the two homopolymers adopt the same chain conformation in the solid state, they differ significantly in their absorption characteristics and in the nature of their solid-state transitions. At room temperature PM-*co*-HS is found to be mostly disordered with a small amount of a well-ordered crystalline phase in which the silicon backbone adopts an all-trans conformational arrangement as is observed for the PDHS homopolymer. The copolymer does not contain any ordered region similar to that of the PDMS homopolymer. Upon cooling of PM-*co*-HS, there is a slight increase in the PDHS-like structure, and between −10 and −20 °C the conformationally disordered phase partly crystallizes into a trans-like structure with a much larger intersilicon-backbone spacing than either PDMS or PDHS. The absorption characteristics of the copolymer and PDHS are similar, and, upon heating above 42 °C, the copolymer exhibits the same solid-state transition observed in PDHS.

Introduction

Recent papers have described the structure and properties of many of the symmetrically substituted poly(di-*n*-alkylsilylenes).[1-10] Of particular interest in these materials has been the relationship between the silicon bond conformation and the electronic properties of the polymers. In addition, several of these homopolymers exhibit strong thermochromic[1,7] and piezochromic[10,11] behavior. The electronic and photochemical properties of these polymers are summarized in a recent paper.[12] The synthesis and solution characterization of several copolymer systems containing *asymmetrically* substituted monomers have been reported,[13-20] but only recently have copolymers formed from two *symmetrically* substituted monomers been examined.[21-24] Since the solid-state structures and properties of the symmetrically substituted polysilylene homopolymers can differ significantly despite strong similarities in molecular structure, the corresponding characteristics of their copolymers cannot be predicted a priori. In this paper we report the characterization of poly(dimethylsilylene-*co*-di-*n*-hexylsilylene) (PM-*co*-HS) by solution- and solid-state NMR, X-ray diffraction, DSC, and UV spectroscopy. This copolymer is of particular interest in that while both of the comonomers adopt an all-trans silicon bond conformation in their respective homopolymers,[3,4,9] the electronic properties of the homopolymers, as reflected in their UV absorption characteristics, differ significantly.[5,9] Additional reasons for our interest are that poly(dimethylsilylene) (PDMS) is the lowest homologue of this family and its methyl side chains have no conformational degrees of freedom to influence the structure of the Si backbone; this is in contrast to poly(di-*n*-hexylsilylene) (PDHS), where the long side chains have been shown to play a dominant role.[3,5] In this discussion we will contrast the chain conformation and the absorption characteristics of PM-*co*-HS with the structure and properties of the PDMS and PDHS homopolymers.

Experimental Section

Synthesis of PM-*co*-HS. To an oven-dried, N_2-purged three-necked flask equipped with a gas inlet, condenser, magnetic stirrer, and inlet from a syringe pump was added 20 g (74.3 mmol) of freshly fractionated di-*n*-hexyldichlorosilane and 9.59 g (74.3 mmol) of dimethyldichlorosilane (purified by fractionation from a small amount of diethyl ether to remove trace quantities of methyltrichlorosilane). Dry toluene (90 mL) and dry heptanes (10 mL) were then added, and the resulting solution was heated to brisk reflux. A mineral spirits dispersion of Na (18.78 g of 40% by weight dispersion, 327 mg·atom) was added via a syringe pump at a rate of 200 mequiv/min. Upon completion of the Na addition, the resulting mixture was refluxed for an additional 90 min and then allowed to cool to room temperature. The reaction mixture was then quenched by addition of methanol followed by a large excess of saturated aqueous $NaHCO_3$ solution. After centrifugation to aid in separation of the organic phase from the aqueous phase, the layers were separated and the organic phase was filtered through diatomaceous earth to remove insoluble polymer. The solvent was removed from the resulting clear solution and 10 volumes of ethyl acetate added to the viscous residue to precipitate the crude product. This was redissolved in toluene and reprecipitated with ethyl acetate and then redissolved again in tetrahydrofuran and reprecipitated again with methanol, with removal by filtration each time of small amounts of polymer which could not be induced to redissolve. Finally, the polymer was redissolved in toluene and 15% by volume of acetone added to fractionate the high molecular weight material from the lower molecular weight polymer and other contaminants. After decantation of the solvent, the precipitated polymer was redissolved again in tetrahydrofuran and precipitated again with methanol to give, after drying, 0.73 g (3.8%) of the pure, white, flocculent title polymer having a monomodal molecular weight distribution of M_w = 813 000 (from size-exclusion chromatography standardized with polystyrene).

