Solid-State Structure and Phase Transitions of Poly(dimethylsilylene)

Andrew J. Lovinger,* Don D. Davis, Frederic C. Schilling, Frank J. Padden, Jr., and Frank A. Bovey

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

John M. Zeigler[†]

Sandia National Laboratories, Albuquerque, New Mexico 87185

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ABSTRACT: We have investigated the structure of poly(dimethylsilylene) (PDMS), which is of interest as the first member of the important and widely studied family of dialkyl-substituted Si-backbone polymers. We found that the chains adopt a trans conformation and propose a monoclinic packing with a = 1.218 nm, b = 0.800 nm, c (chain axis) = 0.388 nm, and γ = 91°. This trans conformation is in agreement with our findings from the next lowest homologues (diethyl and di-n-propyl) but does not lend support to energetic predictions of helical conformations or of a requirement of at least six carbon atoms in the side chain to cause planarity of the silicon backbone. Instead, it points to stabilization of the ground-state trans conformation by Si σ-bond delocalization as the conformational driving force. Solid-state NMR showed the trans chains in PDMS to be much more rigid than those in the diethyl polymer. PDMS undergoes two weak thermal transitions at 160 and 220 °C. On the basis of our UV, X-ray, and electron diffraction results, we find the first of these to involve preservation of the trans conformation and adoption of orthorhombic packing on a metrically hexagonal lattice. The second thermal transition involves additionally some conformational and orientational disordering. Thus, in contrast to the widely studied poly(di-n-hexylsilylene), the dimethyl analogue exhibits no thermochromism or large-scale conformational disordering at its solid-state transformations, which are primarily *inter*molecular in nature.

Introduction

Polysilylenes, also known as polysilanes, continue to attract increasing interest. This is primarily a result of their complex structures and thermochromic conformational transitions (for a recent review, see ref 1), as well as of their interesting electronic and chemical properties, which make them attractive as, e.g., photoconductors, self-developing photoresists, or nonlinear optical materials.[2,3] The properties of these materials are dominated by σ-delocalization of electrons along the Si backbone and are thus very strongly dependent upon the molecular conformation.[1] For this reason, we have been particularly interested in the intra- and intermolecular structures of these important silicon-based materials.

The earliest and most widely studied of the symmetrically substituted polysilylenes, $(R_2Si)_n$, has been the di-n-hexyl (PDHS), whose preferred solid-state conformation at ambient conditions was found[4,5] to be all-trans. This material undergoes a reversible thermochromic transition to a conformationally disordered,[4,5] liquid-crystal-like[6] phase at ca. 42 °C. We have recently demonstrated that above that temperature it can be reversibly returned to the all-trans structure through a *piezochromic* transition utilizing pressures ≥120 MPa.[7] Trans-planar conformations have also been reported[8] as the stable structures under ambient conditions for the di-n-heptyl and di-n-octyl polysilanes.

The structure of polysilylenes with shorter side chains is more complex. Under ambient conditions, the di-n-pentyl[9] and di-n-butyl[10] members (PDPS and PDBS, respectively) were found to adopt a 7/3 helical rather than a trans conformation in the solid state. However, we found that a partial transformation yielding stable trans sequences could be accomplished by application of pressure of the order of 50–500 MPa.[7,11]

These findings for homologues with four to eight carbon atoms in their side chains made it of great interest to elucidate the general structural characteristics of the di-n-alkylsilane family as a function of side-chain length. A number of semiempirical and ab initio conformational analyses have recently been conducted on members of this family. One study[12] reported that a helical structure should be energetically preferred for the isolated molecule of symmetrically substituted poly(n-alkylsilylenes) and that a critical side-chain length of six carbon atoms is needed to force the Si backbone from such a helical conformation into the all-trans. However, an earlier molecular mechanics calculation on poly(di-n-hexylsilane) (PDHS) yielded the all-trans as the lowest energy conformation.[13] In view of these differing results and of the lack of experimental data, we recently synthesized the diethyl and di-n-propyl homologues (PDES and PDPrS, respectively) and examined these by X-ray and electron diffraction.[14] Analysis of fiber patterns from mechanically oriented films demonstrated that the conformation of both PDES and PDPrS is not helical (as might be expected by analogy with PDBS and PDPS as well as from conformational analysis[12]) but all-trans.[14] However, it was found that small, statistical deviations from exact trans planarity were also present.[14]

These results from polysilylenes with two or three C atoms in their side chains have upset the trend inferred earlier[12] from the longer homologues and, of course, make it now imperative to determine the structure of the *shortest* dialkyl-substituted member, i.e., poly(dimethylsilylene) (PDMS). While this polymer had been synthesized and shown to be crystalline over 10 years ago,[15] its solid-state conformation, crystal structure, UV characteristics, and the existence or absence of thermochromism or solid-state phase transformations are not known. However, extensive calculations have been performed on the con-

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[†] Current address: Silchemy, Inc., 2208 Lester Drive, N.E., Albuquerque, NM 87112.

formational energetics of PDMS chains, resulting in a variety of predictions for its preferred conformation.

Early work by Damewood and West[16] using full-relaxation empirical force-field methods found that the all-gauche (GG) conformation should be the lowest in energy for PDMS, with trans–gauche (TG) and all-trans (TT) slightly higher. Welsh and co-workers[17] employed molecular mechanics methods with full, partial, or no relaxation of internal degrees of freedom (bond lengths, as well as torsional and bond angles). Their results for PDMS did not yield a single preferred conformation. The full-relaxation calculations showed a preference for all-gauche conformations (in agreement with ref 16); no relaxation yielded TG lowest in energy, TT only very slightly higher, and GG substantially higher (ca. 4 kcal/mol); partial relaxation gave intermediate results.[17] More recent studies[18,19] have utilized molecular orbital calculations and concluded that the trans state is preferred over the gauche by 0.6–1.1 kcal/mol. One of these[18] found that the global minimum is actually located slightly away from exact trans, i.e., at 170°. In addition, a number of theoretical calculations of the one-dimensional band structures of polysilane and its variously substituted analogues have recently been conducted.[20-23] The latest of these,[23] utilizing a first-principles approach of a linear combination of atomic orbital local-density function, found that the smallest band gap for PDMS is obtained for an all-trans conformation (2.84 eV) and that this increases by ca. 2 eV as the Si backbone is rotated to an all-gauche structure.

