Macromolecules 1989, *22*, 3055-3063

Solid-State Structures and Thermochromism of Poly(di-*n*-butylsilylene) and Poly(di-*n*-pentylsilylene)

Frederic C. Schilling,[*,†] **Andrew J. Lovinger,**[†] **John M. Zeigler,**[‡]
Don D. Davis,[†] **and Frank A. Bovey**[†]

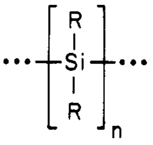
AT&T Bell Laboratories, Murray Hill, New Jersey 07974, and Sandia National Laboratories, Albuquerque, New Mexico 87185.

Received October 14, 1988; Revised Manuscript Received January 13, 1989

ABSTRACT: The relationship between the solid-state conformations and the electronic absorption properties in polysilylenes is of widespread interest. We report the solid-state analyses of two symmetrically substituted polysilylenes, poly(di-*n*-butylsilylene) (PDBS) and poly(di-*n*-pentylsilylene) (PDPS), based upon measurements using X-ray diffraction, ^{13}C and ^{29}Si NMR, UV, and calorimetry. The results indicate that the backbone conformation in PDBS and in PDPS is a 7/3 helix, which is significantly different from the all-trans conformation found in poly(di-*n*-hexylsilylene) (PDHS). A first-order phase transition is observed at ca. 85 and 70 °C for PDBS and PDPS, respectively. Above this solid-state transition the backbone and side-chain conformations are disordered. In contrast to PDHS, there is no dramatic change in the UV absorption characteristics of PDBS and PDPS at their respective solid-state transition temperatures. A correlation is observed between the polymer chain conformation and the UV absorption maxima. We have also considered the thermochromic behavior of these materials in solution. As in PDHS, an abrupt first-order transition-like bathychromic shift is observed in the solution UV spectra of PDBS and PDPS upon cooling. The significant differences observed in the absorption characteristics of PDBS and PDPS in the solid state compared to the solution data or to the data reported for PDHS strongly suggest that the factors that control the solution and solid-state thermochromic phenomena are not closely related.

Introduction

The discovery of strong solution and solid-state thermochromism in many crystalline, symmetrically substituted polysilylenes with the structure



$$\cdots\left[\begin{array}{c} R \\ | \\ -Si- \\ | \\ R \end{array}\right]_n\cdots$$

has generated substantial interest in their solid-state solution conformations and in how these affect the electronic absorption properties.[1-3] Early structural studies,[4-6] which concentrated on the analysis of solid poly(di-*n*-hexylsilylene) (PDHS), provided insight into the structure–property relations of these materials, in particular the relationship between chain conformation and electronic properties. It was established that at room temperature PDHS consists of two phases.[4] In the well-ordered phase I (where the term "phase I" indicates the most ordered phase but does not designate a specific conformation), the silicon backbone conformation is all-trans and the side chains are arranged in a direction nearly perpedicular to that of the backbone and have conformations close to all-trans. Phase II is conformationally disordered but shows rudimentary intermolecular packing. Above ca. 40 °C phase I of PDHS is converted to phase II in which the main chains are packed hexagonally, while the side chains are conformationally disordered but remain packed on planes perpendicular to the direction of the silicon backbone. Supercooling of this high-temperature disordered phase is observed. Despite the intramolecular disorder in phase II, average deviations from the trans conformation of the backbone are small, thus preserving the original molecular direction. Phase II above the 40 °C disordering transition is more ordered compared to the analogous phase II at 23 °C. An electronic absorption at 317 nm is associated with the conformationally disordered phase II, while an absorption at 374 nm is associated with the all-trans backbone chains of phase I.[3]

A preliminary structural analysis of poly(di-*n*-pentylsilylene) (PDPS) has been reported by Miller et al,[7] who found that the backbone conformation of the ordered phase at ambient temperature is a 7/3 helix. In addition, only very small differences in the electronic absorption were found between this ordered phase and the disordered phase at high temperatures, both having peaks near 315 nm. No reports have yet appeared on the structure of the next lower homologue, poly(di-*n*-butylsilylene) (PDBS). A review of thermochromic phenomena and structural studies of PDHS, PDPS, and other polysilylenes in solution and in the solid state has recently been published by Schilling et al.[8]

In this work, we report the results of our solid-state structural analyses of PDBS and PDPS, including measurements using X-ray diffraction, ^{13}C and ^{29}Si NMR, UV, and calorimetry. The results indicate significant similarities in the solid-state structures of PDBS and PDPS but major differences from the structure of PDHS. While the same trend will be demonstrated in their solid-state electronic absorption spectra, we will also show that in solution the thermochromic absorption characteristics of all three polymers are very similar, suggesting a fundamental difference in factors controlling the solid-state and solution behavior.

Experimental Section

Materials. Samples of poly(di-*n*-butylsilylene) and poly(di-*n*-pentylsilylene) were synthesized according to the methods of Zeigler.[9,10] After purification by precipitation from toluene with ethyl acetate (twice) and tetrahydrofuran with methanol, flocculent, pure white, oligomer-free samples of PDBS and PDPS were obtained having monomodal molecular weight distributions with M_w of 695 000 and 562 000, respectively. The molecular weight distributions were determined by size-exclusion chromatography in tetrahydrofuran solution using Ultrastyragel linear columns calibrated with low-polydispersity polystyrene standards.

Methods. Variable-temperature absorption spectra were recorded on hexane solutions approximately 10^{-4} M in monomer units with a combination spectrophotometer/fluorimeter previously described.[11] Neutral density filters (optical density 2.0–4.0) were used in the exciting beam to minimize photodecomposition during spectrum acquisition. Spectra recorded after a series of runs reproduced the initial spectrum within instrumental error,

---

[†] AT&T Bell Laboratories.
[‡] Sandia National Laboratories.

0024-9297/89/2222-3055$01.50/0 © 1989 American Chemical Society

Table I
Thermal Properties of Polysilylenes

polymer	T_d, °C[a]	energy, cal/g	T_g, °C
PDBS	87	2.1	-40, 36
PDPS	70	2.6	-40
PDHS[3]	41	20.0	*b*

[a] Solid-state disordering transition. [b] None detected.

indicating that photochemical degradation of the polysilylenes was negligible under these experimental conditions. Except where otherwise noted, variable-temperature solution spectra were recorded by cooling rapidly to the temperature of interest, acquiring the spectrum, warming back to room temperature, and then cooling again to the next temperature. Such an experimental protocol minimizes precipitation of the polymer on the cuvette walls during cooling of the solution. It was found that this technique was necessary to obtain reproducible solution spectra. Films of the polysilylenes were spin-cast from toluene solution onto quartz plates and annealed briefly at 50 °C under vacuum to remove residual solvent.

Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-4 at scan rates ranging from 1 to 20 °C/min under a nitrogen atmosphere. Transition temperatures were reproducible to within 1 °C over this range of scan rates. After removal of trace amounts of solvent during the first scan, subsequent scans of each sample gave identical results within experimental error.

