Solid-State Carbon-13 NMR Study of the Fold Surface of Solution-Grown 1,4-*trans*-Polybutadiene Crystals†

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ABSTRACT: We report for the first time the application of solid-state carbon-13 NMR spectroscopy to the study of solution-grown polymer single crystals. Two samples of 1,4-*trans*-polybutadiene ($\bar{M}_n = 9.8 \times 10^3$ and 1.7×10^4), grown from 0.01% heptane solution, were employed. With the appropriate use of magic-angle spinning and proton decoupling it is possible to measure chemical shifts, relaxation times, and nuclear Overhauser enhancements (NOE) of carbon nuclei in the crystal stems and amorphous regions; the latter are assumed to consist exclusively of fold surfaces and cilia. Using dipolar decoupling but without magic-angle spinning, we examined the chemical shift anisotropy of the olefinic carbons. The powder pattern is asymmetric with a $(\sigma_{11} - \sigma_{33})$ of ca. 178 ppm. Using magic-angle spinning with dipolar decoupling but without ^1H–^{13}C cross polarization, we have determined the fraction of crystallinity as 0.73 ± 0.01 for both samples, in agreement with estimates from densities. Spin–lattice relaxation of the fold-surface carbons is shown to be predominantly dipolar. The less than maximal NOE values—ca. 2—are consistent with anisotropic chain motion. Both these findings and the chemical shifts of the fold-surface carbons agree with those reported by Jelinski et al.[11] for bulk amorphous polybutadiene. The chemical shifts of the methylene carbons in the folds can be rationalized on the basis of the γ-gauche shielding effect and the accepted rotational isomeric state model for unperturbed 1,4-*trans*-polybutadiene, but the upfield shift of the olefinic carbons is less than expected. It appears that the motions and conformations of the surface folds are similar to those of bulk polymer despite the constraints imposed on the folds by the requirement of adjacent reentry, established in a previous high-resolution study.[10] Upon epoxidation with *m*-chloroperbenzoic acid, the folds give very broad carbon-13 resonances. Evidently, the introduction of oxirane rings immobilizes the chains sufficiently to prevent averaging of ^1H–^{13}C dipolar interactions and ^{13}C chemical shift anisotropies.

Introduction

During the past several years solid-state carbon-13 NMR with magic-angle spinning has been employed in the study of many polymers. Among the materials examined have been several semicrystalline polymers, including polyethylene,[1] polypropylene,[2,3] ethylene–propylene copolymers,[4] and poly(ethylene oxide).[5] In the reports on polyethylene and poly(ethylene oxide) the upfield shoulder on the methylene resonance in the magic-angle spinning spectrum was attributed to the noncrystalline regions of the sample. The magnitude of the upfield shift for the amorphous resonances was satisfactorily accounted for on the basis of differences in chain conformation between the crystalline and amorphous regions. The greater proportion of gauche conformations in the amorphous chains produces a shielding effect. The change in chemical shift results from the three-bond gauche interaction between carbons and is referred to as the γ-effect.[6,7] This interpretation also satisfactorily accounts for the solid-state carbon-13 chemical shift difference observed for the nonequivalent methylene carbons of crystalline syndiotactic polypropylene.[2]

It is evident from these studies that solid-state carbon-13 NMR provides an independent means of observing the morphology of semicrystalline polymers. In addition, comparison of the spectra of different crystalline forms can provide insight into the relationship between carbon-13 chemical shifts and chain conformation in the solid state.

In the present study, we have employed solution-grown crystals of 1,4-*trans*-polybutadiene (TPBD) in a variety of solid-state carbon-13 NMR experiments. This appears to be the first report of the application of solid-state carbon-13 NMR to solution-grown polymer single crystals. With the appropriate use of magic-angle spinning and scalar or high-power dipolar proton decoupling it is possible to measure the chemical shifts, relaxation times, and nuclear Overhauser enhancements (NOE) of carbon nuclei in the crystalline and amorphous regions. It is possible with careful selection of experimental parameters to directly determine the fraction of crystallinity. In addition, chemical shifts and relaxation times permit a measure of the chain conformation and mobility in the noncrystalline regions.

† Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

Experimental Section

Preparation of Samples. Two polymer preparations, designated UH29 and UH45, were used. GPC measurements of $\bar{M}_n$ for UH29 and UH45 yield values of 9.8×10^3 and 1.7×10^4, respectively. The trans content was determined by ^{13}C NMR to be 99.5%. Crystallization was carried out from 0.01% (w/v) heptane solution, using a self-seeding technique.[8] Following precipitation at room temperature UH29 was redissolved at 50 °C and isothermally crystallized at 29 °C, and UH45 was redissolved at 55 °C and isothermally crystallized at 45 °C. The density of UH45 was measured by density gradient flotation and a weight fraction crystallinity of 0.74 calculated therefrom.[8] The crystallinity of UH29 was taken as 0.72, which is an average of the values found for five other TPBD samples crystallized at 29 °C.[9]

NMR Measurements. The 50.31-MHz solid-state ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. For scalar decoupling a proton decoupling field ($\gamma B_2/2\pi$) of 4400 Hz or ca. 1 G was employed. The high-power dipolar decoupling field strength was 45 kHz or ca. 11 G. Sample rotation at the magic angle was 2400 Hz. Optimization of the Hartmann–Hahn match and magic-angle setting was performed by using samples of adamantane and glycine, respectively. The 90° pulse employed was 10 μs. All spectra were recorded at an ambient temperature of 17 °C. The static dipolar-decoupled spectra were recorded with a 40-kHz window in 4 K data points. Scalar-decoupled spectra were obtained with a 20-kHz window in 16 K data points, while magic-angle spinning cross-polarization spectra with dipolar decoupling (MAS/CP/DD) were recorded with a 20-kHz window

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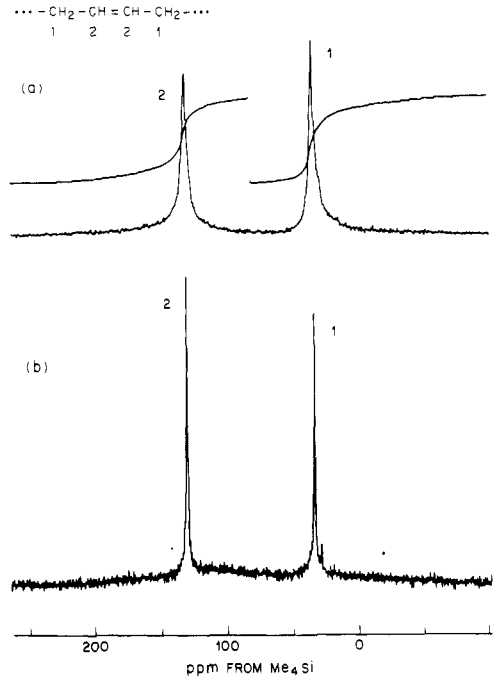


Figure 1. Scalar-decoupled 50.3-MHz carbon-13 spectra of 1,4-*trans*-polybutadiene, sample UH-45: (a) nonspinning; (b) with magic-angle spinning at 2400 Hz.

in 8K data points. Between 250 and 4000 scans were accumulated for each measurement.

Carbon-13 spin–lattice relaxation measurements under conditions of scalar decoupling were made by using a $(180°–\tau–90°)_n$ inversion–recovery pulse sequence with a delay of greater than $5T_1$ betwen repetitions of the sequence. Eight τ values were employed in each T_1 measurement. NOE determinations were made by using the gated decoupling technique, with the delay between each accumulation of data being greater than 10 times the ^{13}C T_1 value.