This diversity of energetic predictions has not been tested up to now because of the lack of a structural analysis of PDMS. We provide such an analysis here and discuss our findings not only in terms of the various conformational calculations but also in relation to the structures of the other symmetrically *n*-alkyl-substituted polysilylenes. We then examine solid-state transformations in PDMS and discuss them in the context of the thermochromic transitions found in other polysilylenes. Because this dimethyl-substituted polymer has the shortest side chains possible, our findings provide a basis for an understanding of the structure and properties of crystalline Si-backbone polymers that are *least* influenced by the effects of substituents (with the exception of the parent polysilane, $(SiH_2)_n$).

Experimental Section

Poly(dimethylsilylene) was synthesized by a modification of the procedure of Trujillo.[24] A 40% v/v solution of purified[15] dimethyldichlorosilane in dry *n*-dodecane was added to a refluxing dispersion of Na metal in dodecane. The insoluble polymer was isolated by filtration of the hydrolyzed warm reaction mixture and triturated with boiling toluene and boiling *n*-dodecane to remove soluble byproducts. The resulting white insoluble solid had an infrared spectrum identical with that reported earlier[15] for PDMS.

Several techniques have been used to prepare PDMS specimens for structural examination. For X-ray diffractometry during heating and cooling, we used the as-polymerized and extracted powder, as well as thin, solution-cast films. The specimens were scanned at 0.5–2° 2θ/min in the reflection geometry, using nickel-filtered Cu Kα radiation. For fiber diffraction patterns, thin PDMS films were deposited from boiling α-chloronaphthalene solution onto fluorinated ethylene–propylene copolymer substrates. The films and substrates were then uniaxially drawn at $T \sim 200$ °C, after which the PDMS area was covered with a thick backing of poly(acrylic acid) from a 10% solution in water. Following evaporation of the water, the glassy poly(acrylic acid) was peeled off the substrate together with the adhering PDMS film. The latter was then removed after deposition of an ultrathin layer of amorphous carbon in a vacuum evaporator, followed by redissolution of the poly(acrylic acid) in water. The carbon-backed, oriented PDMS films were finally picked up onto electron microscope grids for examination by electron diffraction at 100 keV. Fiber patterns at elevated temperatures were recorded by use of a resistance-heated electron microscope sample holder.

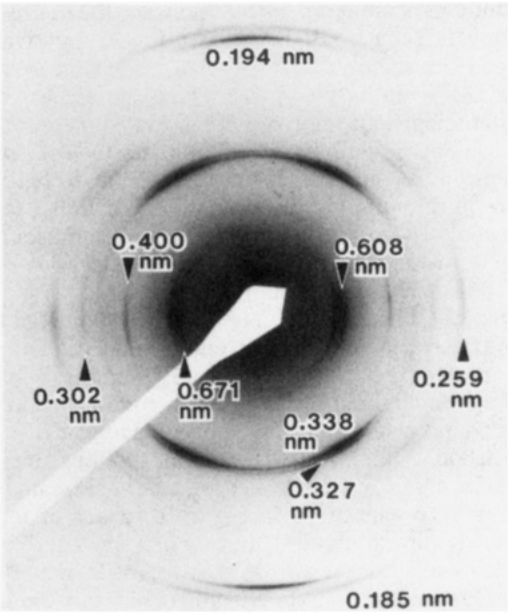

Figure 1. Electron diffraction pattern of a uniaxially oriented thin film of PDMS. The fiber direction is vertical.

Single crystals of poly(dimethylsilylene) were obtained by growth from 0.005% solutions in α-chloronaphthalene at 238 °C. The crystals were deposited onto freshly cleaved mica, shadowed with platinum, coated with carbon, and then transferred onto grids for electron microscopic examination.

Differential scanning calorimetry thermograms were obtained at a heating rate of 10 °C/min under a dry nitrogen atmosphere. Ultraviolet absorption spectra of PDMS as a function of temperature were recorded by using heated nitrogen gas.

For solid-state NMR examination, the 50.3-MHz ^{13}C and 39.75-MHz ^{29}Si spectra were recorded under magic-angle-spinning conditions using Al_2O_3 rotors at speeds of 3 kHz with a proton decoupling level of 65 kHz. The silicon spectra were referenced to the phase II resonance of poly(di-*n*-hexylsilylene) (PDHS) at −24.98 ppm under ambient temperature.[25] The spin–lattice relaxation times were recorded by using the cross-polarization method (CPT_1) of Torchia.[26]

Results and Discussion

(a) Chain Conformation. An electron diffraction pattern of uniaxially oriented PDMS is seen in Figure 1. The pattern is characterized by a large number of sharp reflections, indicating high crystallographic order in all three dimensions. The strongest reflections (at 0.671 and 0.608 nm) characterize the interchain-lattice spacings of the silicon backbones. Remarkably, the meridional reflection is also exceptionally strong and sharp. Its spacing of 0.194 nm and its location on the second layer line associate it *uniquely* with a planar-zigzag, all-trans conformation. As we discussed recently,[14] among the many other conformational possibilities considered, only the 7/3 helical sequence would have a meridional peak at the same spacing as our proposed planar zigzag. However, this helical peak would lie on the *seventh* layer line and be accompanied by a very strong, slightly off-meridional reflection at 0.459 nm on the third layer line. None of these possibilities is consistent with our evidence from Figure 1.