Methods. NMR data were recorded on a Varian Unity-400 spectrometer operating at carbon and silicon frequencies of 100.58 and 79.46 MHz, respectively. Solution samples were prepared at a concentration of 5% in toluene-d_8, and spectra were referenced to internal hexamethyldisiloxane (HMDS). Between 500 and 2000 scans were recorded for each sample. In order to obtain quantitative data, the spin–lattice relaxation times for

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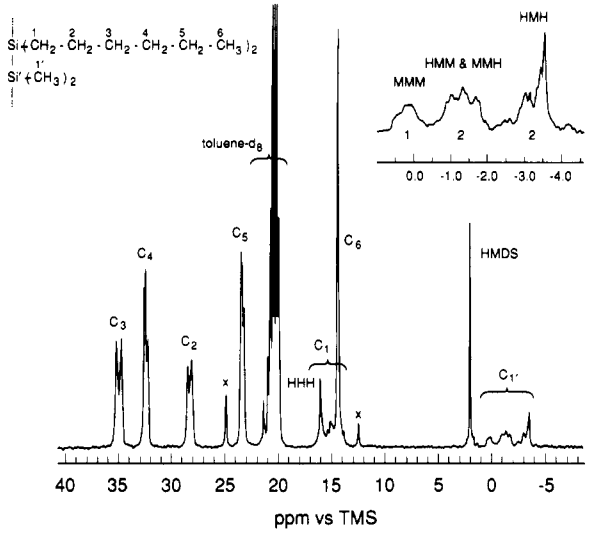

Figure 1. 100.58-MHz ^{13}C NMR spectrum of PM-*co*-HS in toluene-d_8 recorded at 22 °C. The expansion contains the resonances of $C_{1'}$; × indicate solvent impurities.

the carbon and silicon nuclei were recorded for each polymer solution.

The solid-state NMR spectra were obtained using a variable-temperature Doty Scientific magic angle spinning probe with Al_2O_3 and zirconium rotors fitted with vespel end caps. Sample spinning at a rate of 6 kHz and a decoupling field of 55 kHz were employed. Between 100 and 200 scans were accumulated for each spectrum. The silicon NMR spectra are referenced to the phase II (conformationally disordered) resonance of PDHS at −24.98 ppm (+23 °C).[4]

The copolymer was examined by X-ray diffraction in the reflection mode using Ni-filtered Cu Kα radiation. The tacky PM-*co*-HS was easily pressed into a film by application of light pressure with a spatula blade. The film was placed on an X-ray slide capable of being heated electrically or cooled below room temperature by the passage of chilled nitrogen gas. The slide was calibrated with melting-point standards to ±1 °C. X-ray diffractometry at 2° 2θ/min was used to follow the change in crystal structure as a function of temperature. The room-temperature diffraction data of the PM-*co*-HS film and the PDHS powder sample were recorded at 0.5° 2θ/min.

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 at the required temperature (the sample temperature was being 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-nitrogen atmosphere. Variable-temperature solution UV data were recorded on a spectrofluorimeter previously described.[25]

Results and Discussion

Copolymer Microstructure. The ^{13}C solution NMR spectrum of PM-*co*-HS is shown in Figure 1. The assignment of the resonances is based on a comparison with the data for the two homopolymers, PDMS and PDHS.[4] The splittings observed in most of the resonances reflect the distribution of comonomers along the copolymer chain. This chemical shift dispersion results from variations in the silicon bond conformation and changes in the valence angles. The latter reflect the large difference in the steric size of the methyl and *n*-hexyl substituents. The dimethyl centered sequences can be observed in the data of $C_{1'}$ shown in the expansion of Figure 1. The resonances are clearly resolved at the triad level, and each triad signal shows a sensitivity to pentad and possibly heptad sequences. The MMM triad assignment is made by comparison to the chemical shift (−0.6 ppm in the solid