X-ray diffraction fiber patterns of uniaxially oriented specimens were obtained in a vacuum camera to eliminate air scattering. The variation of crystal structure during heating and cooling was monitored by X-ray diffractometry on a heating holder that had been calibrated with melting-point standards to ±1 °C. Unoriented, thin-film specimens were scanned in the reflection mode at 2° 2θ/min by using Ni-filtered Cu Kα radiation.

The 50.3-MHz ^{13}C and 39.75-MHz ^{29}Si solid-state NMR spectra were recorded on a Varian XL-200 NMR spectrometer equipped with a variable-temperature Doty Scientific magic angle spinning probe with Al_2O_3 rotors. A sample spinning rate of 3.0–4.0 kHz and proton decoupling at a level of 45 kHz were employed. Between 100 and 2500 scans were accumulated for each spectrum. Silicon spectra are referenced to the phase II resonance of PDHS at -24.98 ppm (+23 °C),[6] and carbon spectra are referenced to the methyl carbon resonance of phase II PDHS at 14.5 ppm (+23 °C).[6] Samples examined by NMR were powders that were heated well above the solid-state transition temperature and then cooled to room temperature and held for at least 24 h before beginning the measurements.

Results and Discussion

Thermal Properties. Thermal data on the three polysilylenes, obtained by DSC, are summarized in Table I. Both PDBS and PDPS exhibit first-order-like phase transitions at substantially higher temperatures than PDHS and show enthalpies of transition that are nearly a factor of 10 lower than for PDHS.[3,12] In addition, a very weak, glass-transition-like increase in the heat capacity is seen at ca. 36 °C in slow DSC runs with relatively large samples of PDBS. In both PDBS and PDPS a very large, apparent second-order transition occurs at ca. -40 °C. Like PDHS, substantial supercooling (ca. 30 °C) of the high-temperature disordered phase of PDPS occurs, even when very slow scan rates are employed, indicating that the generation of the ordered form is a kinetically slow process.

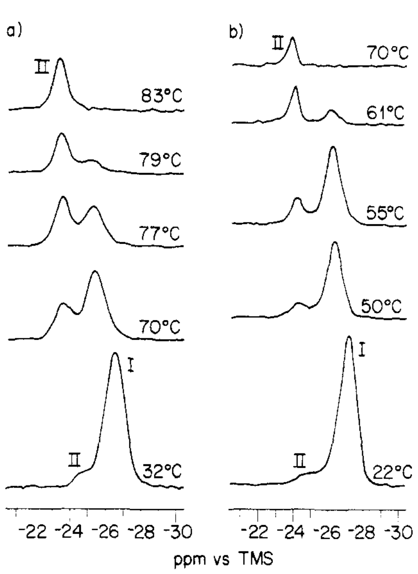


Figure 1. Variable-temperature 39.75-MHz ^{29}Si CPMAS/DD solid-state NMR spectra of (a) PDBS and (b) PDPS.

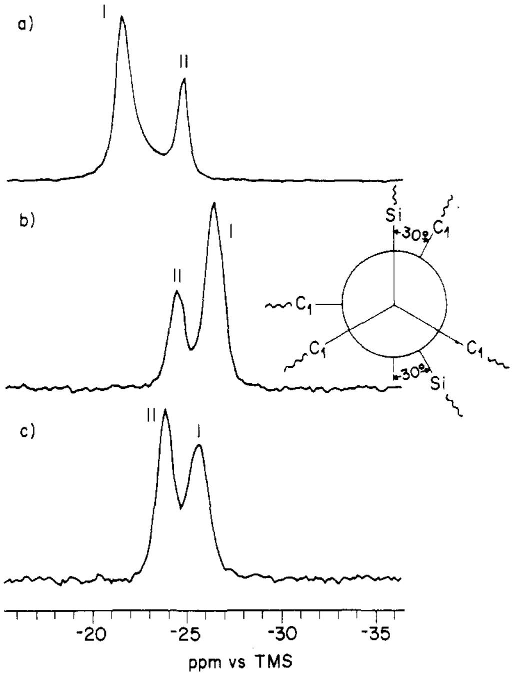


Figure 2. The 39.75-MHz ^{29}Si CPMAS/DD solid-state NMR spectra of (a) PDHS at 37 °C, (b) PDPS at 55 °C, and (c) PDBS at 77 °C. Inset: Newman projection along the silicon–silicon bond in the conformation of the 7/3 helix.

^{13}C and ^{29}Si NMR. We have examined PDBS and PDPS under conditions of magic angle spinning (MAS) using high-power, dipolar decoupling (DD) with and without cross-polarization (CP). In the ^{29}Si CPMAS/DD spectra obtained for PDBS and PDPS below the solid-state phase transition (Figure 1) two resonances are observed and assigned to the silicon nuclei of the ordered phase I and the disordered phase II structures. The midpoint of the transition between these phases may be defined as the temperature at which the phase I resonance is reduced by 50%. We find this midpoint to be ca. +75 °C for PDBS and ca. +55 °C for PDPS; in PDHS, the corresponding temperature was ca. 37 °C.[8] Because of the differences in the local chain motions, the resonance for phase I is strongest when observed with CP, while the more mobile phase II nuclei give optimal spectra without CP (not shown); thus the intensity ratios between phase I and phase II resonances in Figure 1 are not quantitative.

There are additional differences in the silicon NMR spectra of PDBS and PDPS, compared to that of PDHS. These can be observed in Figure 2, where the spectra shown were recorded close to the midpoint of the disordering phase transition in each polymer. The resonances of the disordered phase II of all three polymers are similar in chemical shift (-24 to -25 ppm). In fact, the small observed differences between the phase II resonances can be attributed entirely to the differences in the observation

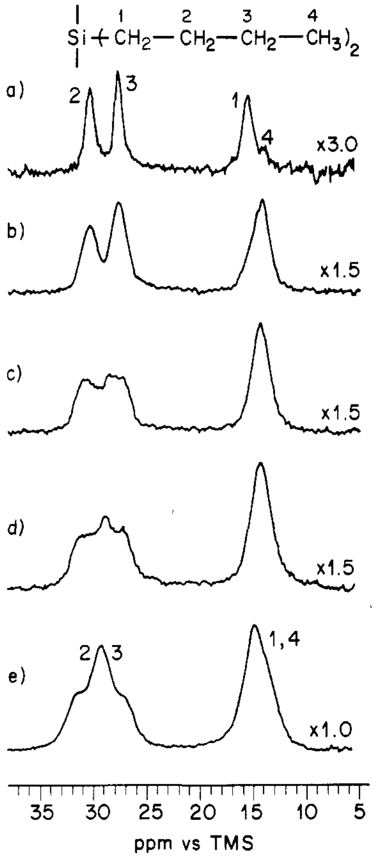


Figure 3. The 50.31-MHz ^{13}C CPMAS/DD solid-state NMR spectra of PDBS at (a) +90 °C, (b) +60 °C, (c) +20 °C, (d) -10 °C, and (e) -60 °C.

temperatures. In contrast, the resonance of phase I in PDHS is found *downfield* (at -21.5 ppm), while in PDBS and PDPS it is *upfield* (at -25.5 and -26.3 ppm, respectively). These higher field positions of the phase I resonances in PDBS and PDPS indicate that in their backbone conformations the silicon nuclei are more shielded than in the trans conformation of phase I in PDHS. This is consistent with the 7/3 helical structure determined by X-ray analysis for PDBS (see below) and PDPS,[7] where each backbone bond is rotated approximately 30° from its trans conformation (see inset in Figure 2). In contrast, the closeness in chemical shift for the phase II resonances of all three polymers indicates a great similarity in the average chain conformation of the disordered phase II in each material, at least over the lengths of conformational sequence of importance to the NMR (ca. five bonds).