The fact that PDMS is thus found to adopt an all-trans conformation in the solid-state is consistent with our recent findings of similar conformations for the diethyl and di-*n*-propyl analogues (PDES and PDPrS, respectively),[14] as well as from suggestions for the solution conformation of PDMS.[27] Cumulatively, the results from these three lowest homologues do not provide support for energetic predictions of helical structures as the lowest energy conformations for such alkyl-substituted silicon chains nor for the requirement of a minimum of six carbon atoms in the side chain to enforce planarity in the silicon backbone. They point instead to a dominance of the *backbone* rather than of the side chains in determining the structure of these polysilylenes. The driving force for this is expected to lie in the maximization of the electron delocalization and the minimization of the ground-state energy that are achieved when a silicon chain adopts the trans conformation. On the other hand, when side chains become longer (i.e., four or five carbon atoms), steric interactions among them (on the same or possibly also on adjacent Si backbones) may cause these to assume a larger role in affecting the backbone conformation. Certainly, when the length of the alkyl side chains is increased to six to eight carbon atoms, their influence on backbone conformation becomes dominant. At the same time, their increased length now leads them to a dense crystallographic packing (akin to that seen in hydrocarbon crystals), thus reinforcing planarity of the silicon backbone to which they are attached.[4,5,8] This is evidenced by the exceptionally high rigidity of PDHS molecules in their trans phase, leading to uniquely long spin–lattice relaxation times in solid-state NMR.[10]

While the dimethyl, diethyl, and di-*n*-propyl polymers all have a trans conformation, there are some important differences among them that we should note. First of all, the exceptional sharpness of *all* reflections in PDMS (see again Figure 1) is in marked contrast with the situation in PDES and PDPrS, where only the *equatorial* reflections were sharp (see Figure 2 of ref 14). The large breadth and diffuseness of the meridional (and other $l \neq 0$) reflections indicated small statistical deviations from exact trans planarity. In PDMS, the trans conformation and the three-dimensional registry among chains appear to be much more regular. Reasons for this difference may be attributable to *intra*molecular packing effects of the alkyl side chains in PDMS on the one hand vs PDES/PDPrS on the other. Molecular models of the dimethyl and diethyl polymers, viewed along the normal to the planar-zigzag backbone, are seen in Figure 2. The terminal methyl groups in these polymers are known to be highly mobile and rotating (see our NMR evidence later in this discussion). For PDMS (Figure 2a), these methyl groups can freely rotate without any interference from each other, as a result of their large mutual separation dictated by the Si–Si bond length and angle. On the other hand, for PDES (Figure 2b) the methyl groups interdigitate and therefore interfere with each other during the rotation. In Figure 2b the ethyl branches are shown in eclipsed conformation, which minimizes the steric interactions among consecutive methyl groups along the Si backbone. For the slightly more stable staggered ethyl conformation, the terminal methyl interactions will be much more severe. For all of these reasons, we expect bond distortions (primarily torsional) to occur along the Si backbone, as well as about the Si–C_1 bond in PDES (and PDPrS). These distortions should cause broadening and diffuseness of the nonequatorial reflections in PDES and PDPrS (as is observed[14]).

A second difference among the planar-zigzag conformations of the di-*n*-alkylsilylenes lies in their actual molecular-repeat distances. Our findings for the three lowest homologues[14] indicate a consistent trend with length of dialkyl substituent, as seen in Figure 3. On this figure is added also the value for the trans repeat of poly(di-*n*-butylsilylene) (PDBS) following piezochromic transformation,[7,11] as well as the the two repeat distances that have been reported[4,5] for PDHS. The increasing trend for the first three members appears to reach saturation for the longer side chains. This slight elongation of the trans backbone is consistent with our argument above, ascribing bond distortions to steric repulsions for alkyl side chains longer than methyl. Moreover, it indicates that these distortions are not relieved through torsional deviations alone but must involve expansion of backbone bond angles (Si–Si bond lengths are least likely to be affected[28]). Si–Si–Si bond angles for PDMS have been reported from semiempirical conformational calculations to be in the range of 114.2–115.4° for trans backbones. Our experimentally determined value (based upon a standard Si–Si bond length of 0.235 nm) is 111.4°. This substantially smaller value is consistent with the minimal steric conflict among the methyl substituents and is in essentially exact

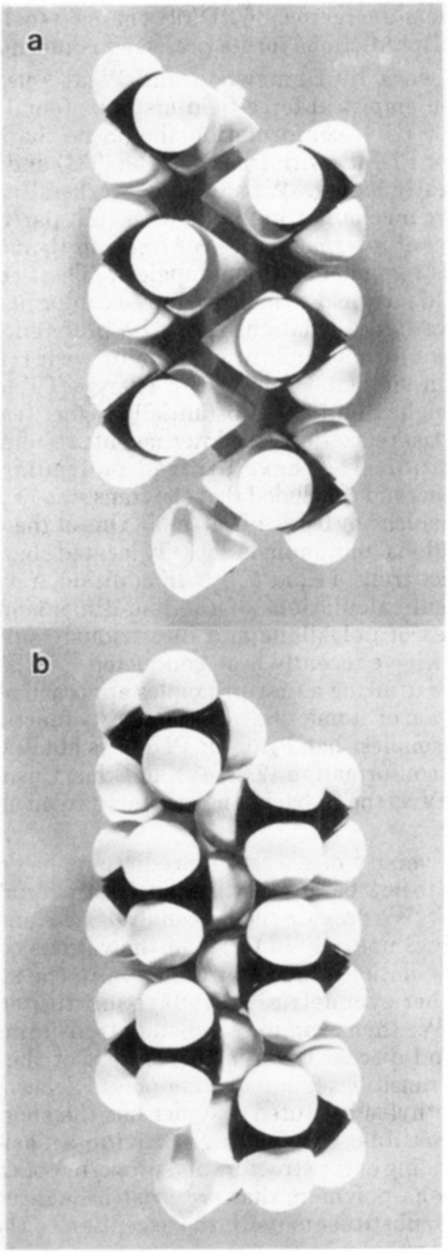

Figure 2. Space-filling molecular models of (a) PDMS and (b) PDES chain segments, viewed normal to the plane of the all-trans silicon backbone.

