(14) It should be noted that the value of the normalized extent of photoisomerization for azobenzene is slightly smaller and that for 4,4′-dinitrostilbene is slightly larger than the ones we previously reported.[2] In the present study, we were able to compensate for the red shift in films by altering the photoisomerizing wavelength. This changed the normalized extent of photoisomerization values slightly.

(15) These films had undergone no physical aging prior to photoisomerization. A publication is in preparation that gives experimental findings on the effect of physical aging on the extent of isomerization of photochromic probes.

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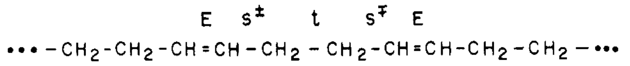
Variable-Temperature, High-Resolution Solid-State Carbon-13 NMR Study of 1,4-*trans*-Polybutadiene

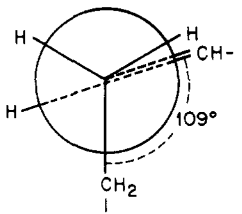
It has long been known[1] that 1,4-*trans*-polybutadiene (TPBD) exists in two crystalline polymorphs. At room temperature, the chain conformation of form I is as follows:[1,2]



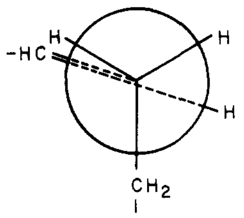
$$\mathrm{E}\quad \mathrm{s}^{\pm}\quad \mathrm{t}\quad \mathrm{s}^{\mp}\quad \mathrm{E}$$

$$\cdots-CH_2-CH_2-CH{=}CH-CH_2-CH_2-CH{=}CH-CH_2-CH_2-\cdots$$

where the double bond is of course trans ("E") and $s^{\pm}$ (or $s^{\mp}$) designates approximate skew conformations:



s^{+}



s^{-}

In the exact skew conformation, the C=C and C—H bonds are eclipsed and the dihedral angle is 120°. The chain packing is a hexagonal array. Above approximately 75 °C the stable form, called form II, is of lower density but with the chains still parallel to each other and still in a hexagonal array.[3–6] They are believed to be in a disordered state, as judged by the blurring of all nonequatorial reflections in the X-ray diffraction pattern, and the marked decrease of the second moment of the wide-line proton NMR spectrum[7] indicates the onset of molecular motion. However, the details of the form II chain conformation and the nature of the motion are not well established. Suehiro and Takayanagi[3] proposed that the chain has a single definite structure, similar to that of form I except that the skew angle is decreased from ±109° to ±80°. They further proposed that the motion consists of large torsional oscillations about the carbon–carbon single bonds. Evans and Woodward[5] employed this conformation to calculate the heat capacity of form II and reported good agreement with experiment below and above the form I → form II transition; they did not consider chain motion nor attempt to calculate the heat capacity during the transition. Iwayanagi and Miura[7] proposed that instead of undergoing large torsional oscillations the chains are rotating about their long axes. Wunderlich et al.[8,9] made thermodynamic calculations similar to those of Evans and Woodward[5] but assumed a conformationally disordered state for form II. De Rosa et al.[6] also proposed a disordered conformation—based on packing energy calculations—consisting of a 50:50 equilibrating mixture of (a) and (b):

$$\text{(a)}\quad \mathrm{E}\quad \mathrm{s}^{\pm}_{(90°)}\quad \mathrm{t}\quad \mathrm{s}^{\mp}_{(90°)}\quad \mathrm{E}$$

$$\text{(b)}\quad \mathrm{E}\quad \mathrm{s}^{\pm}_{(90°)}\quad \mathrm{t}\quad \mathrm{cis}\quad \mathrm{E}$$

This corresponds to a 25% probability of cis for CH–CH_2 bonds.

