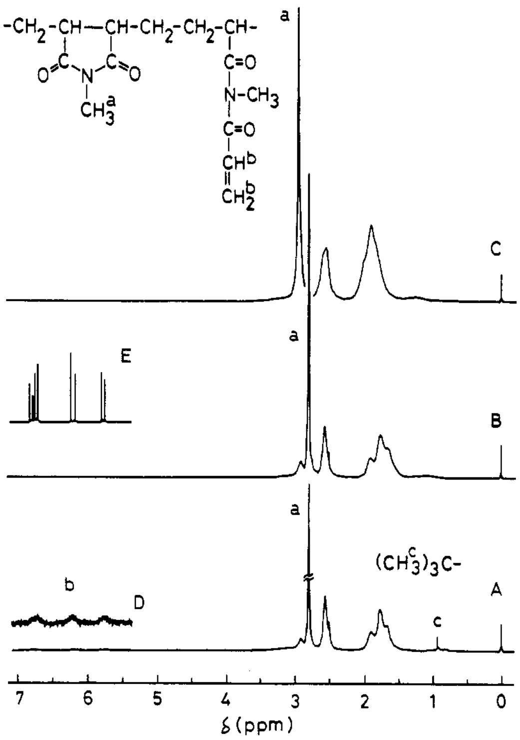

Figure 2. ^1H NMR spectra of poly-MDA and MDA: A, poly-MDA (no. 3 in Table I) in DMSO-d_6; B, poly-MDA obtained by radical polymerization at −78 °C[8] and recorded in DMSO-d_6; C, spectrum measured in $CDCl_3$ for the polymer of spectrum B; D, measured in increased gain for the spectrum A; E, $CH_2{=}CH$ protons of MDA in DMSO-d_6.

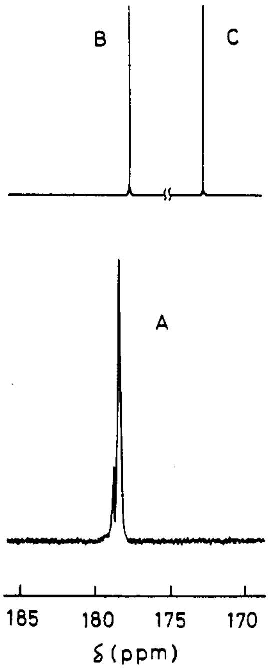

Figure 3. ^{13}C NMR spectra of carbonyl carbon in poly-MDA and cyclic model compounds: A, poly-MDA (3 in Table I); B, MSI; C, MGI measured in DMSO-d_6.

the mechanism of the 5-membered ring formation, further studies are now in progress.

Registry No. MDA, 44889-28-3; MDA (homopolymer), 30641-22-6; MSI, 1121-07-9; MGI, 25077-25-2; *tert*-butylmagnesium chloride, 677-22-5.

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Effect of Pressure on the Solid-State Structure and UV–Visible Absorption Spectra of Symmetrically Substituted Poly(di-*n*-alkylsilylenes)

The unusual and intriguing thermochromic behavior of the symmetrically substituted poly(di-*n*-alkylsilylenes) both in solution and in the solid has been well documented.[1-7] For example, a film of poly(di-*n*-hexylsilylene) (PDHS) at 46 °C shows only a strong UV absorption band centered at 316 nm, but upon cooling below 42 °C it develops an intense red-shifted band at 374 nm.[1] Under these conditions, X-ray and electron diffraction studies[7] indicate the presence of a crystalline component (phase I) having an all-trans silicon backbone together with a conformationally disordered phase (phase II). Above 42 °C the phase I structure is converted to an intermolecularly ordered phase II via a solid-state transformation. The direction of the silicon backbone chain is preserved, but two-dimensional randomization of the hexyl side chains leads to an expansion in cross-sectional area and cylindrical packing on a hexagonal lattice. The red-shifted UV absorption band that is observed below 42 °C is attributed to enhanced σ-conjugation in long sequences of trans silicon bonds.[8-10]