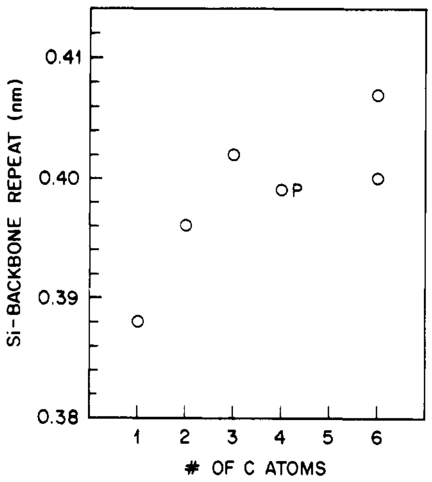

Figure 3. Si-backbone repeat distances for the trans conformation in poly(di-*n*-alkylsilanes) as a function of C side-chain length. The value indicated for PDBS refers to a pressure-transformed specimen.[7,11]

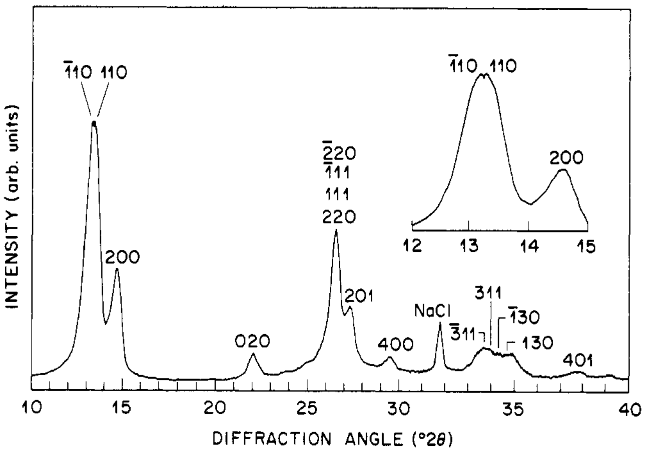

Figure 4. X-ray diffractogram of as-polymerized PDMS. The inset shows the 12–15° 2θ region at higher resolution.

agreement with the equilibrium bond angle determined by ab initio calculations for polysilane oligomers[22] (111.7°).

(b) Unit Cell. From diffraction patterns such as in Figure 1, the observed reflections could be indexed with an orthorhombic unit cell having dimensions a = 1.218 nm, b = 0.800 nm, and c = 0.388 nm. However, higher resolution diffractograms from the bulk specimen, recorded in the reflection mode, provide indications of a lower symmetry (see Figure 4). There is a consistent splitting of the strongest reflection, which we therefore identify as a combined (110, $\bar{1}10$) doublet. The (220, $\bar{2}20$) and (111, $\bar{1}11$) counterparts are not resolved because they all diffract between 0.332 and 0.337 nm (onto which the 201 peak at 0.327 nm is also partly superposed). Another noteworthy feature of the diffractogram in Figure 4 is the sharp reflection at 31.7° 2θ, which we ascribe to the strongest reflection (i.e., the 200) of NaCl (which is a byproduct of the synthesis of PDMS). Since this polymer is insoluble in all solvents at temperature < 210 °C (ref 15), it could not be completely purified by reprecipitation. Our assignment of this peak to NaCl was confirmed by (a) its virtual elimination in bulk diffractograms following prolonged extraction of the polymer in boiling water and (b) its absence in single-crystal electron diffraction patterns (see further in this discussion).

The splitting of the major peak leads to our proposed identification of the observed reflections as indicated in Figure 4: this identification is based upon a monoclinic unit cell having a = 1.218 nm, b = 0.800 nm, c (chain axis) = 0.388 nm, and γ = 91°. These assignments led to an optimal fit with our observed d-spacings. We have attempted to probe directly this possible deviation from orthorhombic packing through electron diffraction patterns of the $hk0$ reciprocal-lattice section from single crystals of PDMS. We succeeded in growing these first single crystals of this polymer by dissolution in α-chloronaphthalene at 251 °C followed by recrystallization at 238 °C. Highly regular, rhombic-shaped single crystals, commonly bounded by {110} facets, were obtained (their morphology will be described separately[29]). While there may be very slight deviations from orthogonality of the a and b axes in some single-crystal patterns, the full diffraction evidence must be considered in detail in a forthcoming publication.[29]

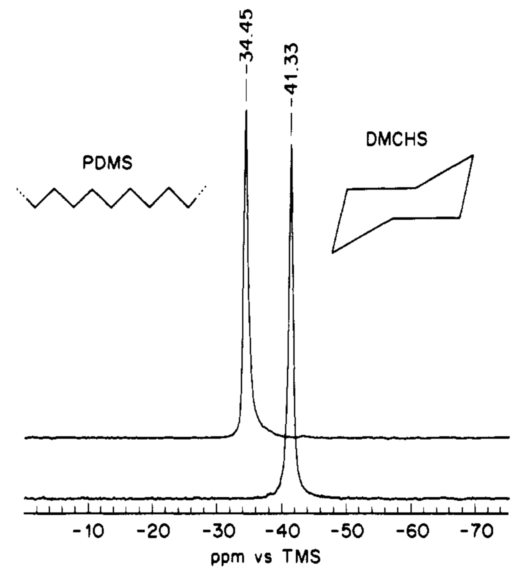

Figure 5. Solid-state ^{29}Si NMR spectra of PDMS and of a cyclic model compound, dodecamethylcyclohexasilane (DMCHS), recorded under magic-angle-spinning conditions and cross-polarization.