No internal reference standard was employed. Chemical shifts were referenced to tetramethylsilane [$(CH_3)_4Si$] by assuming the amorphous methylene carbon resonance to be at 32.79 ppm.[10] It has been previously shown that for amorphous polybutadiene the carbon-13 chemical shifts in chloroform solution and in the solid state are substantially identical.[11]

Results and Discussion

Scalar-Decoupled Solid-State Carbon-13 NMR Spectra of 1,4-*trans*-Polybutadiene. It is well-known that moderately high-resolution carbon-13 NMR spectra can be obtained from solid elastomeric materials without special techniques.[12] Provided the elastomer is examined well above the glass transition temperature, T_g, resonances with ca. 1-ppm line widths can be observed by using the standard pulse sequence employed in the study of solutions. In Figure 1a is shown the nonspinning carbon-13 NMR spectrum of TPBD, sample UH45, recorded at 22 °C with scalar decoupling and a $\pi/2$ sampling pulse. The T_g of the polymer is reported as –18 °C.[13] The line width of the resonances in Figure 1a is ca. 240 Hz or 4.8 ppm. As indicated above, the crystalline content of this sample is estimated to be 74%. For crystals grown from dilute solution it is probable that substantially all of the amorphous content consists of chain folds at the crystal surface and chain ends or cilia, which are excluded from the crystal. It is this amorphous fraction that produces the resonances observed in Figure 1. The observation of resonances in the static scalar-decoupled spectrum indicates significant motion in the chain-fold region. This motion almost completely averages the C–H dipolar interactions and the chemical shift anisotropy. Spinning this sample at the magic angle reduces the line width to ca. 30 Hz or 0.6 ppm, as shown in Figure 1b. The small resonance ~5 ppm upfield of peak 1 represents the methylene carbon of the 1,4-cis unit. Although the cis structure represents only 0.5% of the total butadiene units, it is apparently excluded from the crystalline stems and therefore appears larger relative to the trans unit in the amorphous regions. This small resonance is also visible in Figures 3 and 4. The olefinic carbon of the cis unit differs by <0.5 ppm from the same carbon in the trans unit and is not resolved in our spectra.

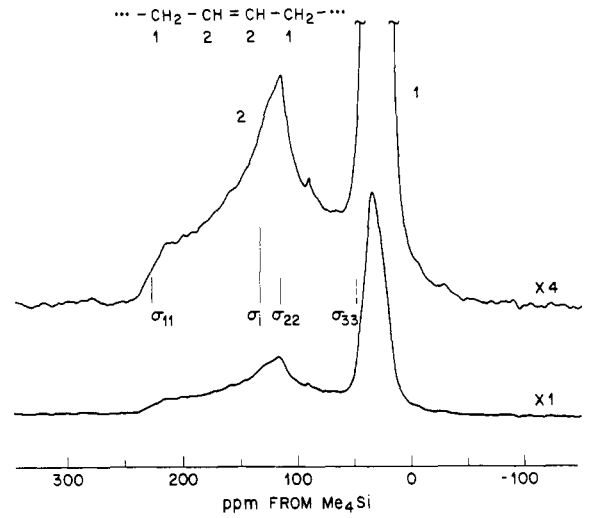


Figure 2. Dipolar-decoupled nonspinning 50.3-MHz carbon-13 spectra of 1,4-*trans*-polybutadiene, sample UH-45. The value of $\sigma_{11} - \sigma_{33}$ is 178 ppm, with σ_{11}, σ_{22}, σ_{33}, and σ_i equal to 228, 116, 50, and 131.2 ppm, respectively.

Table I
Solid-State ^{13}C T_1 and NOE Data for the Mobile Phase of 1,4-*trans*-Polybutadiene (TPBD) Crystals

carbon	T_1, s +21 °C	T_1, s –10 °C	T_1, s –30 °C	NOE $(\eta + 1)$ +21 °C
—CH=	0.40	0.36	0.42	1.95
—CH_2—	0.18	0.16	0.24	2.19

Table I contains a summary of the carbon-13 NOE and spin–lattice relaxation time measurements for the mobile phase of TPBD. The T_1 values for the methylene and olefinic carbons are in a nearly 2:1 ratio; i.e., the NT_1 values are nearly equal (N is the number of directly bonded protons). This suggests that the relaxation is almost entirely dipolar. However, the NOE values are less than the maximum of 3, consistent with anisotropic chain motion. These results are in agreement with those reported by Jelinski et al.[11] for the 1,4-trans sequences in the polybutadiene fraction of ABS resin and for pure amorphous polybutadiene. Thus, chain motions in the fold surface of single crystals are similar to those in the bulk amorphous polymer.