We have previously reported[10] the solid-state ^{13}C NMR spectra of TPBD at room temperature. The results demonstrate that it is possible to independently observe carbon nuclei in the crystalline and the mobile fold surface regions of TPBD single crystals. The olefinic and methylene carbons in the folds appear from their chemical shifts to have essentially the same average conformation as the 1,4-trans sequences in amorphous bulk polybutadiene. In addition, the ^{13}C spin–lattice relaxation times (T_1) of the folds are observed to be the same as for amorphous polymer,[11] indicating that chain motions in the two phases are similar.

In this work we examine the conformational and motional properties of the chains in the crystalline region of TPBD as a function of temperature. The 50.31-MHz cross-polarized (CP), magic-angle spinning (MAS), dipolar-decoupled (DD) spectra were recorded at 23–80 °C on a Varian XL-200 spectrometer by using a Doty Scientific probe with Al_2O_3 rotors and the standard Varian temperature controller. Sample spinning rates of 2.5–5.0 kHz and a high-power, dipolar decoupling level of ca. 10 G were employed. The TPBD sample was a fraction ($\bar{M}_v = 2.5 \times 10^4$) of a polymer synthesized by the rhodium chloride catalyst method.[12] Following solution fractionation the material was dissolved in toluene and precipitated from methanol. The sample morphology is probably multilamellar in nature.[13]

In Figure 1 are shown CPMAS/DD spectra as a function of temperature. The spectrum at 23 °C was obtained by using a 1.0-ms contact time and shows single olefinic and methylene resonances for the crystalline stems of form I. As the temperature is increased new resonances appear at higher field positions for both carbons, reflecting the onset of the solid–solid phase transition. At temperatures where both form I and form II are present a contact time of 2.0 ms was chosen to permit observation of both forms. However, we must emphasize that because of substantial differences in chain mobility (vide infra) the intensities of these resonances do not quantitatively reflect the ratio of these phases. Despite this, we can estimate the midpoint of the transition to be ca. 60 °C; it is essentially complete at 65 °C. It should be noted that the midpoint observed in the initial heating of solution-crystallized TPBD is ca. 50 °C. The higher transition point observed following cooling and subsequent heating is probably the result of crystalline annealing during the first heating.

At 23 °C the chemical shifts of the olefinic and methylene carbons of form I are 130.7 and 35.2 ppm, respectively.[14] Those of form II are more shielded by 1.2 and 1.8 ppm, differences very close to those reported for fold surface (i.e., amorphous) carbons versus crystal stem carbons for form I.[11] Despite the close similarity in chemical shift between the crystal stem carbons of form II and amorphous carbons, individual resonances can be observed in non-cross-polarized spectra. These phases can be clearly differentiated in the course of an inversion–recovery[16] T_1 measurement. In Figure 2 are shown the T_1 spectra for the methylene carbons observed at 70 °C and

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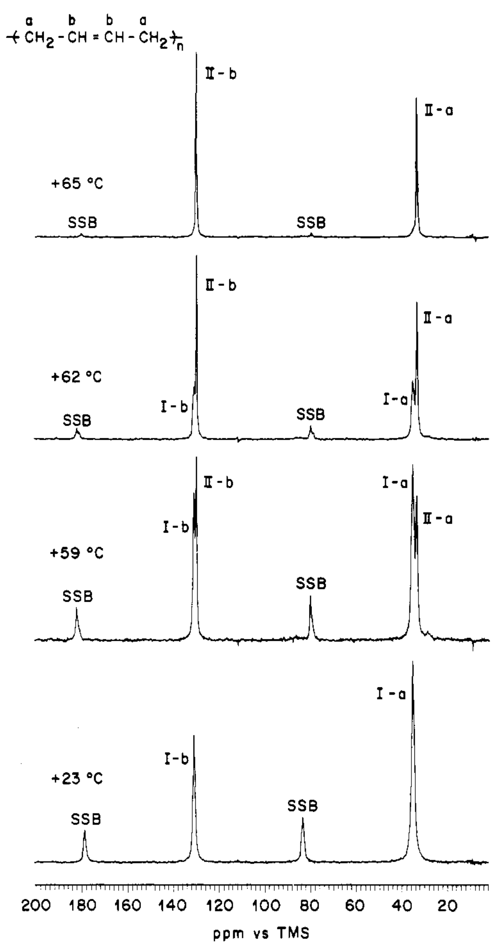