(c) NMR Characterization. The solid-state ^{29}Si NMR spectrum of PDMS at +23 °C is shown in Figure 5. Under the conditions of cross-polarization (CP) a single resonance at −34.45 ppm is observed. Without CP (not shown) a much weaker and somewhat broader peak is found at the same chemical shift, indicating that the majority of the PDMS sample is of a single homogeneous phase. The chemical shift of PDMS is at a higher field position than that reported for any other poly(di-*n*-alkylsilylene). It is about 12 ppm upfield from the silicon resonance of PDES and PDHS, which also adopt the trans conformation along the silicon backbone.[14,25] Unfortunately, a full NMR comparison among these polysilylenes with the same backbone conformation is difficult because of differences in the length of the alkyl side chains. Such comparison would require knowledge of the substituent effects for the silicon atom and determination of side-chain bond conformations in those polymers.

In order to consider the relationship between the silicon chemical shift and silicon bond conformation, we have recorded the solid-state spectrum of dodecamethylcyclohexasilane (DMCHS), which is also shown in Figure 5. An X-ray study[30] indicates that in the solid state the preferred conformation of this molecule is the *chair* sequence. In this arrangement the average torsional angle of the silicon bonds in the ring is 53.5°, which corresponds closely to the gauche conformation. When the chemical shifts of the cyclic DMCHS and the linear PDMS structures are compared, the effects of ring strain or valence-angle changes

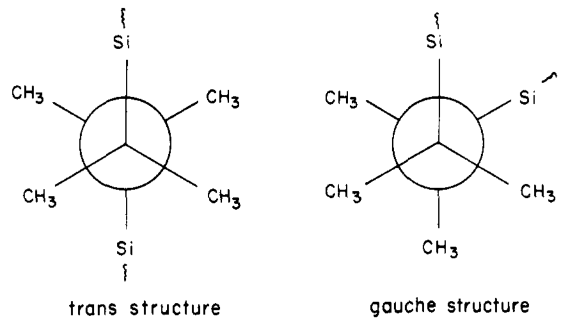

Figure 6. Newman projections of a methyl-substituted silicon backbone, viewed along a Si–Si bond in trans and gauche conformations.

on the chemical shift must be considered. In the case of the silane rings it appears that these effects are small for cyclic structures containing five or more silicon atoms. The average valence angle of DMCHS is 111.9°,[30] i.e., essentially the same as that found by us for the linear PDMS chain (111.4°). The solution chemical shifts reported for the permethylcyclosilanes with four, five, six, and seven ring atoms are −27.56, −42.13, −41.87, and −41.68, respectively.[31,32] These data suggest that there is little difference in molecular geometry for rings of five to seven silicon atoms. For all of these reasons, we believe that it is appropriate to compare the chemical shifts of the linear PDMS and the cyclic DMCHS. The silicon chain of gauche conformations in DMCHS produces a resonance that is 6.9 ppm upfield from the resonance of the trans conformations of PDMS.

The significant difference between these two conformers is that in the trans structure the silicon atom has in each direction along the backbone two methyl carbons that are removed by three bonds and are in a gauche arrangement (γ-gauche interaction[33]). On the other hand, in the gauche structure one of these carbons is replaced with a silicon atom (see Figure 6). Since the silicon atom experiences a change in the γ-gauche interaction[33] in both directions along the backbone chain, the contribution to the chemical shift produced by replacing a single silicon–carbon γ-gauche arrangement with a silicon–silicon interaction is ca. −3.5 ppm, with the negative sign indicating a more shielding arrangement. These observations demonstrate that the silicon chemical shift will be an excellent monitor of backbone conformational changes. In order to understand this relationship in detail, a complete NMR analysis of DMCHS and other cyclic silane model compounds is in progress. However, for polymers with side chains longer than methyl, it will also be necessary to establish the effects of side-chain bond rotations on the silicon chemical shift.

In order to probe the molecular rigidity and dynamics of PDMS, we also measured its silicon spin–lattice relaxation time (T_1). AT 23 °C the T_1 value is 900 s, suggesting a very rigid structure. We have previously reported a value of 11 400 s for the silicon T_1 of PDHS,[10] which represents a record-high value implying extremely high structural rigidity. This is attributed to the crystallographic packing of the *n*-hexyl side chains, which locks the Si backbone into an exceptionally rigid structure. The shorter value observed for the silicon nuclei of PDMS probably reflects the proximity of the freely rotating methyl group. In contrast, the trans structure of PDES, which shows small statistical deviations from exact trans planarity[14] (see also above discussion), has a silicon T_1 value of only 8.8 s. Consistent with the silicon relaxation data, we also find the same trend in the T_1 values for the methyl carbon (11.5 s in PDMS and 1.0 s in PDES). These NMR relaxation data therefore indicate, in agreement with our X-ray and electron diffraction results, that the chain structures of PDMS and PDHS are much more rigid than that of PDES.

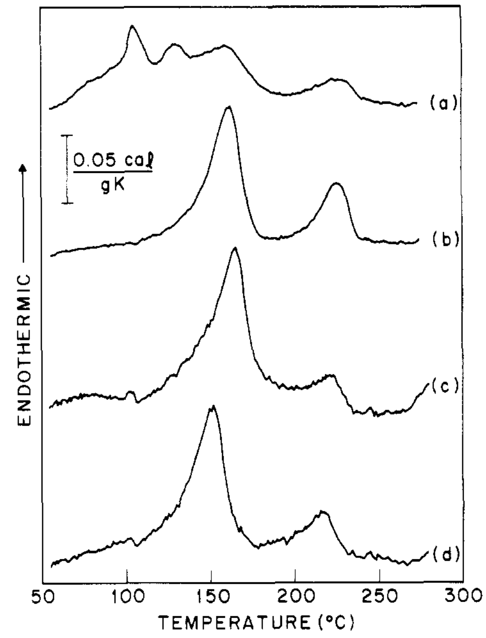

Figure 7. DSC thermograms of PDMS: (a) Initial heating run of as-polymerized powder. (b) Second heating run after quickly cooling to ambient temperature. (c) Initial heating run of single crystals grown from α-chloronaphthalene solution at 238 °C. (d) Second heating run of specimen in c after quickly cooling to room temperature.