We now report that the 374 nm band is generated above the 42 °C transition upon subjecting a film of PDHS to pressure.[11] In Figure 1 this piezochromic effect is shown for nine values of the pressure ranging from 0.1 to 250 MPa (ca. 2500 atm). At the highest pressure the 316 nm band is almost completely replaced by the red-shifted band. When the pressure is released, the spectrum immediately reverts to the original spectrum; this is consistent with a conformational transition between an ordered and a disordered phase. The presence of an isosbestic point in the absorption spectra at different pressures indicates that the pressure-induced transition occurs between two distinct states (conformations) of the polymer and does not involve

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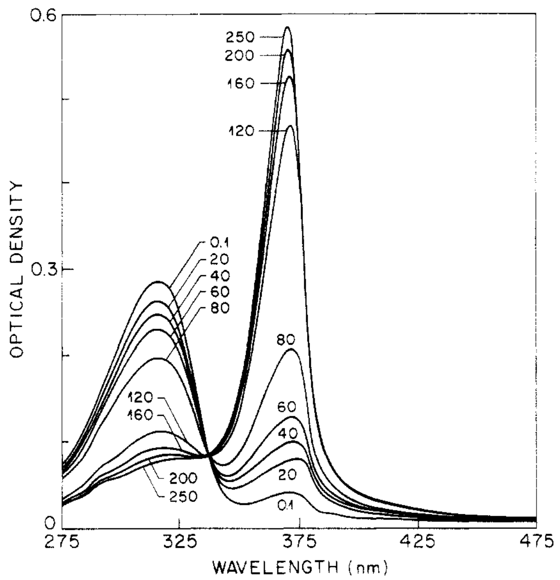

Figure 1. UV spectrum of poly(di-*n*-hexylsilylene) (PDHS) as a function of pressure expressed in MPa observed at 46 °C.

formation of a heterogeneous mixture of species, for which a gradual spectral shift would be expected. At 250 MPa the absorption at $\sim$315 nm is significantly less than it is at temperatures below the 42 °C transition temperature at ambient pressure, implying that pressure shifts the equilibrium toward the ordered phase.

The response of lower members of the symmetrically substituted polysilylene series to pressure is somewhat different. Under ambient pressure poly(di-*n*-pentylsilylene) (PDPS) has a 7/3 helical main-chain conformation and a disordered phase II similar to that of PDHS[12] and exhibits only a single band at 315 nm, with no red-shifted absorption; this remains virtually unchanged at elevated temperature. At 250 MPa pressure and -1 °C a strong absorption band at 362 nm develops and the absorption at 315 nm decreases. If the temperature is held at -1 °C, this band remains unchanged upon the release of pressure, but when the temperature is raised above 26 °C, it disappears over a narrow temperature range. Poly(di-*n*-butylsilylene) (PDBS), which also has a 7/3 helical backbone and a disordered phase II at normal pressures,[13] behaves similarly[14] except that the pressure-induced band is centered at 350 nm and does not disappear fully until the temperature is raised to ca. 62 °C. The absorption at longer wavelengths indicates the presence of trans sequences; differences in the absorption maxima may be related to the length of the trans sequences and the degree of order.

X-ray manifestations of the effects of pressure (imparted on free-standing films in a hydraulic press) were detected by reflection diffractometry at 0.25° 2θ/min using Ni-filtered Cu $K\alpha$ radiation; the resulting diffractograms are seen in Figure 2. Comparison of parts a and b of Figure 2 shows major crystallographic changes imparted to PDBS by pressure. Ordinary PDBS (not pressed) has only one major interchain peak (at 8.02° 2θ or 1.10 nm) corresponding to the quasi-hexagonal packing of the 7/3 helical silicon chains (Figure 2b); the weaker reflections at 19–23° 2θ have both inter- and intramolecular components.[13] Exposure to pressures greater than $\sim$50 MPa causes the appearance of additional crystalline peaks, whose intensities increase at the expense of those of the 7/3 helical phase, until an apparent saturation in the conversion is achieved following pressurization to $\sim$500 MPa. The diffractogram of Figure 2a is typical of this maximal conversion. We have recently obtained even greater conversions by applying pressure at temperatures above the disordering transition of PDBS, but these will be described separately. As seen in Figure 2a, the 7/3 interchain spacing increases slightly to 1.128 nm (7.83° 2θ), while a large number of strong additional reflections, as well as an overall increase in crystallinity, become apparent. In oriented specimens, the peaks at 9.38, 14.69, 17.78, 21.06, and 28.74° 2θ (0.941, 0.603, 0.499, 0.421, and 0.310 nm, respectively) become equatorial. This large increase in the number of equatorial reflections is very reminiscent of the all-trans phase I of PDHS and implies a much more regular interchain lattice than in the 7/3 phase of PDBS. The peaks at 24.04 and 25.01° 2θ (0.370 and 0.356 nm, respectively) become off-meridional, again reminiscent of PDHS phase I. A meridional reflection at 0.399 nm is also visible in oriented samples; its spacing is exactly that of the all-trans repeat of a Si backbone. However, this appearance of the 001 rather than of the 002 reflection is unexpected and not fully understood; it may originate from inequivalent side-chain dispositions along the backbone or from side-chain inclinations with respect to the Si-chain axis. All of these crystallographic changes in PDBS are thus attributable to a partial conversion from a 7/3 helical to an all-trans phase, accompanied by large increases in three-dimensional order.