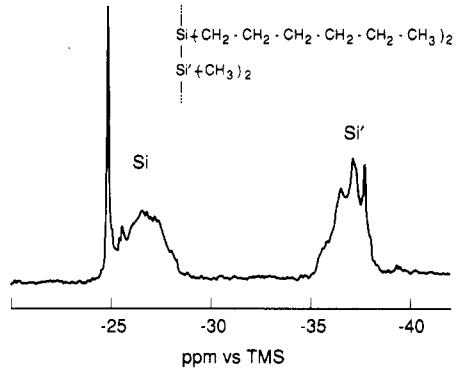

Figure 2. 79.46-MHz ^{29}Si NMR spectrum of PM-*co*-HS in toluene-d_8 recorded at 22 °C.

state) of the methyl carbon in PDMS. The triad centered at −1.4 ppm is assigned to dimethyl units with one di-*n*-hexyl neighbor (HMM and MMH) and the triad at −3.3 ppm is assigned to the dimethyl units with di-*n*-hexyl units on either side (HMH). These assignments assume that the presence of neighboring di-*n*-hexyl units produces an additive upfield shift in the resonance position for the carbon in the dimethyl unit. Integration of the triad peaks of $C_{1'}$ indicates a ratio of 1:2:2 for MMM/HMM&MMH/HMH compared to an expected ratio of 1:2:1 for a completely random polymerization of comonomers in equal molar concentrations that have identical reactivities. These data indicate a tendency toward an alternating copolymer structure. However, it should be remembered that we are examining only the soluble portion of the polymer produced in the PM-*co*-HS synthesis (see Experimental Section).

The C_1 carbon of the di-*n*-hexyl units is also sensitive to comonomer sequences (Figure 1). The assignment of the HHH triad sequence can be made by comparison to the PDHS data.[4] Unfortunately, the overlap of the triad resonances of C_1 with the strong singlet of C_6 prohibits a quantitative measure of the peaks. However, it is clear from the strong intensity of the HHH resonance that the triad distribution is not random.

The different comonomer sequences are also reflected in the ^{29}Si NMR data shown in Figure 2. The silicon nuclei of both the dimethyl comonomer units and the di-*n*-hexyl units produce resonances over a range of ca. 3 ppm. Integration of the two signals indicates a di-*n*-hexyl/dimethyl comonomer ratio of 54:46. By comparison to the data of the PDHS homopolymer,[4] the sharp signal at −24.85 ppm can be assigned to long (>5) sequences of the di-*n*-hexyl units. Integration of this resonance indicates that these sequences of the di-*n*-hexyl comonomer represent ca. 13 mol % of the di-*n*-hexyl portion of the sample and 7 mol % of the total copolymer sample.

This carbon and silicon NMR analysis of the microstructure demonstrates that the distribution of the two monomer units in the soluble fraction of PM-*co*-HS does not appear random. There are indications of both a tendency toward alternating units and the formation of long runs of the di-*n*-hexyl unit. Nonrandom comonomer sequencing has been previously reported in the synthesis of this copolymer.[23,24] These observations are not unexpected since the reactivities of the two monomers probably differ and the propagation step in the polymerization of PDMS is thought to be very fast.[26] We note again that our sample characterized by NMR is only the soluble portion from the PM-*co*-HS synthesis and is not representative of the polymer fraction of the reaction product. The insoluble portion not examined is most probably rich in the dimethylsilyene units.

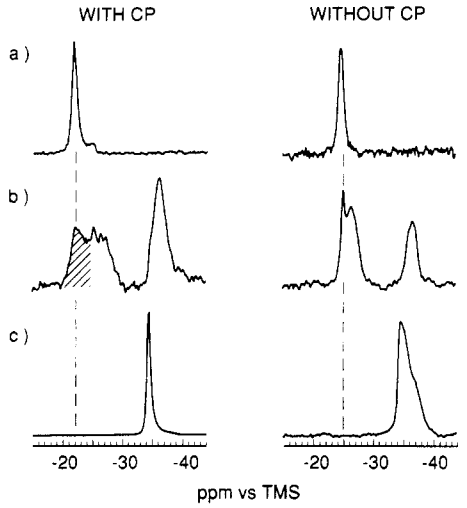

Figure 3. 79.46-MHz solid-state ^{29}Si NMR spectra recorded with and without cross-polarization (CP) at 22 °C for (a) PDHS, (b) PM-*co*-HS, and (c) PDMS.