(d) Thermal Behavior. Having discussed the ambient-temperature structure of PDMS, we now examine its thermal characteristics as a prelude to the structural study of phase transformations (which follows in the next section). The DSC behavior of the as-polymerized material is complicated and shows a number of weak endotherms (see Figure 7a). Second and subsequent heating scans show only two well-defined peaks at 162 and 226 °C (see Figure 7b). The increase in these peaks compared to curve a indicates that the original broad background reflected to a major extent the existence of very small, irregular, or strained crystals that underwent annealing during the first heating run (although some oligomeric species have also been invoked for low-temperature endothems[15]). The two peaks observed in the second and subsequent heating runs are typical of the PDMS polymer under a variety of crystallization conditions. For example, single crystals grown by prolonged crystallization of a PDMS solution in α-chloronaphthalene at 238 °C (followed by cooling to room temperature, filtration, and drying) yield the DSC scan in Figure 7c. The primary peak is now shifted to 165 °C, reflecting the increased thickness and perfection of these solution-grown single crystals. A subsequent scan after cooling to room temperature (Figure 7d) yields the same two endotherms, but shifted to lower temperatures.

The heat of the primary thermal transition of PDMS at 150–165 °C ranges between 2.50 and 2.75 cal/g, while that of the secondary endotherm at higher temperatures is 0.35–0.80 cal/g. Clearly, the first of these represents the major solid-state transformation occurring in PDMS and may be compared to the disordering transitions of other poly(di-*n*-alkylsilanes). Such a comparison is made in Table I. The heat of transition for PDHS is by far the highest, reflecting both the high rigidity of its trans structure and the disordering contributions of its long side

Table I
Primary Thermal Transitions of Poly(di-*n*-alkylsilylenes)

side chain	*T*, °C	Δ*H*, cal/g
dimethyl	162	2.6
diethyl	123	6.0
di-*n*-propyl	125	5.6
di-*n*-butyl	87	2.1
di-*n*-pentyl	70	2.6
di-*n*-hexyl	42	20.0

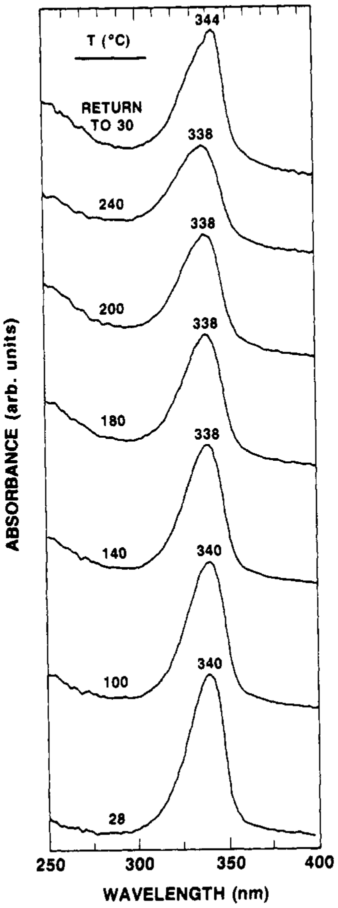

Figure 8. Ultraviolet absorption spectra of PDMS recorded during heating from room temperature to 240 °C and after return to ambient temperature.

chains. The much lower values for PDBS and PDPS have already been discussed[10] in terms of their helical conformation, high side-chain mobility, and limited crystallographic changes through the transition region. For PDMS, the very low enthalpy of transition obviously reflects the fact that there is no conformational disordering possible for the side chains and may also imply limited changes in backbone conformation and chain packing at the transition. Further evidence for this is given in the next section on the basis of our UV and diffraction results.

(e) Phase Transitions. The molecular processes underlying the endothermic transitions detected by DSC were investigated by using UV absorption spectroscopy, X-ray, and electron diffraction. The UV absorption spectra of PDMS are shown as a function of temperature in Figure 8. At 28 °C, a single, narrow (half-width ≃ 22 nm) peak is observed. In view of the trans conformation of PDMS at room temperature, the position of this peak is unexpected: as is well-known, PDHS absorbs at ca. a 30 nm longer wavelength. However, this longer wavelength may reflect the extraordinary rigidity of the Si backbone[4] arising from the tight crystallographic packing of the side chains. Polysilylenes with shorter side chains (e.g., PDES and PDPrS) have a much more flexible and mobile trans backbone and show absorption maxima at 330–340 nm. Recent calculations[19,23] have demonstrated the very high sensitivity of the electronic absorption peak to the torsional backbone angle. Therefore, small departures from 180° along the Si chain (aided perhaps by the highly mobile methyl substituents) might be at the root of this shorter wavelength absorption for PDMS. Changes in valence angles are also possible contributors to shifts in absorption wavelength. Very low molecular weight is another well-known cause for shift of absorption wavelength to lower values, although for our material (cf. also ref 15) this should not be a dominant factor.