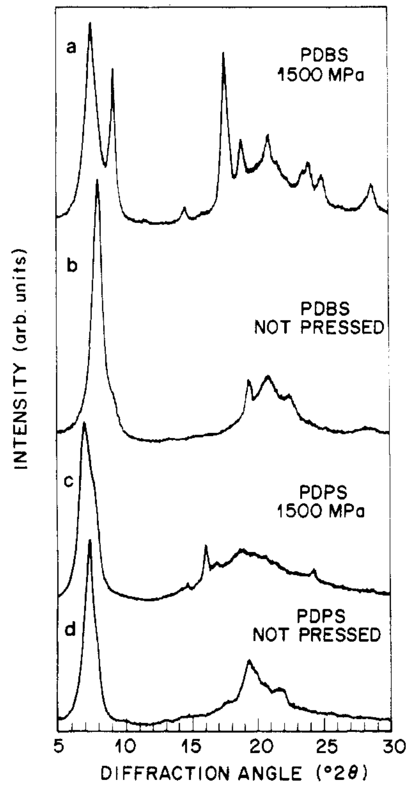

Figure 2. X-ray diffractograms of PDBS and PDPS before and after treatment to the indicated pressures. All diffractograms were recorded at atmospheric pressure and at 25 °C, except (c) which was recorded at 10 °C because PDPS undergoes a phase transformation at ambient temperature (see text).

Parallel X-ray observations on PDPS (parts c and d of Figure 2) also reveal structural changes following application of pressure, although to a smaller degree. The main reflection of the nonpressed specimen at $\sim$7.37° 2θ or 1.19 nm (Figure 2d) again corresponds to the quasi-hexagonal packing of 7/3 helical backbones. After a pressure treatment of 1500 MPa (Figure 2c) this spacing increases to $\sim$1.24 nm and a secondary strong reflection becomes evident as a shoulder at $\sim$7.8° 2θ (or 1.13 nm). Additional

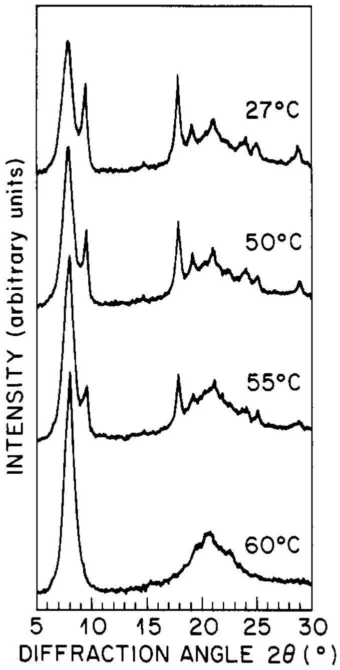

Figure 3. X-ray diffractograms of a film of poly(di-*n*-butylsilylene) (PDBS) pressure-treated to 1500 MPa and then observed at atmospheric pressure while being heated to the indicated temperatures.

peaks arise also at 14.65, 16.10, 16.88, 18.79, and 24.27° 2θ (i.e., 0.604, 0.550, 0.525, 0.472, and 0.367 nm, respectively). Nevertheless, these peaks do not approach the intensities observed in PDBS after pressurization, and the background beyond ~13° 2θ becomes more diffuse than originally. These X-ray manifestations suggest a lesser extent and regularity of the transformation to the new phase than in PDBS.