Solid-State Structures. PDHS has been characterized as containing at room temperature predominantly a three-dimensionally ordered phase I structure (all-trans) and a smaller amount of conformationally disordered phase II structure. Above 42 °C the phase I PDHS is converted to phase II which increases rapidly in intermolecular order as the temperature is increased to yield a pseudohexagonal packing of conformationally disordered chains.[3,4] In PDMS the sample has the phase I all-trans structure which is retained even at very high temperatures.[9] The solid-state ^{29}Si NMR spectra of PDHS, PM-*co*-HS, and PDMS are compared in Figure 3. In the spectrum of PDHS (Figure 3a) recorded without cross-polarization (CP) a single resonance that represents phase II is observed at −25 ppm. Resonances also appear in this chemical shift region in the spectrum of PM-*co*-HS (Figure 3b) recorded without CP and result from the di-*n*-hexyl centered sequences that are conformationally disordered. The sharp signal at −25 ppm is assigned to long sequences (>5) of the di-*n*-hexyl comonomer. The additional chemical shift dispersion observed for the copolymer reflects the sensitivity of the silicon nuclei to the different comonomer sequences as was observed in the solution spectrum (see above). The band of resonances at −36 to −38 ppm in the copolymer spectrum recorded without CP is in the same position as the high-field portion of the resonance of PDMS (Figure 3c) and represents mobile, conformationally disordered dimethylsilylene units.

In the spectrum of the copolymer recorded with CP additional peaks (shaded area) are observed at −22 ppm that by comparison to the spectrum of PDHS (Figure 3a) are assigned to a well-ordered, crystalline phase of the copolymer. Peaks are also observed in the copolymer spectrum (with CP) at −34 ppm, as in PDMS, suggesting that some dimethyl units are also involved in the phase I structure of the copolymer. Thus, phase I of the copolymer is rich in di-*n*-hexyl units, and the chemical shifts indicate that the silicon chains adopt the all-trans conformation as in PDHS. Phase II represents only ca. 25% of the PDHS sample and produces a very weak silicon resonance at −25 ppm under conditions of CP (Figure 3a). On the contrary, the observation of strong signals for phase II in PM-*co*-HS at −25 to −28 ppm (Figure 3b) indicates that this is the majority phase for the copolymer sample at room temperature.

X-ray diffraction data also demonstrate the presence of an ordered phase in PM-*co*-HS at room temperature. The

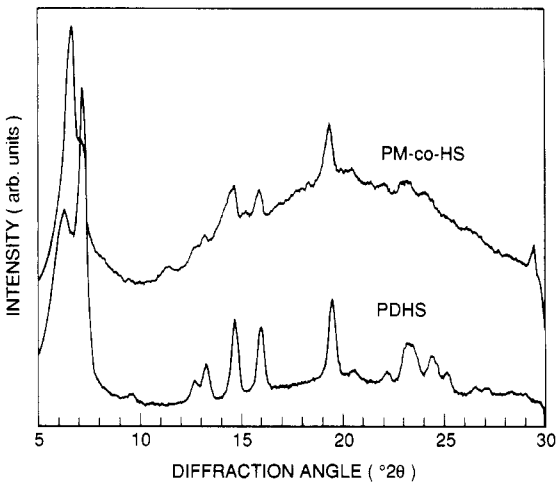

Figure 4. X-ray diffractograms of PM-*co*-HS and PDHS recorded at ambient temperature.