Dipolar-Decoupled (DD) Solid-State Carbon-13 NMR Spectra of 1,4-*trans*-Polybutadiene. In Figure 2 is shown the nonspinning spectrum of crystalline TPBD under high-power (ca. 11 G) proton decoupling. The positions of the principal values of the chemical shift tensor of the olefinic carbons and the isotropic chemical shift are indicated. The position of σ_{33} cannot be precisely ascertained because of overlap with the aliphatic carbon resonance. Nonetheless, it is evident that the olefinic chemical shift tensor powder pattern is axially asymmetric with a value of $\sigma_{11} - \sigma_{33}$ of approximately 178 ppm. The position of σ_{33} is estimated on the basis of the relationship

$$\sigma_i = \tfrac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

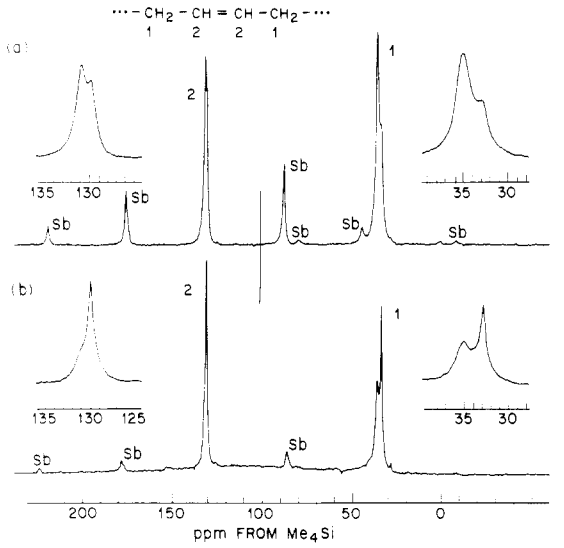


Figure 3. Magic-angle spinning dipolar-decoupled 50.3-MHz carbon-13 spectra of 1,4-*trans*-polybutadiene, sample UH-29: (a) with cross polarization; (b) without cross polarization.

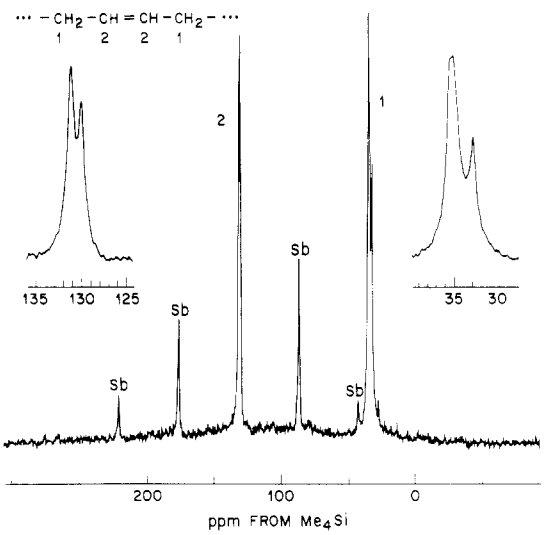


Figure 4. Magic-angle spinning dipolar-decoupled 50.3-MHz carbon-13 spectrum of 1,4-*trans*-polybutadiene, sample UH-29, using a 200-s pulse interval without cross polarization.

where σ_i is the isotropic chemical shift. Taking σ_i from Figure 3a, we can solve for σ_{33}. It is possible that the mobile amorphous phase will also contribute to the spectrum. However, we do not expect a very noticeable contribution from the amorphous phase, since it does not cross polarize efficiently and has a line width of ~240 Hz. This may explain the slight distortion of the pattern near σ_{22}. The olefinic chemical shift tensor is similar to but not identical with that reported by Fleming et al. for 1,4-*cis*-polybutadiene below its glass transition temperature.[5]

The positions of the principal values of the chemical shift tensor of the methylene carbons cannot be accurately determined from the spectrum of Figure 2. At 17 °C there is sufficient motion even within the crystal to partially average the smaller anisotropy of this carbon. Only at very low temperatures would the full methylene anisotropy be observed.