To investigate the side-chain structures in PDBS and PDPS, we have examined their ^{13}C NMR spectra. The results of the CPMAS/DD measurements for PDBS at several temperatures are shown in Figure 3. In the spectra recorded at -60 °C the resonances of C_1 and C_4 are unresolved, while the resonances of C_2 and C_3 overlap. Above -40 °C, at which temperature an apparent second-order transition is observed in the thermal data (see above), the shape of the C_2 and C_3 peaks begins to change. At -10 °C a splitting of these resonances is observed with a magnitude similar to that observed for the C_2 and C_5 carbon resonances of phase I in PDHS.[5] For PDBS we are not able to observe specific resonances for phase I and phase II as was the case in PDHS. In MAS spectra of PDBS recorded without CP (not shown) one observes broad, composite resonances at temperatures below +60 °C, which probably reflects the overlap of phase I and phase II resonances at these temperatures. At +90 °C the four carbon resonances are narrow and well resolved. These observations suggest that the conformational and motional characteristics of the alkyl side chains in phase I and phase II are not too dissimilar for PDBS, in marked contrast with the behavior we found earlier[4,5] for PDHS. This is supported by our X-ray results (see below). Note also that most of the line narrowing of the carbon resonances seen in Figure 3 occurs well below the phase I to phase II transition temperature found in our ^{29}Si NMR, X-ray, DSC, and UV data (see below). This suggests that below -40 °C the hydrocarbon side chains are glassy in nature with little local motion. Above -40 °C increased motion is reflected in the narrowing of the resonances and also in the obvious decrease in signal-to-noise ratio obtained with CP. The increase in local chain motion above -40 °C begins to average the carbon–hydrogen dipole–dipole interactions and reduces the enhancement in the CP experiment. At +60 °C, the motion in the side chains is sufficient on the NMR time scale to average differences of chemical environment and conformation; this yields single resonances that are narrowed as compared to the +20 °C spectrum. The fact that the carbon chemical shifts show little change above the transition temperatue of +75 °C (as determined by NMR) indicates that there are only small differences in the average bond conformation of the side chains below and above this temperature. This is not to imply that the side chains are not affected by the phase transition at +75 °C. In fact, the motion of the methyl carbon, C_4, is enhanced above the transition to such a degree that the C_4 resonance is very weak unless the contact time in the CP experiment is significantly increased. Moreover, additional narrowing and loss of intensity for the C_1–C_3 peaks are observed above +75 °C, indicating a substantial increase in local chain motion.

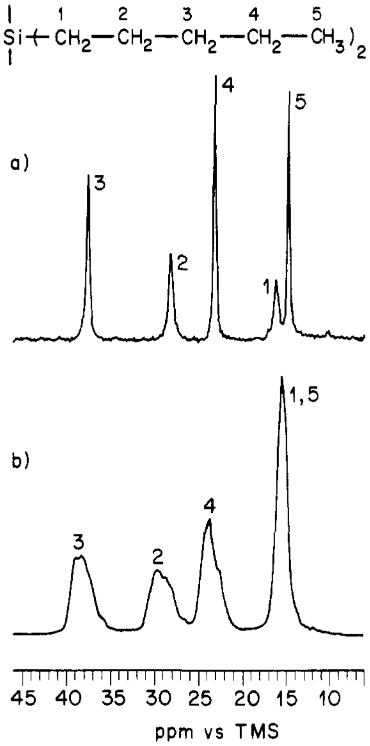


Figure 4. The 50.31-MHz ^{13}C CPMAS/DD solid-state NMR spectra of PDPS at (a) +61 °C and (b) +23 °C.

The solid-state ^{13}C NMR spectra of PDPS are shown in Figure 4. The asymmetric shape of the C_2–C_4 peaks at +23 °C indicates an overlap of several broad resonances. As in the case of PDBS, we are not able to resolve the carbon resonances of phase I and phase II. At +61 °C, above the solid-state phase transition, the resonances narrow significantly, as seen in Figure 4a. As observed in

Table II
^{29}Si Spin–Lattice Relaxation Times (Seconds)

	phase		
polymer	I[a]	II[b]	II[c]
PDBS	350	10.1	5.9
PDPS	240	7.8	6.0
PDHS	11400		5.5

[a] CPT_1 data at +23 °C. [b] IRT_1 data at +23 °C. [c] IRT_1 data above solid-state transition.

Table III
^{13}C Spin–Lattice Relaxation Times (Seconds)

polymer	C_1	C_2	C_3	C_4	C_5	C_6
	+23 °C: Below Solid-State Transition					
PDBS[a]		1.2	0.5	1.4		
PDBS[b]		3.8	0.9, 2.1 0.4, 0.7	2.4, 4.9		
PDPS[b]		3.5	1.0, 1.4	0.7, 1.4		
PDHS[b]	160	140	150	150	110	
	+61 °C: Below Solid-State Transition					
PDBS[a]	0.26	0.5	0.6	1.6		
PDBS[b]		4.8	1.2	5.1		
	Above Solid-State Transition					
PDBS[a,c]	0.17	0.23	0.41	1.60		
PDBS[b,c]	0.18	0.23	0.44	1.40		
PDPS[b,d]	0.16	0.19	0.36	0.72	1.3, 3.5	
PDHS[a,d]	0.15	0.18	0.29	0.55	0.94	2.20

[a] IRT_1 data. [b] CPT_1 data. [c] +83 °C. [d] +61 °C.

the carbon spectra of PDBS and PDHS, there is an obvious increase in line width of carbon resonances of PDPS for nuclei close to the silicon backbone. This reflects the reduced local chain motion resulting from the steric crowding around the polymer backbone. The reduced motion cannot provide complete averaging of the carbon–hydrogen dipole–dipole interactions even at temperatures as high as +100 °C.

