istry program (Grant No. DMR-8553275 to J.E.R.). Additional support through the NSF Presidential Young Investigator (J.E.R.) program was obtained from American Cyanamid, Doty Scientific, Electronic Navigation Industries, the Exxon Education Foundation, General Electric Corporate Research and Development, General Electric NMR Instruments, and the Monsanto Co.

Registry No. $H_2NN{=}C(CH_3)C(CH_3){=}NNH_2$, 3457-52-1; $(CH_3(CO)_2CH_3)(H_2NN{=}C(CH_3)C(CH_3){=}NNH_2)$ (copolymer), 122408-43-9; $N{=}C(CH_3)C{=}N(CH_3)$ (SRU), 54047-69-7.

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Solid-State Carbon-13 NMR Study of the Structure and Mobility of the 1,4-*trans*-Polybutadiene–Perhydrotriphenylene Matrix System and of the Extracted Polymer

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ABSTRACT: 1,4-*trans*-Polybutadiene has been studied by high-resolution solid-state carbon-13 NMR spectroscopy as its crystalline inclusion compound with perhydrotriphenylene (PHTP). The polymer was formed by ^{60}Co γ-irradiation of the inclusion compound with monomer butadiene. The chemical shifts and spin–lattice relaxation times (ca. 10 s) of the polymer are consistent with a high degree of chain mobility and a substantial content (about 25%) of the cis (versus skew) conformation at the $-CH_2-CH=$ single bonds. The NMR characteristics are very similar to those of the crystalline polymer in its high-temperature modification (form II). The unusual environment of the PHTP canals prevents interchain interactions while interaction with the matrix is nonspecific and permits mobility of the polymer down to very low temperature. The spin–lattice relaxation times of the carbons of the pure matrix (200–350 s) are reduced by half when polymer is present because of increased mobility in the inclusion compound. The splitting of the PHTP carbon resonances of the inclusion compound is diagnostic of altered crystal packing in the presence of polymer.

Introduction

1,4-*trans*-Polybutadiene can be produced by different methods. Ziegler–Natta catalysts based on VCl_3–$Al(Et)_3$ complexes lead to a polymer containing greater than 99.7% trans monomer units, as observed by ^{13}C NMR.[1,2] Inclusion polymerization has been widely employed as an alternative method of synthesis, leading to high molecular weight, highly ordered products. Many authors regard polybutadiene obtained in urea and in perhydrotriphenylene (PHTP) inclusion complexes as reference compounds for characterization methods.[2,3] This process involves an initiation step, brought about by γ-irradiation of the inclusion compound formed by butadiene and the matrix, and a propagation step in which the monomer molecules residing in the canals of the inclusion compound are linked together, leading to a new inclusion compound with the polymer.[4]

The crystal structure of PHTP is not destroyed during the polymerization process, but a solid–solid crystal transformation occurs, which can be followed by X-ray

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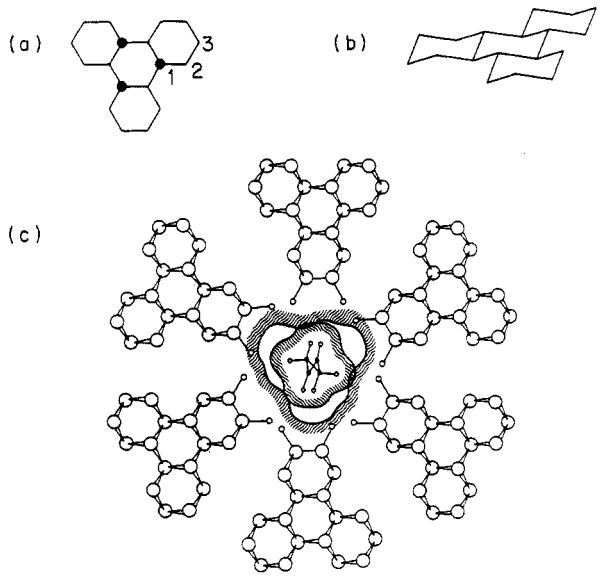

Figure 1. (a) Projection of PHTP; black dots represent axial hydrogens; (b) conformation of PHTP; (c) schematic representation of a 1,4-*trans*-polybutadiene chain in the PHTP inclusion compound, as determined by X-ray diffraction.[5] The polymer is contained in canals perpendicular to the plane of the paper. The projections of the van der Waals limiting surface for the polymer and the contour of the canal are shown.

diffraction.[5,6] Side reactions are eliminated. By ESR one observes stable propagating radicals existing long after irradiation has ceased,[7,8] consistent with the occurrence of long-lived radicals and very slow propagation in the solid state.