As already mentioned, the structural transformations in both PDBS and PDPS are stable after reduction of pressure to atmospheric. However, a solid-state transition to the 7/3 helical phase is seen in PDBS upon heating to ~53 °C (see Figure 3). At 60 °C, the X-ray diffractogram shows no more peaks from the trans phase (the corresponding temperature in our UV study was 62 °C). For PDPS, this transformation occurs sharply around 26–27 °C; for this reason the pressurization, specimen handling, X-ray, and NMR characterizations of this polymer were performed well below ambient temperature (i.e. at 0–10 °C). X-ray diffractograms of pressure-treated PDPS after heating to ~30 °C show that the 7/3 helical phase adopted is less well ordered than after direct crystallization at ambient conditions.

The 39.75-MHz ^{29}Si CP/MAS/DD[15] solid-state NMR spectra of pressure-treated PDPS are shown in Figure 4. The spectrum at −10 °C (Figure 4a) shows resonances for the trans and 7/3 helical sequences at −23.2 and −27.4 ppm, respectively, and a weak peak for the disordered phase II at ca. −25 ppm. Thus, the trans portions of the chains are long enough to be clearly evident by NMR (and by UV, vide supra) although of limited three-dimensional regularity as seen by X-ray (Figure 2). When the temperature is increased, the trans resonance disappears very abruptly between 26 and 27 °C (Figure 4b,c) while the phase II peak becomes somewhat more prominent. The silicon nuclei in phase II do not cross-polarize as readily as those in the ordered phase I structures; thus the intensity of the phase II resonance does not correctly represent its proportion in the sample. When the pressurized sample is cooled once again, the trans resonance does not return (Figure 4e). In the ^{29}Si NMR spectrum for pressurized PDBS we observe a large silicon resonance at −24.6 ppm that is assigned to the trans structure and a very weak resonance at ca. −26 ppm that is assigned to the residual 7/3 helical structure. This suggests nearly complete conformational conversion of the 7/3 helical structure rather than the partial transformation indicated by the X-ray data (vide supra).

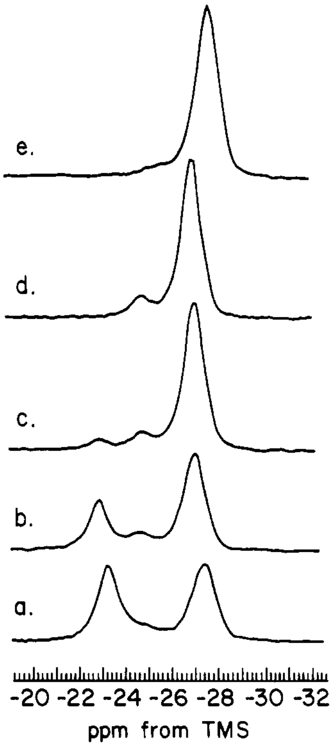

Figure 4. 39.75-MHz ^{29}Si CP/MAS/DD[15] spectra of poly(di-*n*-pentylsilylene) (PDPS) in the solid state as a function of temperature. The polymer has been subjected to 250 MPa pressure (ca. 2500 atm) and then inserted into the magic angle spinner at −10 °C (spectrum a) and the temperature increased: (b) 26 °C; (c) 27 °C; (d) 32 °C; a sharp transition occurs between 26 and 27 °C; at (e) the sample is once again cooled to 10 °C. See text for peak identifications.

These observations are consistent with the following conclusions:

1. Under pressure, the conformationally disordered phase II of PDHS, which constitutes the entire sample above 42 °C, is almost entirely transformed into the all-trans crystalline form, phase I, having a UV absorption band at 374 nm. This is consistent with the smaller specific volume of the latter. Upon release of pressure the chain conformation rapidly reverts to its normal disordered state.