diffraction patterns of the copolymer and PDHS homopolymer are presented in Figure 4. The data for the copolymer contain a number of crystallographically sharp peaks superimposed on a very broad background. A comparison of the two patterns indicates that the copolymer contains an ordered phase that is very similar to the all-trans, three-dimensionally ordered phase I observed in PDHS, although the extent of order is much less. As in the homopolymer of all poly(di-*n*-alkylsilylenes), the conformationally disordered phase II of the copolymer retains intermolecular order indicated by the peak at 6.6° 2θ. The strength of this peak and of the broad one encompassing the 10–30° 2θ region indicates that most of the copolymer is unable to adopt crystallographically regular packing, presumably because of the irregular sequence distribution. The crystallographically sharp, PDHS-like peaks probably arise from sequences rich in the di-*n*-hexyl component. Because of their great side-chain length, these sequences will obviously dominate the intermolecular packing. Even if sufficient runs rich in the dimethyl constituent were present, they would not be able to come together sufficiently closely to crystallize because of the effects of the *n*-hexyl side chains. It is therefore very reasonable that the copolymer adopts predominantly a conformationally disordered quasi-hexagonal interchain arrangement, with only limited PDHS-like crystallinity and no PDMS-like regions.

As reflected in the diffraction patterns shown in Figure 5a, the extent of order in PM-*co*-HS is increased upon cooling. At +26 °C the peaks at 6.6 and 7.2° 2θ represent phase II and phase I, respectively, exactly as in PDHS. As the sample is cooled to −10 °C the peak at 7.2° 2θ increases in intensity and so do the smaller peaks at larger angles, indicating increased three-dimensional order.

More interestingly, an unexpected additional transformation occurs at temperatures below −10 °C (see again Figure 5a). The dominant peak of the conformationally disordered quasi-hexagonally packed phase II at 6.6° 2θ is seen to diminish greatly at −20 °C and to continue to be reduced at temperatures down to −40 °C (lower temperatures were not experimentally accessible). At the same time, a new peak appears at 5.6° 2θ, which increases substantially as the specimen is cooled from −20 to −40 °C. This peak obviously represents a new, longer-range order of the Si backbones; its spacing (1.58 nm) is larger than that of the PDHS homopolymer. Moreover, this new interchain peak is accompanied by weaker additional reflections at 8.8, 16.8, 19.0 (shoulder), 20.5, 22.3, and 23.0° 2θ, corresponding to *d* spacings of 1.00, 0.53, 0.47, 0.43,