The polymer thus formed is not observed to be accompanied by an amorphous phase because polymerization does not occur outside the crystal canals. In the case of PHTP, the inclusion compound with the polymer is recovered after stripping away the excess monomer. It exhibits a melting point of at least 180 °C. Polybutadiene chains are confined in restricted regions kept several angstroms apart from one another (Figure 1c). If the inclusion compound is instead formed by melting the polymer and the pure matrix together and recrystallizing, the melting point and heat of melting are considerably depressed.

These peculiarities of inclusion polymerization stimulated us to study by solid-state carbon-13 NMR the properties of polybutadiene in the PHTP matrix. In addition we have studied in this way (a) the matrix itself, both with and without the polymer; (b) the 1,4-*trans*-polybutadiene as directly recovered from the matrix by dissolving the latter; and (c) the polymer after solvent recrystallization. In the course of this investigation we have for the first time studied by high-resolution solid-state ^{13}C NMR the motional behavior of individual polymer chains trapped in a crystalline environment not constituted by the polymer itself.

In order to extend this study to the use of solid-state deuterium (^2H) NMR, desirable because of the unique sensitivity of this method to a wide range of molecular mobilities, we also synthesized 1,4-*trans*-poly(butadiene-*1,1,4,4-d*$_4$) by inclusion polymerization in PHTP. The deuterium spectroscopy of this polymer is reported in a separate publication.[9]

Experimental Section

The racemic trans-anti-trans-anti-trans-anti isomer of PHTP (Figure 1a,b) was synthesized as described elsewhere,[10] precipitated as an inclusion compound with heptane, and purified by sublimation at 10^{-4} Torr and 80 °C. It was checked by GLC, NMR, and DSC and found to be >99% pure. Butadiene was a 99% product obtained from Aldrich Chemical Co. Butadiene-*1,1,4,4-d*$_4$ was supplied by Merck MSD Isotopes (98% isotopic purity). The inclusion compound was formed by condensing the degassed monomer under high vacuum in a vial containing PHTP. The sealed vial was conditioned at 0 °C for 24 h and then irradiated using a ^{60}Co source for 45 min for a total dose of 0.8 Mrad. A further period of a week at 0 °C without irradiation was allowed in order to complete the polymerization. The polymer was recovered by using a Soxhlet extractor and heptane or boiling methanol (vide infra).

1,4-*trans*-Polybutadiene prepared by inclusion polymerization in PHTP and isolated by extraction of the PHTP is insoluble to the extent of ca. 30% when stirred for 3 days in boiling heptane or toluene. This insoluble fraction is of high molecular weight and prevents complete GPC analysis. The same behavior was observed for polymer prepared in a urea matrix by Tseng et al.[2] The GPC analysis performed by these authors on the soluble part of their samples gave an $\bar{M}_n$ of 1.2×10^5; this can be taken as a minimum value for our samples. DSC analysis was performed on a Perkin-Elmer DSC-4 calorimeter equipped with a Model 3600 data station.