To gain additional insight into the nature of the chain motions of the polysilylenes, we measured the spin–lattice relaxation time, T_1, of the silicon and carbon nuclei in PDBS and PDPS and compared the results to those obtained for PDHS. These data are reported in Tables II and III. Measurements were made using both the standard inversion-recovery (IRT_1) pulse sequence[13] and the cross-polarization method (CPT_1) of Torchia.[14] The CPT_1 method is used to probe motions in the ordered phase I structures, while the IRT_1 experiment measures motions in the disordered phase II structures. Looking first at the silicon data in Table II, we observe that at room temperature the T_1's of phase I in PDBS and PDPS are 30- and 50-fold less than the extremely long T_1 in PDHS. These data may reflect some increased local motion in the backbones of PDBS and PDPS, but more likely the shorter T_1's are the result of the substantially increased motion of the side chains in these two polysilylenes (see below). Side-chain motions are particularly important in these polymers since it is primarily the dipolar interaction with the side-chain protons that causes the relaxation of the silicon nuclei. At 23 °C, silicon nuclei of the disordered phase II in PDBS and PDPS have much shorter T_1's than those of phase I, reflecting the substantial local chain motion involved in conformational averaging. Because of the large differences in relaxation times and silicon chemical shifts (see Figure 1) in PDBS, PDPS, and PDHS, it is possible, by using the ^{29}Si NMR experiments, to probe selectively phases that differ in molecular motion. Above the solid-state phase transition of each polymer we observed nearly identical silicon T_1 data, indicating similar backbone and side-chain motions in the high-temperature disordered phase II of these three polysilylenes.

In Table III, the carbon relaxation data at 23 °C reveal T_1's in PDBS and PDPS that are ca. 50-fold shorter than in PHDS. The 110–160 s T_1's for PDHS are similar to those measured in highly ordered crystalline hydrocarbon polymers.[15,16] In comparison, the much shorter T_1's of PDBS and PDPS indicate substantial side-chain motion even in the ordered phase I structures. In the CPT_1 and IRT_1 data of Table III where two T_1 values are reported, the slope of the relaxation curves showed a clear nonlinear character, indicating the presence of two components. For PDBS we were able to obtain individual T_1 results for the two peaks of the C_3 nuclei at +23 °C and found that they were different. In contrast, the T_1's of each component of the doublets observed for both the C_2 and the C_5 resonances of PDHS[5] were identical. Also, one may note that for PDBS different results are obtained in the CPT_1 and IRT_1 experiments. This demonstrates that several motional states are present in this polymer, i.e., those of phase I and phase II. However, the T_1's of these phases are not greatly different, and the chemical shifts of the two phases are apparently similar. As a consequence, it is not possible to vary the parameters of the carbon NMR experiment to probe selectively these distinct motional states in PDBS and PDPS as is the case in PDHS.

At +61 °C, still below the phase transition for PDBS, we continue to observe differences between the CPT_1 and IRT_1 data. At this temperature, the C_3 peak is no longer split and all resonances have narrowed considerably as compared to +23 °C (Figure 3). Therefore, despite the observation of single, relatively narrow carbon resonances at +61 °C (which implies similar average side-chain conformations in phases I and II) the side chain motions in these two phases are different. Only above the transition do the CPT_1 and IRT_1 data of PDBS agree, reflecting a single motional state. In the high-temperature phase II of PDBS, we observe very short T_1's for all the carbon nuclei; these values are very similar for all three polymers. This demonstrates again that the phase II structures of these polysilylenes above their individual solid-state transition temperatures are motionally very similar. On the basis of the carbon relaxation data one can conclude that at room temperature the correlation time of the phase I side-chain nuclei for PDHS is in the microsecond regime, while for PDBS and PDPS it is ca. 100 ns. In all three polymers the correlation time for phase II carbon nuclei above the solid-solid transition is ca. 1 ns.

X-ray Diffraction. The ambient-temperature diffraction pattern of uniaxially oriented PDBS is seen in Figure 5. The pattern is dominated by two strong reflections—a broad equatorial one centered at 1.098 nm and another quasi-meridional one at 0.459 nm (the latter is indeed split into two off-meridional reflections at shorter exposures). The three weaker reflections in the first, second, and third layer lines have *d* spacings of 0.431, 0.424, and 0.397 nm, respectively. The pattern is almost exactly analogous to the one obtained from PDPS,[7] with the exception of the smaller interchain spacing. The structure is consistent with a 7/3 helix, as has been proposed for PDPS[7] and as was also calculated to be the energetically preferred conformation for poly(di-*n*-hexylsilylene) (PDHS).[17] However, we should note that the exact conformational arrangement (particularly as regards the side chains) may be different from that schematically drawn in Figure 1 of ref 17; this is discussed in greater detail (and an alternative is proposed) in ref 18. The smaller average interchain packing in PDBS vs PDPS (1.18 nm)[7] is the

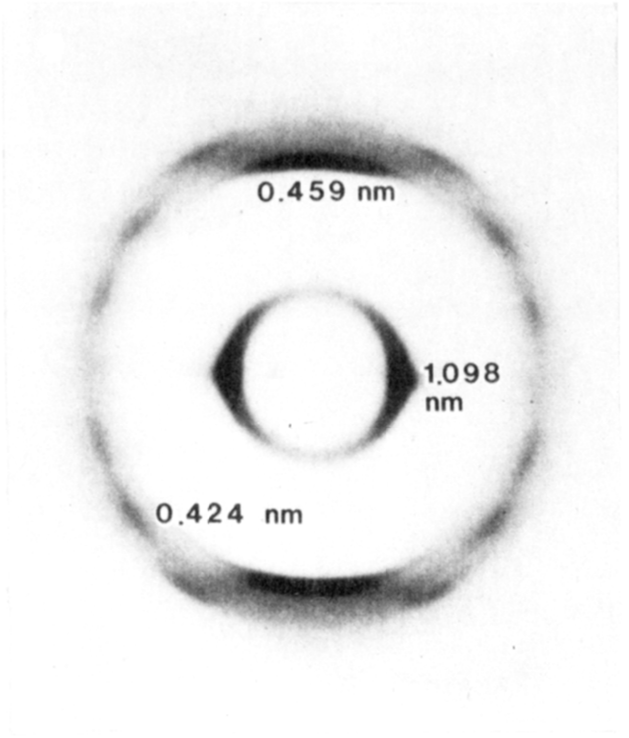


Figure 5. Flat-plate X-ray diffraction pattern of uniaxially oriented PDBS; fiber axis is vertical.

result of the shorter alkyl side chains. Adoption of the same backbone conformation in both PDBS and PDPS suggests that there are no systematic structural differences in polysilylenes based upon odd vs even numbers of carbons in side chains of similar lengths. The fact that PDBS adopts a helical conformation, while PDHS crystallizes in a planar zigzag,[4,6] probably results from the more efficient packing of the longer side chains in a trans-like arrangement, which might also favor better *inter*molecular packing.