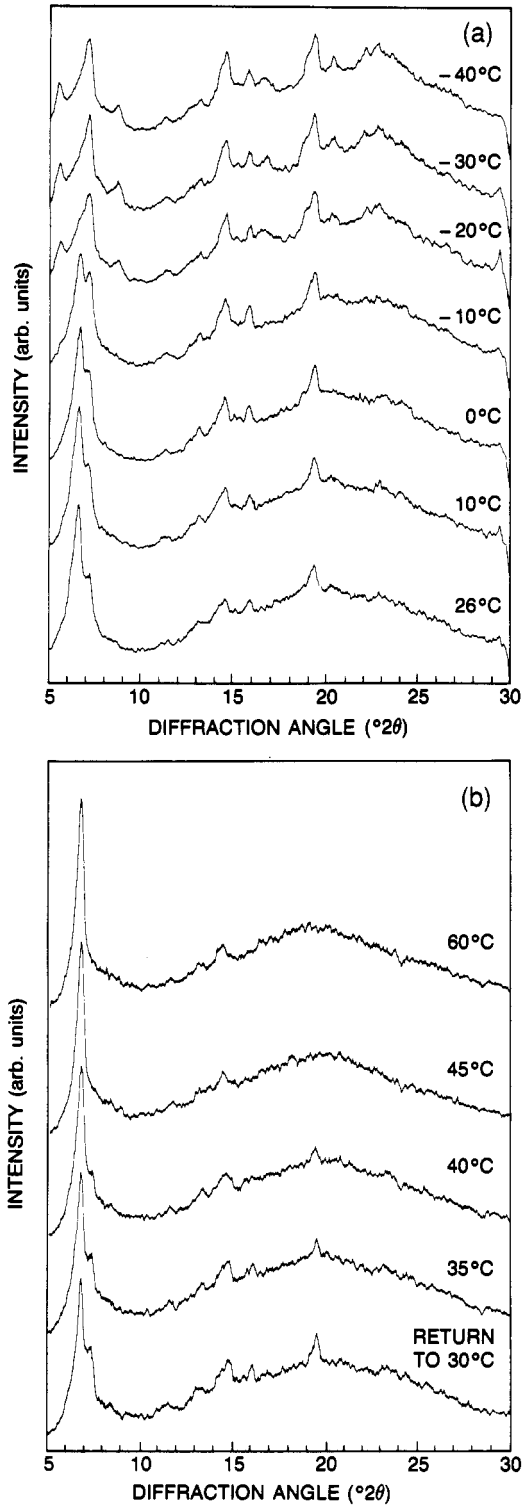

Figure 5. X-ray diffractograms of PM-co-HS recorded at the indicated temperature during (a) cooling from +26 to −40 °C and (b) return to +30 °C and finally heating to +60 °C.

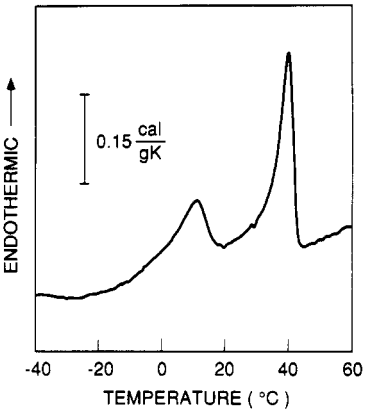

Figure 6. DSC thermogram of PM-co-HS.

0.40, and 0.39 nm, respectively (see again Figure 5a). Therefore, the new low-temperature phase (phase III) is ordered not just in a liquid-crystal-like fashion but three-dimensionally. Because of the severe overlap with the peaks of phases I and II, it is not possible at this stage to suggest a unit cell for this structure. Since the phase I peaks remain between −10 and −40 °C, this new phase III may represent a differently packed analogue of phase I arising by crystallization from the disordered phase II. The large increase in the Si-backbone spacing over that of PDHS (1.58 vs 1.20 nm, respectively) may suggest some additional participation of PDMS regions in a regular manner or more highly extended and less interdigitated n-hexyl arms than in PDHS homopolymer.

Upon heating from −40 °C back to +30 °C (Figure 5b) the diffraction pattern of the copolymer reverts back to that observed at 26 °C before cooling, demonstrating full reversibility of the phase II → phase III transformation and of the increased trans order. Subsequent heating of the sample above +30 °C produces additional changes in the diffraction data. As seen in Figure 5b the peak at 7.2° 2θ and the other peaks characteristic of phase I disappear between 40 and 45 °C. Above this temperature range only the intramolecularly disordered phase II remains. This suggests an order–disorder phase transition at ca. 42 °C, identical to that observed in the PDHS homopolymer.[3,5] In essence, therefore, the limited PDHS-like crystallinity behaves as in the homopolymer in reverting to the conformationally disordered, quasi-hexagonally packed phase (which in the copolymer is already present in the majority of the specimen even below the 42 °C transition temperature).

These changes in the structure upon cooling and heating are also reflected in the thermal characteristics of the copolymer (Figure 6). Upon heating from −40 °C endotherms are observed in the DSC data at 11 and 40 °C with a ΔH of 1.34 and 2.47 cal/g, respectively. The first endotherm is probably associated with loss of the increased order indicated in the X-ray diffraction data below −10 °C (Figure 5a and discussion above). The hysteresis of 20–30 °C in the formation of the ordered structure is typical for polymeric structures. The larger endotherm at 40 °C reflects the primary order–disorder transition described above. The value of ΔH for this transition is an order of magnitude lower than that observed in PDHS and is similar to the value found in PDMS, poly(di-n-butylsilylene), and poly(di-n-pentylsilylene). The lower value compared to PDHS probably reflects the decrease in order and crystal perfection resulting from the packing of both methyl and n-hexyl substituents in the crystal structure of the copolymer.