Solid-state NMR spectroscopy was performed at 50.3 MHz on a Varian XL200 instrument. The cross-polarized (CP), magic angle spinning (MAS), dipolar decoupled (DD) spectra were recorded by using a Doty Scientific probe with Al_2O_3 rotors spinning at rates ranging from 3 to 4 kHz. Optimization of the Hartmann-Hahn match and magic angle setting were performed with adamantane and hexamethylbenzene, respectively. The temperature was controlled over a 20–100 °C range with a standard Varian controller. The high-power decoupling was performed at approximately 10 G. CP/MAS/DD spectra were recorded with a 20-kHz sweep width in 8K data points. The number of scans ranged from 1000 to 15 000. Spin–lattice relaxation times (T_1) were measured on the polymer in the matrix using a 180°–τ–90° inversion–recovery pulse sequence with seven different τ values ranging from 0.05 to 5 times the T_1 value and with a delay of $5T_1$ between repetitions of the sequence. The CP T_1 sequence[11] was used for the measurement of the relaxation times of the PHTP and of the recrystallized polybutadiene. Chemical shifts were referenced to TMS by recording the spectrum of poly(oxymethylene) (POM) before and after each spectrum and taking its signal as being at 89.1 ppm with respect to TMS.

Results and Discussion

DSC Analysis. In order to evaluate the filling of the canals, the PHTP–polymer inclusion compound was analyzed by DSC after stripping away the excess monomer. The thermogram (Figure 2a) shows two endothermic transitions. The smaller transition, at about 125 °C, is due to excess PHTP, the canals of which do not contain polymer. From a comparison of the enthalpy of melting to that of pure PHTP (ΔH = 17.0 cal/g), one can estimate that in this sample 96% of the volume available for the polymerization is filled by polymer. This inclusion compound shows a melting point of 186.2 °C (Table I) with a ΔH of 24.5 cal/g. The enthalpy of melting of pure inclusion compound can therefore be calculated as 25.5 cal/g. No transitions were detected in the temperature range from −130 to 120 °C (not shown in Figure 2a), leading to the conclusion that no free polymer is present. On a second melting, after crystallization by cooling at 0.5 deg/min, a higher content of pure PHTP is detected. The endotherm for the inclusion compound occurs at a slightly lower temperature (179.5 °C) and corresponds to a lower heat of melting (19.0 cal/g). This indicates a less complete filling of the canals and a less regular morphology (Figure 2b).

After extraction of the PHTP with boiling methanol, a crystalline polymer (native) was recovered that gave the thermogram shown in Figure 3b. The two endotherms correspond to the crystal–crystal transition at 67 °C and to the melting point at 133 °C. They are compared to a

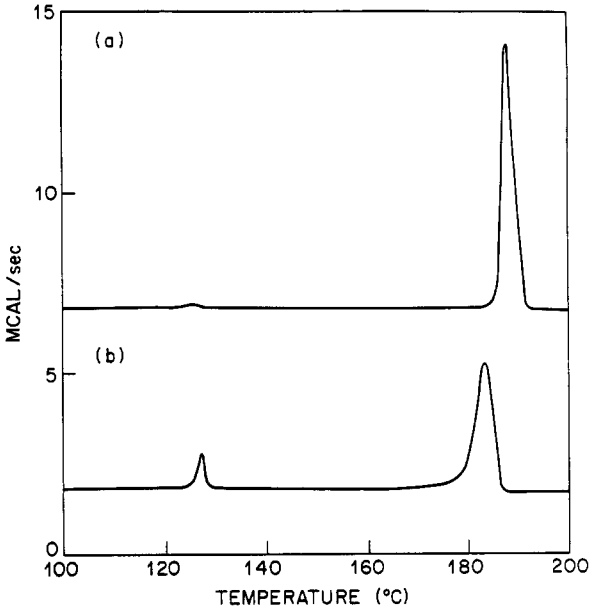

Figure 2. DSC analysis of the inclusion compound formed by PHTP and 1,4-*trans*-polybutadiene: (a) direct product from the polymerization; (b) after recrystallization at 0.5 deg/min.