Figure 1. ^{13}C NMR CPMAS/DD spectra, 50.31 MHz, of 1,4-*trans*-polybutadiene (I = form I; II = form II).

therefore representing only form II. The fully relaxed spectrum (τ = 25 s) shows partial resolution of the two phases. Near the null one observes both positive and inverted resonances, clearly indicative of two phases relaxing at different rates. As a result of the partial overlap of the methylene resonances in Figure 2, accurate T_1's cannot be determined from this inversion–recovery data. The T_1 data measured by the cross-polarization method (CPT_1)[17] is shown in Table I. The form II stem carbons exhibit values of 10.5 and 12.2 s for CH_2 and CH, respectively. The value for the methylene carbons in the fold is estimated from the null point in Figure 2 to be ca. 0.7 s. These carbons are more shielded than the stem carbons by 0.6 ppm. It should be noted (Table I) that for form I at 23 °C the T_1 values are 0.33 and 0.65 s for the surface fold CH_2 and CH, respectively, while the crystal stem carbons exhibit much longer values having two components: 55 and 130 s for CH_2 and 53 and 123 s for CH. The shorter values may correspond to monomer units near the crystal surface.[18] The markedly greater shielding of the form II stem carbons is difficult to understand on the basis of the conformation proposed by Suehiro and Takayanagi,[3] nor can the profound difference in carbon T_1 values for form I and form II stems be explained merely by torsional oscillations. Both observations seem consistent, however, with the disordered conformation suggested by De Rosa et al.,[6] possibly combined with chain rotation, as proposed by Iwayanagi and Miura.[7]

Additional insight into the nature of the chain motion in TPBD can be obtained from observing the nonspinning ^{13}C spectra as a function of temperature. The CP/DD spectrum at 23 °C in Figure 3a, corresponding to form I, shows that the olefinic carbon has an axially asymmetric chemical shift anisotropy, as previously reported.[11] The value of $\sigma_{11} - \sigma_{33}$ is ca. 178 ppm. The spectrum of form II recorded at 83 °C without CP[19] (Figure 3b) shows a dramatic narrowing in the powder pattern as a result of chain motion. The form of the pattern at 83 °C indicates a very anisotropic motion since the shift tensor does not simply average to the isotropic value, σ_i; instead the pattern of both the olefinic and methylene carbons shows an unsymmetrical change in addition to a growth in intensity at the isotropic positions. Of course, without CP a fraction of the intensity observed at σ_i must be attributed to the amorphous carbons.

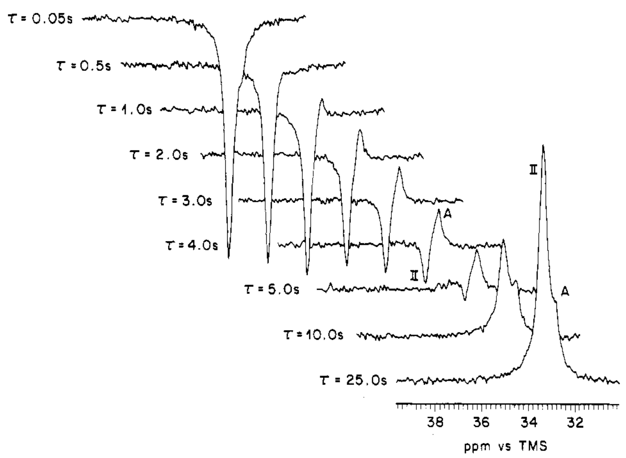

Figure 2. ^{13}C NMR inversion–recovery spectra, 50.31 MHz, of the methylene carbons in 1,4-*trans*-polybutadiene at 70 °C (II = form II; A = amorphous).