Changes in the degree of order and local motion with temperature are also observed in the solid-state ^{29}Si NMR data recorded with cross-polarization (CP). The spectra presented in Figure 7 include the resonances at −22 to −23 ppm of the immobile, well-ordered phase I. Upon cooling from 0 °C (bottom spectrum) to −60 °C we see a substantial increase in the size of these resonances consistent with the X-ray data described above. This change may also reflect the formation of the three-dimensionally ordered phase III as discussed above. The conformationally disordered phase II produces the peaks at −25 to −28 and

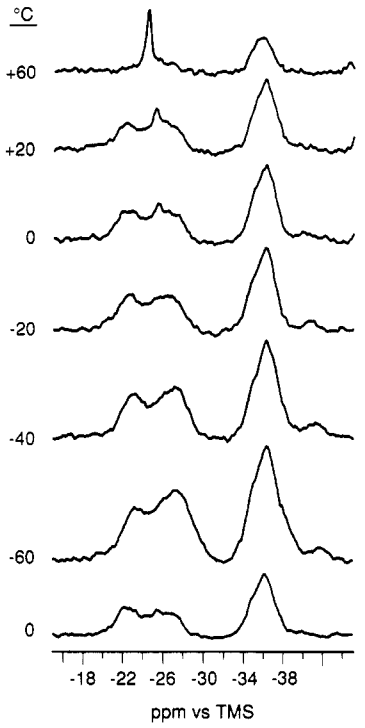

Figure 7. 79.46-MHz solid-state ^{29}Si NMR spectra of PM-*co*-HS recorded with cross-polarization (CP) at the indicated temperatures. The cooling–heating cycle is from the bottom to the top of the figure.

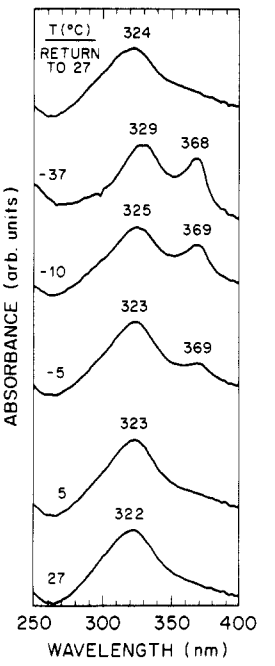

Figure 8. Solid-state UV absorption spectra of PM-*co*-HS recorded during cooling from +27 to −37 °C and after return to +27 °C.

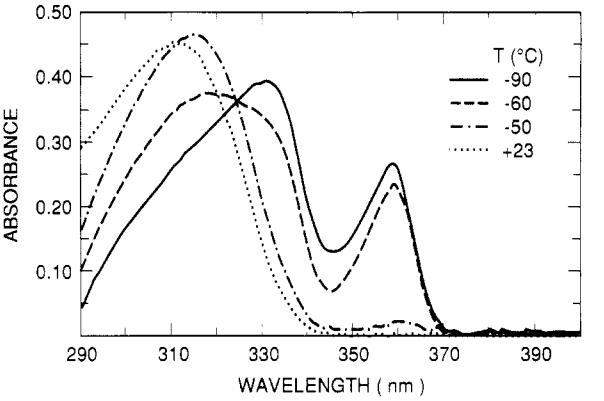

Figure 9. UV absorption spectra of PM-*co*-HS in toluene recorded during cooling from +23 to −90 °C.

−35 to −38 ppm. Their increased intensity at the lower temperatures results from a reduction in local chain motions that generates a signal enhancement in the cross-polarization experiment. In heating the copolymer from −60 °C back to 0 °C the spectra show a decrease in the intensity of the signals at −22 to −23 ppm as the extent of trans is reduced. Further heating to 20 °C shows an additional loss of signal strength at −22 ppm and a narrowing of the phase II resonance at −25 ppm. Finally, at 60 °C, above the order–disorder transition, we do not observe a resonance for phase I at −22 ppm. The strong resonance at −24.3 ppm represents silicon nuclei in runs of the di-*n*-hexyl units in phase II. The nuclei of the di-*n*-hexyl units in other comonomer sequences are too mobile at this temperature to be measured by a cross-polarization experiment. We do detect those resonances at −25 to −28 ppm in data recorded without CP (not shown).