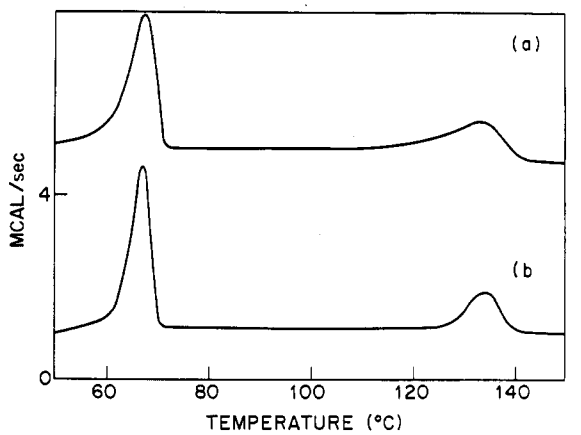

Figure 3. DSC analysis of 1,4-*trans*-polybutadiene: (a) polymer of $\bar{M}_v = 2.5 \times 10^4$, recrystallized from dilute heptane solution;[12] (b) polymer as purified by extraction of PHTP with boiling methanol, with no other treatment.

Table I
Calorimetric Data for 1,4-*trans*-Polybutadiene

	melt temp, °C	ΔH_m, cal/g	crystallinity, %
Inclusion Compound			
1st melt	186.2	24.5	96
2nd melt	179.5	19.0	75

	transitn temp, °C	ΔH_{tr},[b] cal/g	T_m	ΔH_m[c]	crystallinity,[d] %
Native Polymer					
methanol, 60 °C[a]					
1st melt	66.8	26.3	134.0	12.0	75
2nd melt	68.0	23.7	126.1	10.6	68
heptane, 20 °C[a]					
1st melt	50.2	16.4	136.5	13.1	47[e]
2nd melt	67.1	19.2	120.7	9.2	56

[a] The solvent and the temperature of extraction are indicated. [b] Solid–solid transition. [c] Melting transition. [d] The crystallinity is evaluated by taking ΔH_{tr} = 34.5 cal/g for 100% crystalline form I.[19] [e] The crystallinity at the melting point is about 75%.

reference specimen of 1,4-*trans*-polybutadiene[2,12] (Figure 3a). Between 70 °C and the melting point the crystalline portion of the polymer exists in a less ordered polymorph designated form II.[12,13]

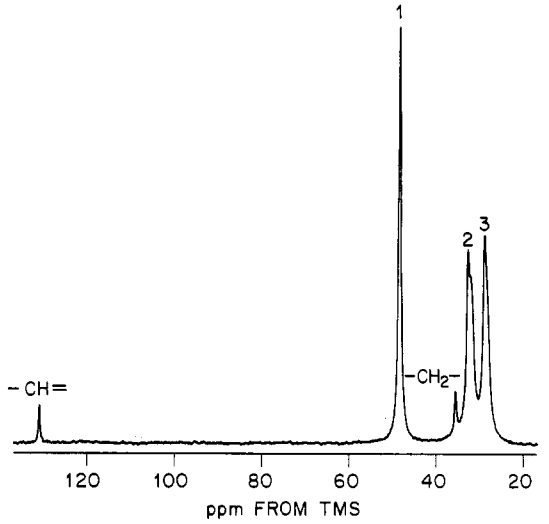

Figure 4. 50.3-MHz ^{13}C NMR spectrum of the inclusion compound PHTP/1,4-*trans*-polybutadiene; CP/MAS/DD; delay time, 5 s; contact time, 2 ms.

Table II
Chemical Shifts and T_1 Values for 1,4-*trans*-Polybutadiene

carbon	chem shift, ppm	T_1,[a] s 21 °C	60 °C	90 °C
Inclusion Compound				
CH=	130.9		10.0	10.0
	129.3[b]		6.4[b]	6.8[b]
CH_2	35.6		8.0	
CD_2	34.5		~14.0[c]	

carbon	chem shift, ppm form I	form II	T_1, s 21 °C, form I	70 °C, form II
Native Polymer[d]				
CH=	132.4	131.3	116	15.5
			123[e]	12.2[e]
CH_2	36.7			10.5[e]
CD_2	35.9	34.1	192	26.8

[a] ±10%. [b] Refers to small peak arising from oligomers. [c] Estimated from null point (±20%). [d] The form I to form II transition temperature agrees well with that of ref 12. [e] From ref 12.