Table I
Carbon-13 Cross-Polarization T_1's (s) for 1,4-*trans*-Polybutadiene

		stem		fold	
temp, °C	form	CH_2	CH=	CH_2	CH=
23.0	I	55, 130	53, 123	0.33[a]	0.65[a]
50.5	I	28, 69	40, 75		
60.0	I	23, 56	28, 66		
60.0	II	8.5	9.1		
70.0	II	10.5	12.2	~0.7[b]	

[a] Inversion–recovery measurement. [b] Estimate from inversion–recovery null point (Figure 2).

Additional evidence for the presence of conformational disorder is found in the differential scanning calorimetry (DSC) for TPBD, recorded on a Perkin-Elmer DSC-4 employing a heating rate of 10 °C/min. A large endotherm at 67 °C is associated with the form I → form II transition and a much smaller endotherm at 133.2 °C is associated with melting. The entropy of the solid–solid transition (ΔS_{tr}) in TPBD has been shown experimentally to be 1.6–2.0 times the energy of melting (ΔS_m) depending on sample preparation.[20] A similar observation is reported in the DSC study of cyclic alkanes. For cyclotetraeicosane[21] a large endotherm associated with the onset of conformational averaging is observed to accompany the first-order solid–solid transition at 24 °C. The conformational averaging results from a "bicycle chain" motion within the crystal (i.e. rotation about an axis perpendicular to the plane containing the cyclic molecule). At 49 °C a much smaller endotherm, associated with the melting process, is observed.

In an earlier report[10] it was shown that the treatment of TPBD crystals with *m*-chloroperbenzoic acid results in the epoxidation of the surface folds only and not the crystal stems. The solid-state ^{13}C NMR spectra showed that the

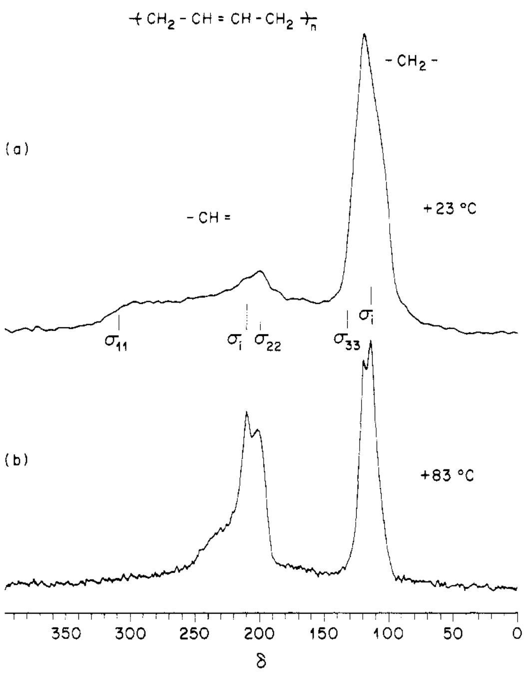

Figure 3. ^{13}C NMR nonspinning DD spectra, 50.31 MHz, of 1,4-*trans*-polybutadiene: (a) form I with CP and (b) form II without CP.