The paucity and relative diffuseness of reflections, particularly when compared with the rich pattern of sharp reflections in PDHS (see, e.g., Figure 5a in ref 4), imply a more poorly ordered crystalline structure for the di-*n*-butyl polymer. This applies particularly for the side chains, since the only major reflections are those at 1.098 and 0.459 nm, which are related respectively with the packing and molecular repeat of the *main* chain. These diffraction characteristics also hinder determination of the full crystalline structure. To a first approximation, we may consider the strongest reflection at 1.098 nm as representing an essentially hexagonal or tetragonal intermolecular packing of 7/3 helices. To discriminate between these two possibilities, we utilized long X-ray exposures, whereupon two additional, weak equatorial reflections could be observed (these are not visible in Figure 5). Their spacings are ~0.643 and 0.555 nm, which (within experimental error) identify them respectively with 200 and 220 of an orthohexagonal lattice having a = 1.284 nm and b = 2.224 nm. The c axis is taken as 1.39 nm from the layer-line spacing (this identifies the strong quasi-meridional reflection at 0.459 nm as 103).

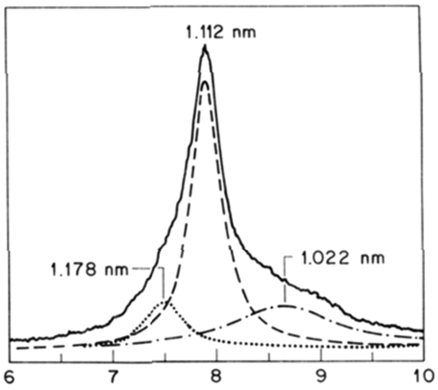


Figure 6. High-resolution diffractometric trace of the major intermolecular reflection of PDBS and its deconvolution into three Lorentzian constituents.

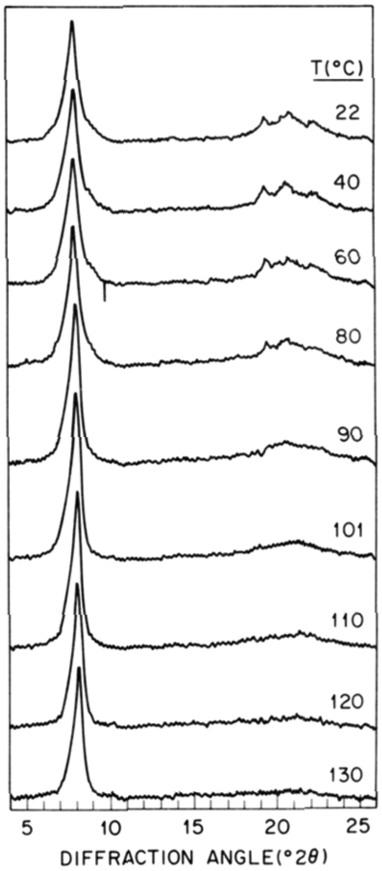


Figure 7. X-ray diffractograms (reflection mode) of PDBS during heating from +22 °C to above the solid-state transition temperature.

The above *ab* plane dimensions would require the major reflection (020, 110) to be centered at 1.112 nm (i.e., slightly higher than observed in the diffraction pattern of Figure 5); this would not be unreasonable on the basis of the breadth of that reflection. For this reason, we attempted high-resolution diffractometric examination of this peak (at a scanning rate of 0.25° 2θ/min) at ambient temperature. As seen in Figure 6, this peak is indeed centered at 1.112 nm but contains two distinct shoulders. The composite peak may be deconvoluted into three Lorentzians centered at the indicated positions (of course, other combinations of peaks having different Gaussian/Lorentzian ratios are also possible). The peaks at 1.178 and 1.022 nm may represent a deviation from strictly hexagonal packing or the presence of a small amount of a different phase.

The effects of heating and subsequent cooling on the crystalline structure of PDBS are seen in Figures 7 and 8, respectively. The observed changes are very small and gradual, especially when compared with the pronounced and discrete manifestations exhibited by PDHS at its first-order thermochromic transition.[4,6]

The *intra*molecular changes accompanying this transition are seen in the behavior of the weak peaks in the

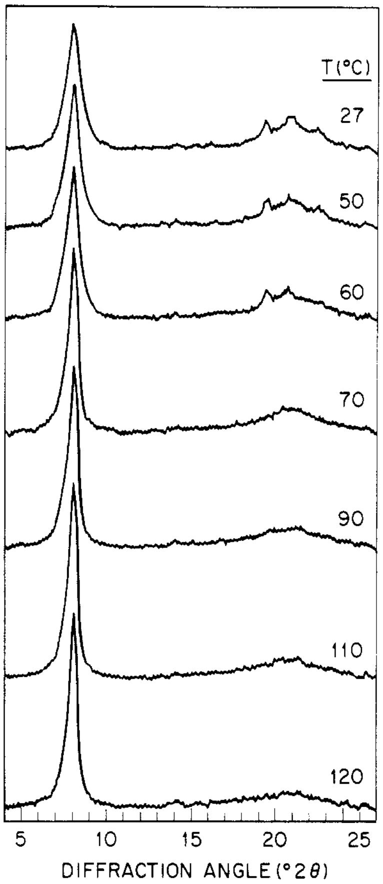


Figure 8. X-ray diffractograms (reflection mode) of PDBS during cooling from +120 to +27 °C.

19–22° 2θ region of Figure 7. These peaks are replaced by a broad, amorphous-like background at temperatures above 80 °C, indicating randomization of the side chains. The fact that the strong, quasi-meridional 013 reflection (seen at ~19° 2θ in Figure 7) is also lost at high temperatures implies a change from the 7/3 helical conformation of phase I to a disordered one (phase II). These intramolecular manifestations of the transition are reversible upon cooling as seen in Figure 8. However, the high-temperature phase II is seen to survive to temperatures at least as low as 70 °C, implying its metastability and the first-order nature of this transition.

As regards the *inter*molecular structure, Figures 7 and 8 demonstrate that crystallographic packing is preserved at all temperatures, even above the disordered transition. This is in agreement with our earlier results from PDHS.[4] However, in contrast to PDHS, there are no large changes in either d spacing or intensity of the intermolecular peak between phases I and II. This is to be expected, since in PDBS the molecular envelope is fairly similar in the 7/3 helical and the disordered conformations.