When the polymer is isolated by dissolving away the matrix in heptane at room temperature, its melting point is 136.5 °C, and the crystallinity just below the melting point is comparable to that of the polymer obtained from methanol extraction at 60 °C. It shows a markedly lower melting point (120.7 °C) after recrystallization from the melt. This in turn suggests that an extended chain morphology, i.e., without chain folding, is produced by both methanol and heptane extraction at room temperature[6,14,15] and that lamellae with chain folding result from the melt recrystallization. The calorimetric data are given in Table I. The form I–form II transition is depressed (by about 17 deg) if the extraction is performed near room temperature with heptane.

^{13}C NMR of Polybutadiene in the PHTP Matrix. A major problem that may occur in the study of inclusion compounds by high-resolution ^{13}C NMR arises from the fact that the matrix resonances are so large as to overwhelm most of the informative portion of the spectrum. Fortunately, in our case, due to the symmetry of the monomer units, 1,4-*trans*-polybutadiene gives rise to only two sharp peaks, thus increasing their relative intensity. In addition, since PHTP is a saturated hydrocarbon, it leaves the downfield region of the spectrum free. In Figure 4 and Table II, the CP/MAS/DD NMR spectra and the chem-

Table III
Chemical Shifts and T_1 Values for PHTP

Inclusion Compound			
carbon no.[a]	1	2	3
chem shift, ppm	48.4	32.7, 31.9	28.8, 28.3
T_1 (±10%), s	177	156	110
Pure PHTP			
carbon no.[a]	1	2	3
chem shift, ppm	49.2, 48.6	32.1, 31.5	28.9, 28.0
T_1 (±10%), s	386	324	258

[a] See Figure 1.

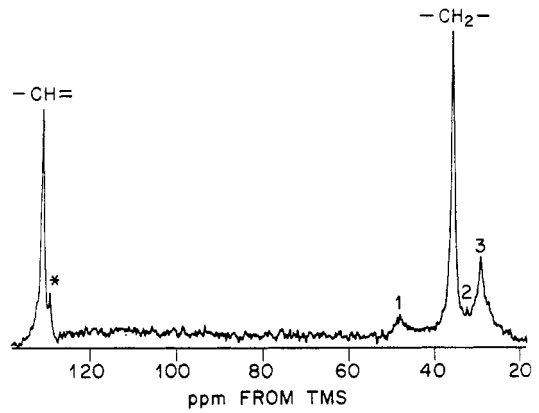

Figure 5. 50.3-MHz MAS/DD ^{13}C NMR spectrum of the inclusion compound PHTP/1,4-*trans*-polybutadiene; delay time, 1 s.

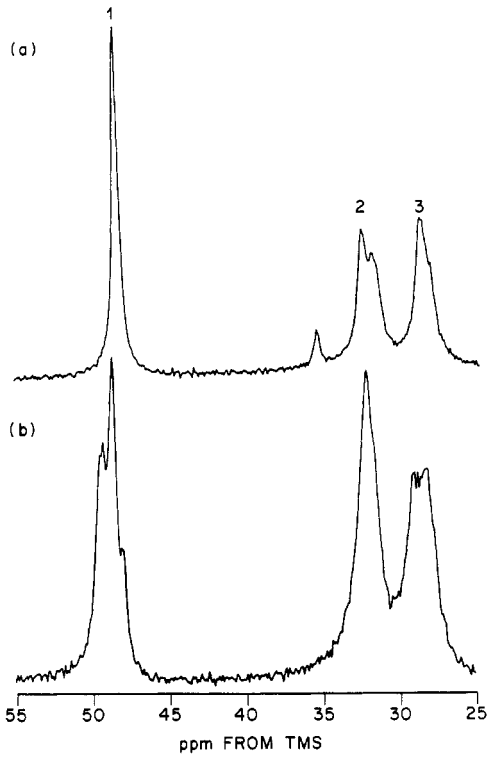

Figure 6. Expansion of the aliphatic region of the CP/MAS/DD ^{13}C NMR spectrum of (a) PHTP matrix with included polymer and (b) pure PHTP. See Figure 1 for numbering of the PHTP carbons. The resonance at ca. 35.6 ppm is that of the polymer CH_2.