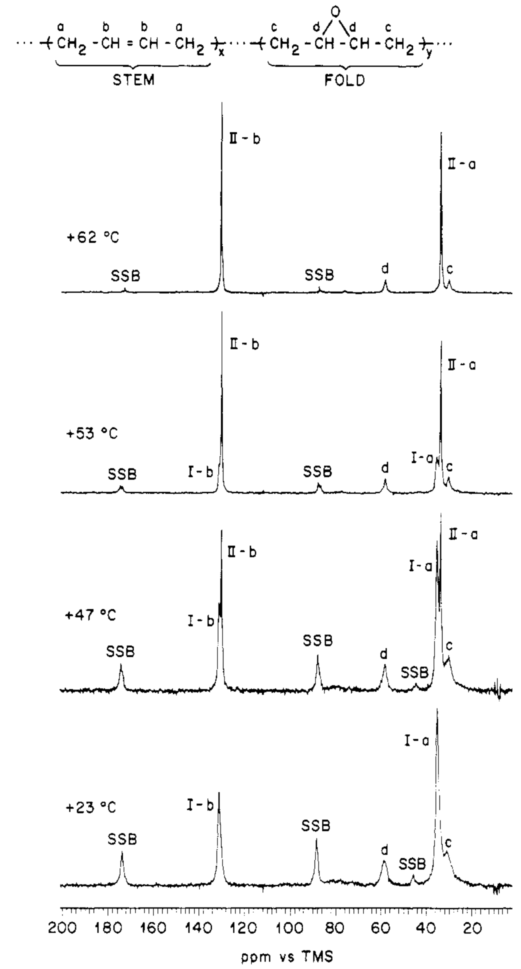

Figure 4. ^{13}C NMR CPMAS/DD spectra, 50.31 MHz, of crystal surface epoxidized 1,4-*trans*-polybutadiene (I = form I; II = form II).

epoxidation results in the immobilization of the surface folds and that the oxirane rings have probably raised the T_g of the fold surface above room temperature. In the present work we find this conclusion is supported by the observation of a ^{13}C T_1 of ~5 s for the oxirane carbons as compared to 0.6 s for the CH carbons in the folds of nonepoxidized TPBD. We have also examined the epoxidized polymer (28% total epoxidation) at various temperatures to observe the effect of this treatment upon the solid–solid transition. There is little change in the behavior of the sample as compared to that of untreated TPBD. The ^{13}C CPMAS/DD spectra shown in Figure 4 indicate the midpoint of the transition is ~47 °C, similar to the midpoint observed in the initial heating of the nonepoxidized TPBD material. Subsequent temperature cycling of the epoxidized sample does not change the midpoint of the transition because the immobilized surface prevents thickening of the crystals by annealing. In addition, examination of the X-ray diffractograms of TPBD and epoxidized TPBD shows identical crystalline structures for the two materials as indicated by the position of the main reflection at $2\theta = 22.5°$. The fact that the presence of immobilized oxirane rings on the surface of the crystal does not prevent or even perturb the solid–solid phase transition indicates that the folds are not involved in the phase transition of TPBD in any significant manner. We also conclude that there is probably little motion along the direction of the crystalline stem in form II. Such motion would require movement of the oxirane folds, which appear to be immobile at 47 °C, as evidenced by the broadened resonances (Figure 4) for the oxirane CH and CH_2 carbons.

High-energy irradiation of TPBD crystals is observed to initiate an expansion of the crystal lattice at room temperature in a manner similar to that observed at the form I → form II transition. We expect that such irradiation will cause cross-linking, which in turn will inhibit motion within the crystalline regions of this analogue of form II. The details of this new structure, in addition to a more complete discussion of the relaxation data and chemical shift anisotropy of TPBD, will be given in a subsequent publication.

Registry No. TPBD, 9003-17-2; 3-$ClC_6H_4CO_2H$, 535-80-8.

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Sol-Gel Transition of Hydrolyzed Polyacrylamide + Chromium III: Rheological Behavior versus Cross-Link Concentration

Sol-gel transition investigations usually proceed by measuring the time evolution of the relevant quantities[1] during the chemical reaction leading to gelation and the results are compared to the predictions of the theoretical models assuming that the experimental parameter (the time) and the theoretical one (the number of cross-links) are linearly related in the vicinity of the transition. This assumption is not obvious and we have studied a system polymer + cross-linker in which we have been able to determine the number of cross-links formed as a function of the concentrations of polymer and cross-linkers.[2] This system consists of high molecular weight hydrolyzed polyacrylamide ($M_w \cong 6 \times 10^6$, degree of hydrolysis $\cong$24%[3]) and chromium(III) salt in an aqueous solution containing 20 g/L of NaCl, which is a good solvent for the polymer.[4] In addition, it is a good example of the various systems of practical interest.