The minor extent of the intermolecular changes accompanying heating and cooling of PDBS is seen in Figure 9. The d spacing between Si chains is seen to increase slightly during initial heating, as expected from thermal expansion. At the transition region (80–90 °C), there is a small but abrupt contraction as the disordered structure is adopted, with this trend continuing at a slower rate at increasing temperatures. The tighter molecular cross section in phase II is consistent with the ^{29}Si NMR evidence (Figure 1), which shows a downfield shift of ca. 2 ppm (i.e., reduced departure from trans conformers) as the high-temperature structure is adopted. The X-ray manifestations of the interchain spacing are qualitatively reversible upon cooling, and the expected hysteresis in the transition is seen at 60–70 °C (Figure 9b). The interchain peak line width also shows discontinuous changes at the respective transition temperatures during heating and cooling, as seen in Figure 9a,b. The observed narrowing with increasing temperature implies improved lateral coherence, which is consistent with the increased mobility and cylindrical packing of these molecules. We have previously shown similar behavior in PDHS.[4]

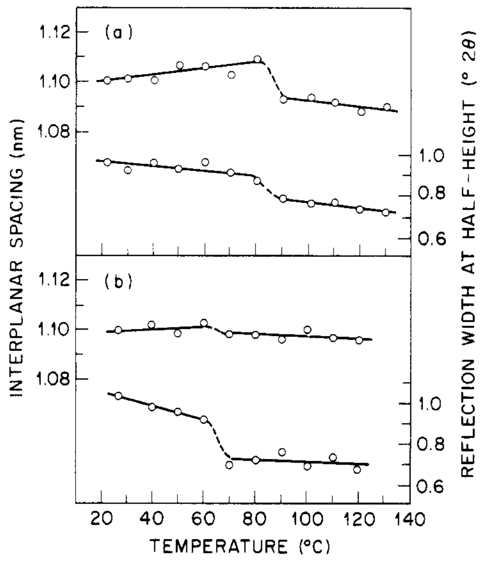


Figure 9. Variation of d spacing and peak width for the major intermolecular reflection of PDBS (at ca. 8° 2θ) during (a) heating and (b) cooling.

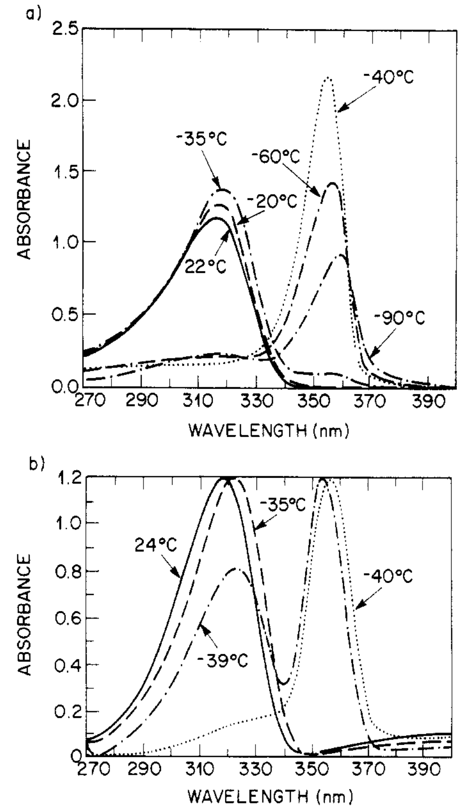


Figure 10. Variable-temperature UV absorption spectra of (a) PDBS and (b) PDPS in hexanes.

Solution UV Spectra. Variable-temperature UV spectra of PDBS and PDPS are shown in Figure 10, parts a and b, respectively. As in the homologous PDHS,[1,2] the spectra of these polymers exhibit abrupt bathychromic shifts in solution, indicative of conformationally associated phase transitions. The absorption maximum of PDBS in hexane solutions shifts drastically from 319 to 355 nm and narrows at a transition temperature of ca. −36 °C, while that of PDPS undergoes a shift from 320 to 353 nm at ca. −39 °C. Trefonas et al. have previously presented variable-temperature solution spectra for PDBS,[2] in which they report extreme breadth for the thermochromic transition (−10 to −61 °C). We were unable to duplicate this result with our materials and experimental procedures. By comparison, PDHS has been reported to exhibit a shift in its solution UV spectrum from 320 to 355 nm at a transition temperature of −31 °C.[1] Consistent with the observed increase of the PDHS transition temperature in toluene solution to −20 °C,[19] this temperature rises to about ca. −23 °C when PDPS is studied in the same solvent.[20] Although it is conceivable that these bathychromic shifts could result from precipitation of the dissolved polymer, the lack of any immediate loss of integrated intensity on going through the transition argues against this interpretation. The absence of any concentration dependence of the transition temperature for PDHS and the presence of an approximately 30-min time lag before the onset of scattering fluctuations in the UV spectrum[1] also point to a phenomenon that is, at root, single chain (i.e., a solution phenomenon) in nature.

The determination of these transition temperatures is sometimes complicated by partial precipitation of the polysilylene after the transition temperature has been reached. This phenomenon is particularly evident when spectra are obtained in sequence without rewarming above the transition temperature between each spectral recording or when the solutions are cooled slowly to the temperature of interest. As can be seen in Figure 10a, after the transition temperature of PDBS is reached (−40 °C), further sequential cooling results in a continued slight red shift to 360 nm at −90 °C, accompanied by a substantial decrease in the integrated absorption intensity. These events are most readily rationalized as resulting from precipitation of the polymer on the cuvette walls, since warming to room temperature followed by rapid cooling to −40 °C reproduces the original −40 °C spectrum identically. Indeed, solutions that have been allowed to stand at temperatures below −40 °C deposit a visible coating of solid polymer on the cuvette walls. Precipitation occurs less rapidly with PDPS; for PDHS, it requires 30 min to become detectable in the absorption spectrum in hexane at a monomer unit concentration of 5×10^{-5} M. This solution behavior can greatly complicate the interpretation of variable-temperature UV experiments performed at low concentrations (10^{-5}–10^{-4} M in monomer) on these materials and even become dominant when higher concentrations are necessary (e.g., for light scattering).

Solid-State UV Spectra. The solid-state variable-temperature UV spectra of PDBS and PDPS are shown in Figure 11. At 23 °C, the spectrum of PDBS has a λ_{max} at 313 nm and a full width at half-maximum ($\omega_{1/2}$) of 20 nm. At around 70 °C, the spectrum broadens to $\omega_{1/2}$ of 34 nm and shifts to 315 nm. Additional broadening and bathychromic shifts occur with further heating until, at 85 °C, the $\omega_{1/2}$ is 45 nm with a λ_{max} of 320 nm. Spectra recorded from −50 to +23 °C are nearly identical. Thus, in contrast to the case of PDHS, the spectra of which undergo relatively abrupt changes over a few degrees near the 42 °C disordering temperature,[6] the thermochromic transition of PDBS is much more gradual and less pronounced, consistent with our NMR and X-ray results.

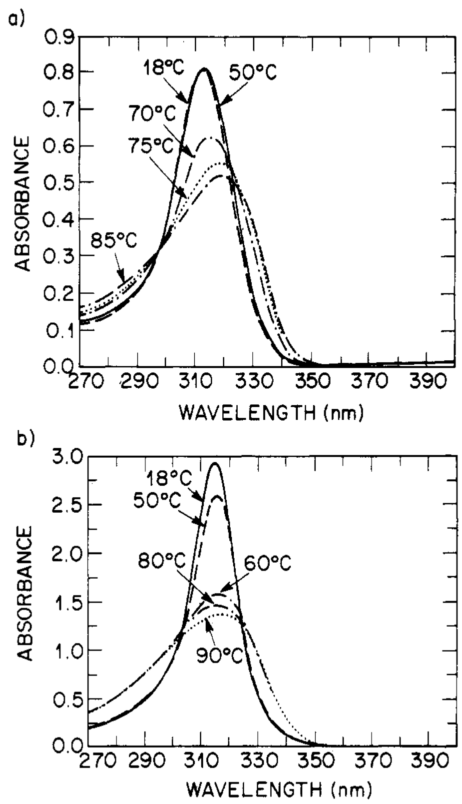


Figure 11. Variable-temperature solid-state UV absorption spectra of (a) PDBS and (b) PDPS.