ical shifts of the polymer in the inclusion compound are shown. The principal signals are due to the matrix and can be recognized by comparison to the spectrum of pure PHTP. The spectrum contains three resonances corresponding to the three singlets (at 26.58, 30.17, and 47.27 ppm) of PHTP in solution, but with a downfield shift of ca. 1.5 ppm. The signals due to polybutadiene appear at 130.9 and 35.6 ppm. These values differ slightly from previous data on solution-crystallized 1,4-*trans*-polybutadiene[1] because earlier values were referenced assuming the amorphous CH_2 signal to be coincident with the corresponding solution chemical shift. We find the chemical shifts referenced to POM (see Experimental Section) to be 1.2 ppm downfield from the previously reported values.[1] The chemical shifts thus measured for the polymer in the matrix are close to those of the high-temperature crystalline form (form II) and are clearly upfield from those of form I (see Table II). Direct comparison of the resonances for the extracted and recrystallized polymers confirms this point (vide infra). The relatively small deviations (0.4 and 0.6 ppm) with respect to form II can be attributed to the unusual environment in which the polymer is embedded, i.e., to the different intermolecular magnetic interactions in the bulk polymer compared to those in the crystalline inclusion compound, and need not be attributed to differences in conformation. The absence of spinning sidebands for the olefinic resonance is consistent with the presence of a mobile form similar to form II. Because the ^{13}C T_1 values for the polymer in the matrix are much shorter than those of the matrix itself (see Tables II and III), we can enhance the polymer resonances by using a short delay (1 s) in the MAS/DD experiment. The matrix signals are in this ways almost eliminated (Figure 5). The polybutadiene chemical shifts can thus be measured more accurately. They correspond to those of the CP/MAS/DD spectrum (Table II). In addition, a small signal at 129.3 ppm (marked with an asterisk in Figure 5) is observable. This cannot be due to cis double bonds or spinning side bands. It disappears after extraction of the matrix and is probably due to oligomers removed by methanol.

Spin–lattice relaxation time measurements were performed on the polymer in the matrix by the MAS/DD inversion–recovery method (see Experimental Section). This may be less precise for the upfield (methylene) signal due to interference from PHTP signals. The results are given in Table II. (The T_1 of the minor resonance at 129.3 ppm was approximately 6 s.) These T_1 values (8–10 s) are very close to those found for form II at 60 and 70 °C (9–12 s) and are in contrast to the much longer times (123–130 s) exhibited by the rigid, crystalline form I.[12]

In the selectively deuterated polymer, in which CD_2 groups replace CH_2 groups, the carbon-13 NMR observations are nearly the same except that the CD_2 ^{13}C resonances are shifted upfield by about 1 ppm and the T_1 values are increased, as expected. The presence of deuterium should broaden them by about 40–50 Hz due to ^2H scalar coupling, but this is within the normal solid-state broadening. A reduced tendency to cross polarize is reflected in a reduction of the $^{13}CD_2$ signal in the CP/MAS/DD spectrum when short contact times are employed.

^{13}C NMR of PHTP. The chemical shifts and T_1 data for pure PHTP and PHTP in the inclusion compound are given in Table III. Expansions of the spectra in the aliphatic region are shown in Figure 6. The assignments correspond to the numbering of the carbon atoms in Figure 1. It is clear that the splitting of the PHTP resonances differs in the two cases. In the solid state the carbon atoms of PHTP, both in the pure substance and in the inclusion compound, are not connected by the same elements of symmetry as for PHTP in solution.[16] This is indicated by the splitting in the solid state of the sharp singlet resonances observed in solution. We do not believe, however,