2. The lower homologues, PDPS and PDBS, whose conformationally ordered crystalline phases are normally 7/3 helical, also transform to an all-trans crystalline form, but less completely, with the 7/3 helical phase remaining prominent in PDPS. Upon release of pressure at lower temperatures (−10 to 0 °C for PDPS or room temperature for PDBS) both crystalline phases remain. But when the temperature is raised, a phase transformation takes place (at ca. 26.5 °C for PDPS and 53–60 °C for PDBS), and the all-trans form disappears, yielding a slightly less ordered version of the 7/3 helical polymorph.

3. The absorption maxima of 350, 362, and 374 nm for the trans conformation in pressurized PDBS, PDPS, and PDHS, respectively, demonstrate that there is not a perfect correlation between specific bond conformations and the UV spectral peaks in the polysilylenes. This has also been observed in poly(dimethylsilylene),[16] poly(diethyl-

silylene),[17] and poly(di-*n*-propylsilylene)[17] where trans conformations have been documented yet the absorption maxima were found at 342, 332, and 344 nm, respectively. In addition, the $\lambda_{\max}$ in poly(di-*n*-tetradecylsilylene) is 347 nm, even though its conformation has been reported as tgtg′.[18] These results demonstrate the problem in correlating the UV absorption maxima with specific conformations or with lengths of conformational sequences.

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Registry No. PDHS, 94904-85-5; PDPS, 96228-24-9; PDBS, 95999-72-7.

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Azo Dye Stereoisomerization at Polyethylene–Solution Interfaces

The extent to which solvents interact with polymers is an important parameter that can affect many aspects of a polymer's behavior. However, while many aspects of the behavior of polymers in solution are well established, there is less known about how solid polymers and in particular how surface functionalized polymers behave in contact with solvents. This is due, in part, to the problems of synthesizing such interfaces and of monitoring the chemistry and dynamics of molecules at such interfaces. More recently, details about the chemistry of macromolecules and solvents at solid–liquid interfaces are in part being addressed by recent developments in studies of Å-level interactions of polymers adsorbed on mica surfaces, in various physical studies of interfaces, and in studies of organic thin films.[1-4] Studies that yield similar information about functional group behavior for a functionalized polymer's solid–liquid interface are also actively being pursued by several groups.[5,6] Here we describe experiments which show that thermal geometric isomerization of an azo dye can be used to probe solvent–polymer interaction at functionalized polymer–solvent interfaces.

Geometric isomerization of azo dyes is a facile reaction and occurs both thermally and photochemically.[7] Such isomerizations have been studied for small molecules in solution and for macromolecular derivatives in either the solid state or solution. In solution, such isomerizations follow simple first-order kinetics. However, in polymeric solids more complicated kinetics are seen.[7-12] Typically the isomerization under these conditions proceeds by two or more first-order processes. The most common observation of an initial fast first-order isomerization followed by a second slower first-order isomerization reportedly only occurs below T_g. Similar isomerizations also occur in dye-labeled chromic acid etched and entrapment-functionalized polyethylene.[9,10,12] Further, the extent of isomerization can be correlated with the behavior of other probes of solvent–polymer interactions at functionalized polyethylene–solution interfaces.[13,14] While we have examined both chromic acid etched high density polyethylene labeled with an azo dye and entrapment-functionalized polyethylene that incorporates an azo dye and seen similar behavior for each system, we have used entrapment-functionalized materials for quantitative studies. This is primarily because quantitative studies with a labeled chromic acid etched polymer are frustrated by the small amount of chromophore present. Comparison of isomerization data of an entrapment-functionalized polymer with rotational correlation times measured for ESR spin labels of similarly functionalized polyethylene suspended in the same solvents shows that the extent of the initial, faster stage of the isomerization is correlated with these τ_C values.[13] However, the total amount of isomerization seen is better correlated with solvation of these interfaces as measured with a fluorescence probe.[14]

In previous work we had reported that terminally functionalized ethylene oligomers can be blended with additive-free polyethylene to produce functionalized polyethylene powders and films. The product films and powders have been shown to form such that the terminal functional groups are largely accessible to solvent and reagents in solution. The degree to which the product films and powders are "surface" functionalized depends on various experimental parameters that have been discussed in a prior paper. Spectroscopic and chemical behavior of the product-functionalized polymer parallel that of similar derivatized etched polyethylene films although the depth