Miller et al.[7] have previously reported that in PDPS the solid-state UV absorption position remained unchanged but the half-width more than doubled to 58 nm above 80 °C. No intermediate-temperature spectra were reported. The room-temperature spectrum of PDPS in Figure 11b is essentially identical with that reported in the previous work.[7] The thermochromic phenomena in this polymer resemble those in PDBS, in that they occur over a wide temperature range, result in considerable broadening of the spectrum with only a small shift of the absorption maximum, and show no obvious relationship to the disordering temperature detected by DSC. At 60 °C, 10 °C below the first-order disordering transition, the spectrum is very similar to that obtained at 90 °C, 20 °C above this transition. As expected from the degree of supercooling observed in the DSC, recovery of the original room-temperature spectrum of PDPS following disordering is largely incomplete even after 18 h at 23 °C. The relative narrowness of the solid-state spectra of PDBS and PDPS, quite similar in breadth to that of highly crystalline PDHS,[11] which has been shown to adopt an all-trans conformation in the solid state,[3-6] suggests a relatively highly ordered, albeit different, solid-state structure for these two polysilylenes, at least out to backbone lengths of about 30 silicon–silicon bonds; beyond this the absorption maximum becomes insensitive to further silicon catenation.[21] These observations are consistent with the X-ray and NMR results discussed above.

The long-wavelength limit in the *solid state* is substantially different for PDBS and PDPS (about 320 and 315 nm, respectively) vs PDHS (374 nm), while the limiting wavelength in *solution* for these two materials (355 and 353 nm, respectively) is essentially identical with that of PDHS (355 nm). These observations suggest that the low-temperature solution structures of PDBS and PDPS are similar to that of the low-temperature solution form of PDHS but that the solid-state structures are substantially different from that of PDHS. This constitutes strong evidence that the solution and solid-state thermochromic phenomena are *not* strongly related and questions those interpretations of the solution effects that invoke side-chain microcrystallization[2] as an explanation. Indeed, the recent report of well-defined abrupt thermochromism in atactic poly(*n*-propylmethylsilylene)[22] and other atactic polysilylenes[23] argues strongly against such an interpretation, since these polymers would be expected to be extremely reluctant to form structures with well-defined side-chain order, given their inherent configurational disorder.

Conclusions

The solid-state structures of PDBS and PDPS are very similar. X-ray diffraction studies of these materials indicate that the backbone conformation is a 7/3 helix, which is significantly different from the all-trans conformation found in PDHS. The crystalline structure of PDBS is less ordered than that of PDHS and has quasi-hexagonal intermolecular packing. A first-order phase transition is observed at ca. 85 and 70 °C for PDBS and PDPS, respectively. The 7/3 helical conformation of these polymers is changed to a disordered structure above this solid-state transition, as is observed in PDHS. At all temperatures studied the interchain packing of PDBS is preserved and, in contrast to PDHS, almost no change in the lattice dimensions is observed when phase I is converted to phase II.

The average molecular conformation and the local chain motions of the backbone and side chains of phase II in these three symmetrically substituted polysilylenes are very similar, at least over the lengths of bonds probed by NMR. In PDHS it is observed that ordered backbone and side-chain structures of phase I become conformationally disordered at the same temperature. On the basis of NMR chemical shift and relaxation data, we can conclude that in PDBS and PDPS the side chains begin to disorder at temperatures significantly lower than the disordering temperature of the silicon backbone. In PDBS the side chains apparently begin to do so at ca. −40 °C. This may contribute to the much lower enthalpies observed for the solid-state disordering transitions of PDBS and PDPS (as compared to PDHS) and the paucity and weakness of their X-ray peaks.

As in PDHS, an abrupt first-order transition-like bathychromic shift is observed in the solution UV spectra of PDBS and PDPS upon cooling. The observation of a constant integrated intensity on moving through this transition in solution strongly suggests that this phenomenon is a single-chain property not associated with precipitation of the polymer. This thermochromism is apparently the result of a conformational transition from a random coil[24] to an extended conformation whose primary conformer is trans. A reversible transition between extended and random coil conformations is rarely if ever seen in polymer chains other than those of biological or biorelated origin, such as the polypeptides and polynucleotides. These symmetrically substituted polysilylenes seem to provide uniques examples of such behavior in σ-bonded synthetic polymers of relatively simple structures in which hydrogen bonding does not play a part. The thermochromism observed in these polysilylenes is similar to that reported for the π-bonded polydiacetylenes.[25,26]

In contrast to PDHS, where upon cooling an abrupt bathychromic shift is also observed at the solid-state disordering transition, there is no obvious correlation in the absorption characteristics of PDBS and PDPS with their respective solid-state transition temperatures. The longer wavelength absorption observed for the phase I structure of PDHS is clearly associated with the all-trans backbone conformation, a structure not found in either PDBS or PDPS. The solid-state thermochromic manifestations of PDBS and PDPS are strikingly different from either their behavior in solution or from that of the homologue PDHS. Unlike PDHS, whose thermochromism in the solid state is similar to its solution thermochromism (i.e., abrupt and bathychromic), the solid-state transitions in PDBS and PDPS occur over a broad range, show no discernible connection to the DSC-determined disordering transition, and move with temperature in the opposite direction from the solution effects. These data provide strong evidence that the solution and solid-state thermochromic phenomena are not governed by the same factors.

We are continuing our studies of the relationship between the solid-state structures and thermochromism of the symmetrically substituted polysilylenes, with particular interst in the effects of temperature and pressure in producing specific structures and absorption characteristics. The initial results of these studies are published elsewhere.[18]

Acknowledgment. We thank P. P. Ward for assistance in acquiring UV thermochromism data. The work performed at Sandia National Laboratories was supported by the U.S. Department of Energy under Contract No. DEAC04-76DP00789.

Registry No. PDBS (homopolymer), 97036-65-2; PDBS (SRU), 95999-72-7; PDPS (homopolymer), 97036-66-3; PDPS (SRU), 96228-24-9.

References and Notes

(1) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.

(2) Trefonas, P.; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.

(3) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.

(4) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657.

(5) Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2660.

(6) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413.

(7) Miller, R. D.; Farmer, B. L.; Fleming, W.; Sooriyakumaran, R.; Rabolt, J. *J. Am. Chem. Soc.* **1987**, *109*, 2509.

(8) Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Zeigler, J. M. In *Advances in Chemistry Series*; Zeigler, J. M., Fearon, F. G., Eds.; American Chemical Society: Washington, D.C., in press.