that the presence of the polymer itself changes the magnetic environments of the carbon atoms, for we observe that the carbon atoms designated as C-1, which are the most internal and are at a distance of about 5 Å from the polymer, are those showing the clearest alterations in splitting. In addition, the splittings cannot be due to a conformational change in the trans-anti isomer of PHTP because this molecule is very rigid and not subject to conformational modifications.[10] We therefore attribute the differences in splitting entirely to packing effects. The crystal structure of PHTP and of its inclusion compounds has been studied previously. Upon inclusion of linear hydrocarbons the unit cell is modified, changing from $P2_1/m$ to $P6_3/m$.[5,13] We are unable at this time to explain quantitatively the splittings on the basis of the internuclear distances of the carbon atoms in the crystal lattice, but we can rule out another possible reason for the splittings, i.e., the chirality of the PHTP molecule. X-ray shows that the unit cell of the inclusion compound contains molecules of both chiralities.[17] This could lead to different distributions of carbon–carbon distances and thus to different chemical shifts, but actually a sample of (−)-PHTP–1,3-pentadiene inclusion compound shows the same matrix resonances as in Figure 6a.[18]

CP T_1 measurements[11] (see Experimental Section) give values of ca. 250–380 s (Table III) for pure PHTP, as expected for a very rigid crystal structure. The values are the same for the split signals corresponding to a given carbon type. When the polymer inclusion compound is formed, an ca. 2-fold decrease of matrix T_1 values is observed for all the signals. This shows that it is not the polymer that directly interacts with the carbon atoms of the matrix, because it is unlikely that they would all be affected to the same extent by the presence of the polymer. A better explanation is that the overall motion of the PHTP molecules in the inclusion compound is increased due to the mobility of the polymer and to looser crystal packing. This is not in contradiction with the higher melting point of the inclusion compound, because higher mobility in the solid state decreases the entropic advantage gained in melting.

^{13}C NMR of the Native Polymer. It is well established that inclusion polymerization leads to "native" polymers—i.e., isolated from the matrix but not recrystallized[4]—having an extended chain conformation. According to Chatani,[6] small-angle X-ray diffraction does not show any periodicity up to a dimension of 200 Å in polybutadiene prepared by urea matrix polymerization, in contrast to the conventional lamellar structure of normally crystallized polybutadiene. This is consistent with the unusually high melting point (147 °C) of the same product reported by White.[14] Poly(1,3-pentadiene) prepared in a PHTP matrix shows similar properties.[15]

The CP/MAS/DD spectrum of the native polymer obtained from methanol is shown in Figure 7a. The chemical shifts of the main signals at 132.4 and 36.7 ppm correspond to those of form I polybutadiene.[1,12] In the expanded spectrum an upfield shoulder can be seen. This corresponds roughly to the chemical shift of the amorphous or loop region of crystallized polybutadiene.[1] In this sample, however, it is not clear that the usual folds or loops should be present, as conventional crystallization can hardly be visualized from so poor a solvent as methanol. These shoulders are more clearly seen by employing short pulses without cross polarization in the MAS/DD experiment (not shown). They may be due to disordered chains connecting different crystallites or possibly to disordered portions produced by irregular collapse of the chains during extraction of the matrix. The amorphous content, when evaluated quantitatively by performing the MAS/DD experiment without CP and with very long delay times in order to allow the crystalline portions to relax completely (see ref 1), is comparable to that of a solution-crystallized sample and constitutes 20–30% of the sample. We may conclude from the similarity of Figure 7a to previously published spectra[12] that the native polymer has the skew$^+$-trans-skew$^-$ conformation established for form I.[12]