Rheological measurements have been performed by using a magnetic sphere rheometer[5,6] whose ranges of shear rates and deformations and times of measurements as long as 2000 s allow the determination of the steady-state zero-shear viscosity and the steady-state linear elastic modulus up to the vicinity of the transition. Since the cross-link formation proceeds through a ligand substitution reaction on chromium(III), the kinetics are very slow. We have been able to follow the evolution of the rheological quantities and to determine accurately the equilibrium values which are reached about 50 h after the preparation of the samples achieved by mixing equal volumes of polymer and chromium solutions. The equilibrium concentration of cross-links has been determined by a UV-visible spectrophotometric study of the chromium complexes. We have made a comparison with a low molecular weight model of the polymer to ensure that no complexation enhancement occurs in the range of concentrations where the rheological measurements are performed.[2] Figure 1a presents the results of a systematic study done with 2500 ppm in polymer (about 2 times the chain overlapping concentration) as a function of the concentration in cross-links (c_l). The divergence of the viscosity and the smooth increase from zero of the elastic modulus are characteristic of critical behavior.

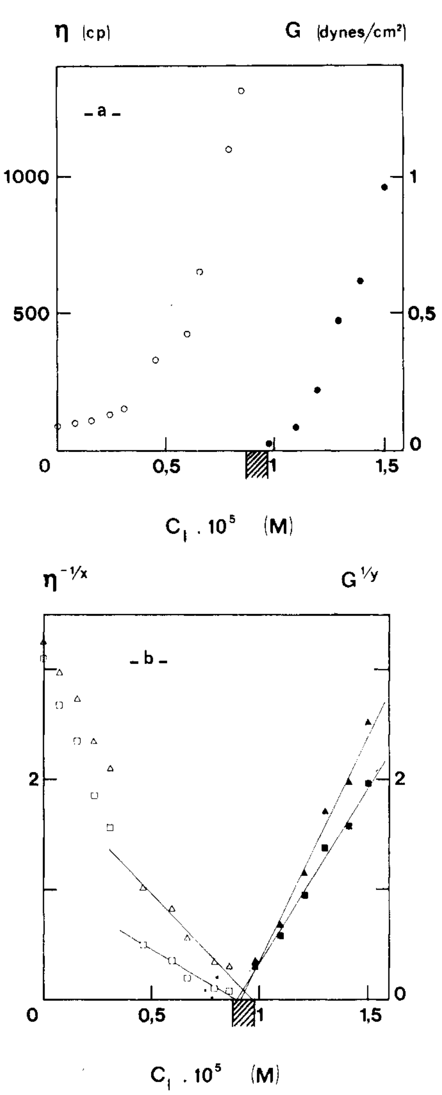

Figure 1. (a) Variations of the viscosity (○) and of the elastic modulus (●) versus concentration in cross-links. (b) Variations of $\eta^{-1/X}$ and $G^{1/Y}$, in arbitrary units, for different values of X and Y: (□) $X = 0.7$; (△) X = 1.1; (▲) Y = 1.8; (■) Y = 2. The chosen values of κ and θ are those for which the experimental points lie on a straight line intersecting the c_l-scale within the interval in which $c_{l,c}$ is located (shaded range).

The gel point, $c_{l,c}$, is unambiguously located between the last point in the viscous regime (8.7×10^{-6} M) and the first one in the elastic regime (9.7×10^{-6} M). If the molecular weight of the polymer is taken into account, the number of cross-links per chain at the threshold is found to be of the order of 11. This value is much larger than the value predicted by the classical theory which is one per chain[7] (it corresponds to c_l equal to 0.8×10^{-6} M). We have attributed this large discrepancy to the formation of small intrablob loops: indeed, the binding probability between the monomers of the same chain in a good solvent falls off quickly with the chemical distance.[8] Assuming that the sizes of the loops are related to the persistence length, the number of monomers in the loops is only 1% of the total number of monomers. Therefore, the contour length of the chain and consequently its mechanical properties are negligibly affected by the loops. This result has been corroborated by viscometric measurements performed in the dilute regime.[9] Moreover, at a constant polymer

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