Absorption Characteristics. Despite a similarity in the chain conformation for PDMS and PDHS, the two homopolymers differ in their absorption characteristics. At room temperature, PDMS[9] and PDHS[5] exhibit a λ_{max} of 340 and 374 nm, respectively. The UV absorption spectra for PM-*co*-HS are shown in Figure 8. At 27 °C the spectrum shows a broad absorption band centered at 322 nm with a weak shoulder in the 360–370-nm region. The large band is attributed to the disordered copolymer and the absorption at longer wavelengths to phase I material. Upon cooling a distinct band with a λ_{max} of 369 nm is observed. This band continues to increase in intensity as the temperature is lowered to −37 °C, paralleling the increase in the amount of the well-ordered phase I. The peak at 329 nm is narrowed and reduced in intensity as the sample is cooled, and phase II is converted to phase III with trans-like absorption characteristics. After the sample is heated back to 27 °C the spectrum again shows only a weak shoulder in the longer wavelength region, reflecting the reduction in trans content. Thus the absorption characteristics of trans sequences in PM-*co*-HS are very similar to those of phase I in PDHS.

The solution UV behavior of PM-*co*-HS also bears similarities to that of PDHS. As shown in Figure 9, the ambient-temperature spectrum of the copolymer peaks at 310 nm. At −50 °C, the position of the main absorption shifts to 315 nm and a small band at about 359 nm is seen. At −60 °C, the 359-nm band grows to a well-defined sharp absorption (cf. 355 nm for the low-temperature solution form of PDHS), while the shorter wavelength band changes to a broad, flat absorption at 320 nm. The shape of this band is suggestive of the presence of two species with overlapping absorption bands. This interpretation is supported by the observation that at −90 °C the shortest-wavelength part of the broad, flat absorption decreases in intensity and a well-defined peak at 331 nm develops, while the long-wavelength band grows somewhat in intensity but remains positioned at 359 nm. Thus, this copolymer exhibits the same kind of abrupt red-shift thermochromism as PDHS, but the transition is at lower temperature (onset at −50 °C vs −23 °C for PDHS in this solvent) and does not go completely to the long-wavelength form. A similar behavior has been reported for PDBS in toluene,[7] in which case the third form absorbs at 337 nm. The apparent third solution species observed in these experiments is

not found in PDHS but does parallel the finding of a third crystalline form in the solid state of this copolymer. Of course, the nature of the conformations leading to these various absorptions is not known with certainty. However, it can be safely said that the longer-wavelength forms must have greater effective "conjugation lengths" and hence be more ordered than the high-temperature, short-wavelength form. It has been suggested previously that a perfectly alternating structure is necessary for this copolymer to exhibit abrupt thermochroism.[24] These experiments show that such a phenomenon can be induced merely by a change in solvent from the hexanes of the previous work to toluene in this work.

Conclusions

The standard Wurtz coupling reaction of equal molar concentrations of dichlorodimethylsilane and dichlorodi-n-hexylsilane produces a copolymer in which the distribution of comonomer units in the soluble fraction is not random, exhibiting instead a tendency toward alternating units and containing long runs of the di-n-hexyl units. In the solid state PM-co-HS contains a three-dimensionally ordered phase (phase I) at room temperature that is very similar to the phase I structure of PDHS. This phase has a high concentration of the di-n-hexyl comonomer unit, and the copolymer chain adopts the all-trans arrangement. The amount of phase I is increased when the material is cooled. Below −10 °C a three-dimensionally ordered phase III is crystallized from the disordered phase II. The spacing of the silicon chains in this phase is larger than that of phase I and may indicate participation of PDMS regions in a regular manner or more highly extended and less interdigitated n-hexyl side chains compared to phase I. The low-temperature transformation of phase II to phase III and the increase in trans content order are fully reversible upon heating. The copolymer shows an order–disorder transition at ca. 42 °C, as is observed for PDHS. Above this temperature the phase I is converted into the conformationally disordered phase II that retains intermolecular order. In addition, the absorption characteristics of PM-co-HS in the solid state and in solution are very similar to those of PDHS. The λ_{max} of the well-ordered, crystalline phase I of PM-co-HS is at 369 nm, and in solution the copolymer exhibits a low-temperature, red-shift thermochromism. In a subsequent publication[27] we will discuss two other types of copolymers: (1) a copolymer in which both comonomers adopt a 7/3 helical arrangement as homopolymer; (2) a copolymer in which one comonomer prefers the all-trans conformational arrangement while the other comonomer adopts the 7/3 helical structure as homopolymer.

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