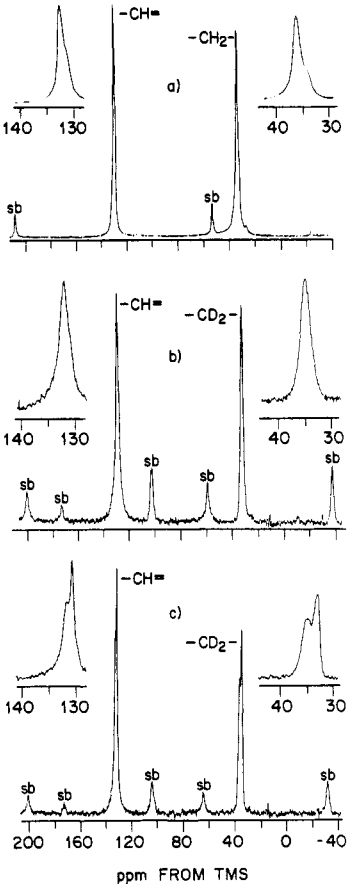

Figure 7. 50.3-MHz CP/MAS/DD ^{13}C spectra of (a) native 1,4-*trans*-polybutadiene after isolation using methanol, observed at 23 °C; (b) native 1,4-*trans*-poly(butadiene-*1,1,4,4-d*$_4$) after isolation using methanol, observed at 23 °C; (c) same as (b), but recorded at 59 °C, i.e., at the midpoint of the form I–form II transition.

The deuterio native polymer (Figure 7b) shows corresponding ^{13}C resonances at 132.4 and 35.9 ppm (Table II) with only slightly greater line width for the $^{13}CD_2$ resonance. The most striking feature, however, is the presence of very strong spinning sidebands centered on the aliphatic signal. Even second-order sidebands are visible, one of them at ca. 175 ppm. These result from modulation of the ^{13}C–^{2}H dipolar interaction by sample spinning.

The form I–form II transition at 59 °C[12] is unaffected by the presence of deuterium. Figure 7c shows the spectrum at this midpoint temperature. We again observe strong side bands centered on the form I signals. The sidebands are not observed for the deuterio polymer in the matrix (not shown), a further indication of its mobility.

General Remarks. We have seen (under ^{13}C NMR of PHTP) that polymerization of butadiene in the matrix causes a change in the space group from $P2_1/m$ to $P6_3/m$, but the unit cell is actually very little changed.[5] X-ray reflections are not detected from the monomer in the PHTP–butadiene inclusion compound or from the polymer in the PHTP–polymer inclusion compound. It has been

suggested[5] that this may be due to a coincidence of the repeat distance in form I polybutadiene (4.85 Å) and the repeat distance in stacked PHTP molecules (4.78 Å). This interpretation now seems less convincing because the included polymer is now seen to be similar to form II polybutadiene, which has a shorter repeat distance of 4.66 Å. We therefore believe it more likely that the dynamic disorder of the polybutadiene in the matrix is responsible for the absence of reflections. Deuterium NMR shows[9] that the mobility of the polymer is maintained down to −160 °C, whereas crystalline *trans*-1,4-polybutadiene loses mobility at ca. 60 °C, a spread of over 200 °C. The absence of molecular recognition or specificity in this inclusion compound accounts for the difference in behavior.

The presence of methyl groups, as in poly(1,3-pentadiene), is found to markedly retard the mobility of the polymer in the matrix, as judged both by ESR[7] and deuterium NMR.[20]

Conclusions

We have shown by high-resolution solid-state ^{13}C NMR that there is a close analogy between the 1,4-*trans*-polybutadiene formed in the PHTP matrix at room temperature and form II polybutadiene. The spin–lattice relaxation times and the absence of spinning sidebands demonstrate that both polymers have a substantial degree of mobility. The deuterium spectroscopy described in ref 9 leads to the same conclusion. Chain mobility is also indicated by ESR spectroscopy on the matrix polymer, using the radical at the growing chain end as a probe.[7] In this case, measurements performed at temperatures ranging from 60 to −150 °C demonstrated restriction of the chain ends only at the lowest temperatures. However, in the present study we observe the whole polymer rather than confining our attention to the chain ends. The deuterium observations[9] show that the matrix polymer retains mobility down to −160 °C. We suggest that in both form II and the matrix polymer there is a statistical distribution of E-skew$^{\pm}$-trans-skew$^{\mp}$-E and E-skew$^{\pm}$-trans-cis-E conformations. This disordered conformation is dynamically averaged. These conformational "defects" may be viewed as traveling rapidly along the chains in the matrix canals, but at present we do not know if such traveling defects or *solitons* are confined to short stretches of the chain or may run more freely along its length.

Registry No. PHTP-PB, 29698-97-3; PHTP, 15074-91-6; PB, 9003-17-2.

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