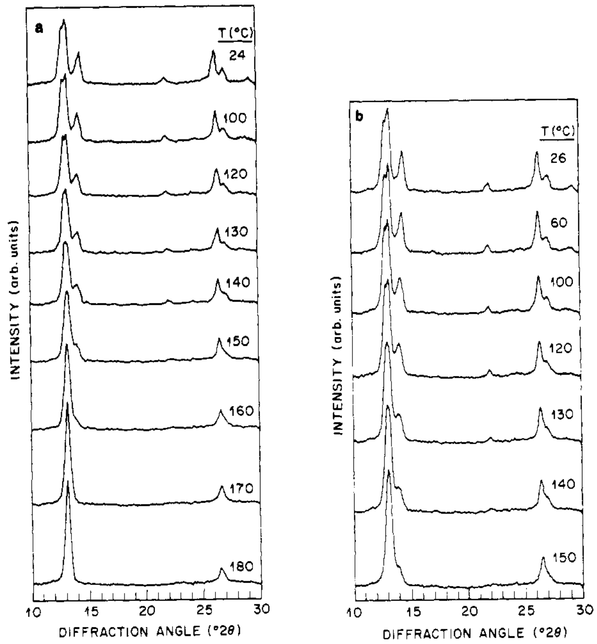

Figure 9. X-ray diffractograms of PDMS recorded at the indicated temperatures during (a) heating from 24 to 180 °C and (b) subsequent cooling to ambient temperature.

When the electronic absorption of PDMS is examined during heating (Figure 8), there is remarkably little change through the first DSC transition (at ca. 160 °C). The peak remains centered at 340 nm and becomes only slightly weaker and broader. This implies that there is no significant conformational disordering at the transition, in contrast to the behavior of PDHS. The overall trans conformation must be preserved to a large extent, with only small disruptions of the σ-conjugation. We therefore infer that the primary transition detected by DSC must be predominantly an *inter*molecular one. The secondary transition at ca. 220 °C is seen in Figure 8 to involve somewhat greater conformational disruption and some degradation as reflected in the more extensive weakening and broadening of the 340-nm peak and the further growth of a large background extending into the deeper UV. The changes are to a substantial extent reversible upon cooling back to ambient temperature, although the deeper UV background (indicative of some degradation) remains. The original peak becomes consistently skewed toward slightly longer wavelengths (see again Figure 8), indicating a small annealing effect on the backbone trans conformation.

Examination of the crystallographic changes occurring during heating and cooling of PDMS can be made with the aid of the X-ray diffractograms in Figure 9. Only the first transition could be probed because temperatures higher than 200 °C were not attainable in our equipment. The heating part of the cycle (Figure 9a) shows that the transition around 160 °C is accompanied by disappearance

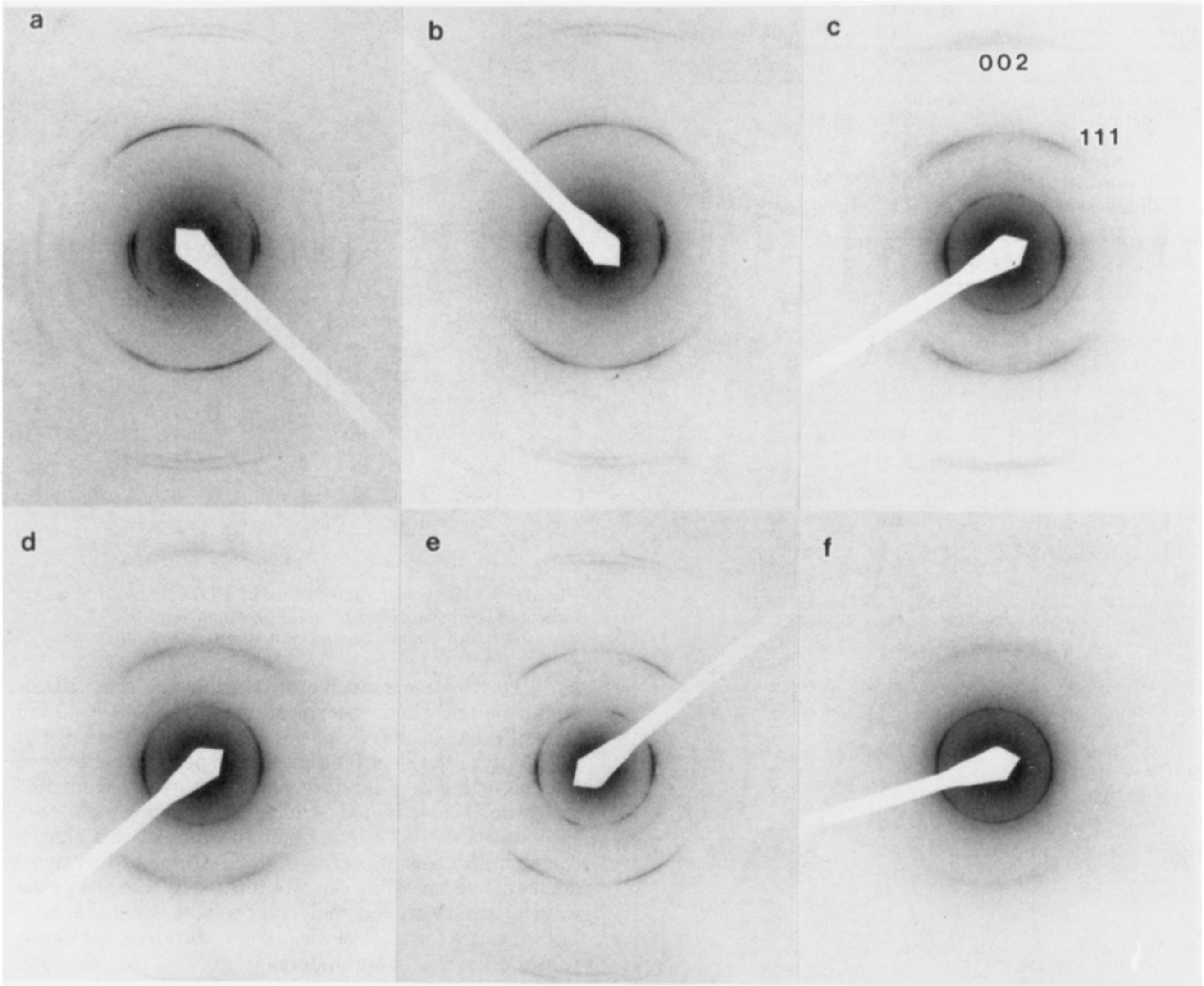

Figure 10. Electron diffraction patterns of uniaxially oriented PDMS recorded during consecutive heating from (a) 27 °C to (b) 130 °C, (c) 167 °C, and (d) 180 °C, followed by (e) cooling to 120 °C, and (f) subsequent reheating to 265 °C.