(9) Zeigler, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 109.

(10) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 424.

(11) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.

(12) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.

(13) Levitt, M. H.; Freeman, R. *J. Magn. Reson.* **1979**, *33*, 473.

(14) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.

(15) VanderHart, D. L. *Macromolecules* **1979**, *12*, 1232.

(16) Axelson, D. E. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; p 193.

(17) Farmer, B. L.; Rabolt, J. F.; Miller, R. D. *Macromolecules* **1987**, *20*, 1167.

(18) Walsh, C. A.; Schilling, F. C.; Lovinger, A. J.; Davis, D. D.; Bovey, F. A.; Zeigler, J. M. *Macromolecules*, in press.

(19) Harrah, L. A.; Zeigler, J. M. In *Advances in Chemistry Ser.*; Zeigler, J. M., Fearon, F. G. Eds.; American Chemical Society: Washington, D.C., in press.

(20) We have also examined the thermochromism of PDBS in toluene. At about −25 °C, the 317-nm absorption begins to be replaced by two new absorptions, at 337 and 358 nm. On further cooling, the 337-nm absorption grows and then declines, to be replaced by the 358-nm absorption. At −90 °C, the 358-nm peak is the major absorption; at the same temperature, the 337-nm band essentially disappears. These effects result in no significant change in the total integrated intensity; thus, precipitation appears to be excluded as a rationalization for the complexity of these phenomena.

(21) Miller, R. D.; Hofer, D.; McKean, D. R.; Wilson, C. G.; West, R.; Trefonas, P. T. In *Materials for Microlithography*; Thompson, L. F., Wilson, C. G., Frechet, J. M. J., Eds.; Am-

Macromolecules 1989, *22*, 3063–3075 **3063**

erican Chemical Society: Washington, D.C.; Symposium Series, 1984; Vol. 266, pp 293–310.

(22) Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, D.C., 1987; pp 482–498.

(23) Harrah, L. A.; Zeigler, J. M. *Bull. Am. Phys. Soc.* **1985**, *30*, 540.

(24) Cotts, P. M.; Miller, R. D.; Trefonas, P., III; West, R.; Fickes, G. N. *Macromolecules* **1987**, *20*, 1046.

(25) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522.

(26) Plachetta, C.; Rau, N. O.; Schulz, R. C. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 141.

Concentration Dynamics in Polymer Blends and Block Copolymer Melts

Kyozi Kawasaki* and Ken Sekimoto

Department of Physics, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan.

Received March 15, 1988; Revised Manuscript Received October 28, 1988

ABSTRACT: The theory of slow dynamics of monomer concentrations in polymer blends and block copolymer melts developed earlier by the present authors is reconsidered when the incompressibility condition is replaced by the condition of constant chemical potential for the total monomer density. This results in modifications of earlier results even for the symmetric polymer blends where the same results are obtained for macroscopic interdiffusion. Linearized equations of motion for concentration deviations from homogeneous states as well as from the equilibrium lamellar state are derived, the latter giving rise to phase equations for long-wavelength deformations of lamellae. For blends in the strong segregation regime, we find the diffusion along interfaces of the type considered by Mullins, giving rise to the $^1/_4$ power law for the domain growth in time. This process, however, is masked by faster hydrodynamic growth process.

1. Introduction

Dynamics of macroscopic phase separation in polymer blends and microphase separation in block copolymers is one of the most interesting but still poorly understood problems in phase transition studies and in polymer sciences.[1] A major source of difficulty resides, of course, in our incomplete understanding of chain dynamics in polymer melts. Nevertheless, a wealth of experimental studies has been accumulated that motivates one to attempt theoretical understanding of these problems. We presented such attempts[2] stimulated by the pioneering works of de Gennes, Pincus, Binder, and others.[3] One of the crucial assumptions made in these theories is that the system is totally incompressible. A consequence of this is that polymer chains cannot move independently even for the mean field type reptation model, but correlations are introduced among moving parts of chains that form temporary rings.[2,4]

Difficulty of polymer chain dynamics in melts, however, precludes a priori judgement of validity of incompressibility, for which we must rely on tests by laboratory experiments or computer simulations.

Experimental tests of the incompressibility assumption have been performed recently for the related but somewhat different problem of interdiffusion in compatible polymer blends. Here two theories have so far been put forward that give quite different predictions. One is based on the incompressibility assumption[5] (slow process) whereas the other assumes the constant chemical potential for the total monomer density[6] (fast process). The available experimental evidence seems to exclude the prediction based on the incompressibility assumption.[6] In Appendix A we discuss the problem of bulk flow in the context of this work. This development thus necessitates reconsideration of earlier theories of phase-separation dynamics, which is the purpose of this paper.

In the next section we summarize the main results of this work and intuitive discussions will be given wherever appropriate. Derivations of these results and some formal developments are contained in the sections that follow. This reconsideration is important even for the so-called symmetric polymer blends[6] where the difference between the two theories vanishes for macroscopic interdiffusion taking place in the homogeneous background (Appendix A). In section 3 we develop a general theory of concentration dynamics for polymer blends and diblock polymers in which only relative monomer concentrations are the slow variables. This means that the total monomer density is eliminated by requiring that the chemical potential associated with the total monomer density is constant. The theory is first applied in section 4 to the simplest problem of dynamics of small concentration deviations from the uniform background in blends and diblocks. Section 5 deals with linear dynamics of small concentration deviations in the equilibrium lamellar phase of diblocks. The result is used in section 6 to investigate dynamics of smooth deformations of lamellar structure, which can be shown to be described by a phase equation. Explicit results are obtained for the weak segregation regime. In section 7 we are concerned with the late-stage phase separation of blends where the problem can be reduced to dynamics of interfaces.

2. Main Results with Intuitive Discussions

In this section we summarize main concrete results of this paper and also give intuitive explanations wherever appropriate. We first take up the slow dynamics of the smooth deformation field $u(\mathbf{r}, t)$ of the lamellar mesophase pattern of the block copolymer system. This is an analogue of the deformation of roll patterns in Rayleigh–Benard convection or of layers in the smectic A phase of liquid crystals.[7] Here, $u(\mathbf{r}, t)$ is found to satisfy the following phase equation[8] when the undeformed lamellae are in the xy plane

$$\frac{\partial}{\partial t}u(\mathbf{r}, t) = \left(D_z\frac{\partial^2}{\partial z^2} + D_\perp \nabla_\perp{}^4\right)u(\mathbf{r}, t) \qquad (2.1)$$

where $\nabla_\perp{}^4 = (\nabla_\perp{}^2)^2$ with $\nabla_\perp{}^2 \equiv (\partial/\partial x)^2 + (\partial/\partial y)^2$. The two terms in (2.1) describe the two types of deformations shown, respectively, by the left and right figures of Figure 1. For the compressible case now under consideration and in the weak segregation regime the coefficients in (2.1) are

0024-9297/89/2222-3063$01.50/0