of the 200, 020, 201, and 400 peaks (these are identified in Figure 4). At the same time, the strong $\bar{1}10 + 110$ reflections merge together, yielding a single, narrow, and sharp peak at 0.675 nm, while the combined {$\bar{2}20$, $\bar{1}11$, 111, 220} reflection is reduced in intensity. These changes are consistent with adoption of a metrically hexagonal packing of the PDMS chains ($a = 0.779$ nm) on a slightly expanded lattice (7.8%). This would imply that the chains assume an approximately cylindrical packing and could in principle be realized through changes in molecular conformation (e.g., to a disordered or helical conformation) or packing (e.g., to a rotator phase); it could also involve only liquid-crystalline order (e.g., a nematic phase). The exact structure of the PDMS molecules above 160 °C cannot be determined from X-ray diffractograms of unoriented specimens alone, but the minimal changes in the UV absorption peak (Figure 8) argue against any major conformational departures. Whatever the crystallographic changes, they are reversible upon cooling, leading to adoption of the original structure at ambient temperature (see Figure 9b).

To obtain a better understanding of the structural origins of the primary DSC transition, we have studied the temperature dependence of electron diffraction patterns from uniaxially oriented PDMS. This also allowed us to probe the secondary transition since its temperature range was readily attainable in our electron microscope heating stage. Selected-area diffraction patterns from one such oriented PDMS film are seen at a number of temperatures in Figure 10. Upon examination of the sequence a–d, (encompassing the first transition), the most noteworthy observation is the very clear preservation of the meridional 002 reflection and the off-meridional {111} reflections (albeit with some broadening). These findings demonstrate that the conformation is not altered substantially but remains essentially all-trans. This is consistent with the UV features observed in Figure 8. The fact that arcing of the reflections is not increased in Figure 10 (a–d) indicates that the molecular orientation of the Si backbones is preserved. Moreover, since the nonequatorial reflections are not streaked parallel to the layer lines, there is a well-developed registry of chains along their molecular axes and therefore not a nematic structure. Finally, the retention of the *original* first layer line demonstrates that the structure cannot be a rotator phase: this would imply *halving* of the molecular repeat, in which case the 1.94-nm meridional reflection would have been on the *first* layer line. All of these results lead us to conclude that the most likely structure of PDMS above its primary thermal transition does not involve true hexagonal packing but is only an orthorhombic arrangement of essentially trans chains on an expanded, metrically hexagonal, lattice.

Figure 10 also shows the effects of cooling below the first DSC transition (part e) and then reheating beyond the secondary transition (part f). In part e, a strong sharpening of the nonequatorial reflections is clearly seen, together with an incipient appearance of the additional equatorial peaks that were present originally. These results demonstrate again the reversibility of the primary transition. When the specimen is heated to 265 °C, i.e., well above the secondary transition (see part f), several major changes are observed. The meridional reflection on the second layer line is no longer visible, and the first layer line reflections have become highly weakened. On the other hand, the equatorial reflection is still strong and sharp, yet much more arced, indicating deterioration of the original molecular orientation. Therefore, we conclude that the secondary transition involves larger scale conformational and orientational disorder, coupled with some degradation and consistent with the more pronounced changes visible in the UV.

Conclusions

From our electron diffraction analysis of oriented poly(dimethylsilylene), we concluded that it adopts a trans conformation in a much more regular three-dimensional lattice than do its diethyl and di-*n*-propyl analogues. We also found a slight but systematic shortening of the trans chain repeat as the side-chain length decreases. Adoption of a trans conformation in the three lowest homologues of this di-*n*-alkyl-substituted polysilane family does not lend support to energetic models predicting helical backbone conformations or requiring a minimum of six carbon atoms in the side chain to stabilize a Si planar zigzag. Indeed, in the case of PDMS the side-chain interactions are minimal (the groups being spherical rather than chainlike), yet the Si backbone is exceptionally rigid, as shown by our solid-state NMR results. These combined findings demonstrate the primacy of interactions *within* the Si backbone in determining the molecular conformation. The driving force for these interactions is the maximization of Si σ-bond electron delocalization and minimization of the ground-state energy.

We found the packing of these trans chains to be consistent with a monoclinic unit cell having $a = 1.218$ nm, $b = 0.800$ nm, $c = 0.388$ nm, and $\gamma = 91°$. The interchain packing will be examined directly by electron diffraction on the first single crystals of PDMS, which we grew from α-chloronaphthalene solution at very high temperatures (238 °C).

The transitional behavior of PDMS results in two low-enthalpy DSC endotherms at ca. 160 and 220 °C. Nevertheless, the UV absorption peak remains at ca. 340 nm throughout the heating, showing only minimal broadening at the first transition and more substantial broadening at the second. These findings imply that the conformation remains essentially all-trans through the first transition and undergoes more significant disordering and some degradation at the second. We confirmed this conclusion by electron diffraction analysis of uniaxially oriented specimens, which demonstrated preservation of the meridional reflection at 180 °C. In addition, our X-ray and electron diffraction results showed that the primary transition is an *inter*molecular one to a slightly expanded metrically hexagonal lattice whose underlying symmetry is lower. Thus, even though PDHS and PDMS both adopt very rigid trans planar conformations at room temperature and undergo solid-state transitions at higher temperatures, the products and processes of these transformations are quite different. In PDHS, there is significant conformational disordering leading to a liquid-crystal-like packing on a hexagonal lattice; in PDMS, on the other hand, the conformation is retained and the packing, while transformed to hexagonal, remains three-dimensionally ordered.

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