Magic-Angle Spinning (MAS) Dipolar-Decoupled (DD) Spectra of 1,4-*trans*-Polybutadiene. As illustrated in Figure 3a, the simultaneous use of high-power proton decoupling and spinning of the sample at the magic angle of 54.7° removes the broadening due to C–H dipolar interactions and chemical shift anisotropy (CSA).[14] The line width of the resonances is reduced to approximately 60 Hz. However, it should be noted that the spinning rate of 2400 Hz is insufficient to average completely the large CSA of the olefinic carbons. As a result we observe in Figure 3a strong sidebands (sb) upfield and downfield of the olefinic resonance, while only very weak sidebands are observed for the methylene carbon.

Figure 3a exhibits a narrow splitting of the center-band resonances of methylene carbons at 33 ppm and olefinic carbons at 130 ppm, whereas the sidebands are not split (note inset expansions). This result demonstrates that we are resolving the resonances of the crystalline and amorphous carbons and that the latter are sufficiently mobile to average the CSA nearly completely, as is indeed already evident from the scalar-decoupled spectra (Figure 1). Since the spectrum of Figure 3a was recorded with cross polarization (CP),[15] the crystalline carbons, which cross polarize efficiently, are enhanced to a greater extent than the mobile carbons of the amorphous phase. By measuring signal intensity as a function of CP contact time, the optimum value of the contact time, corresponding to an enhancement of 2.6, was found to be 500 μs for the crystalline carbons.

If a much longer contact time is used, the relative intensity of the amorphous carbons can be increased. At 3–40-ms contact times, the amorphous carbon intensity increases while that of the crystalline carbons, which are well beyond their optimum contact time, decreases. An alternative method of enhancing the amorphous resonance is to record a MAS/DD spectrum without cross polarization, as shown in Figure 3b. This spectrum was recorded with a pulse delay of 5.2 s. The olefinic carbon-13 T_1 is ca. 35 s (vide infra) for the crystalline phase and ca. 0.4 s for the amorphous phase. Because of the large difference in T_1 values, the amorphous resonance is much larger than the crystalline resonance. In the olefinic region of Figure 3b the crystalline peak appears only as a downfield shoulder on the much stronger amorphous peak. The dramatic change in the crystalline peak intensity is also borne out by the much weaker spinning sidebands in the olefinic region.

In order to observe the crystalline and amorphous carbons quantitatively, we recorded the MAS/DD spectrum without CP, but with a long delay time between signal accumulations. A progressive saturation experiment indicated the longest carbon T_1 to be ca. 35 s, as discussed above. Therefore, a delay of 200 s was chosen to ensure at least a $5T_1$ interval between sampling pulses. The resulting spectrum is shown in Figure 4. The areas of the individual resonances were determined by a computer line-fitting routine. The procedure involves visual fitting of experimental data to computer-drawn resonances in which the resonance position is fixed, while the line width and intensity are varied. The spinning sidebands are assumed to be totally crystalline. The computer-generated curves superimpose well on the experimental results. Good agreement is found between aliphatic and olefinic measurements. This provides a measure of the ratio of crystalline to amorphous carbons. The results indicate an amorphous content of 26.7% and 26.3% for UH29 and UH45, respectively. This compares well to amorphous contents determined from density measurements of 28% for UH29 and 26% for UH45.

Interpretation of Carbon-13 NMR Chemical Shift Data. Chemical shift differences have been observed between amorphous and crystalline carbons in polyethylene[1] and poly(ethylene oxide).[5] The differences in chemical shift can be satisfactorily explained on the basis of the content of gauche conformations in the amorphous

fraction. In a recent publication[16] Cholli et al. reported solid-state carbon-13 data for poly(methylene oxide), which in the crystalline state adopts the all-gauche conformation. The amorphous chains have a distribution of gauche and trans bonds, and as expected the amorphous resonance is found to be downfield from the crystalline resonance. Consideration of gauche conformations[17] also explains the observed doubling of the methylene resonance in the solid-state carbon-13 NMR spectrum of syndiotactic polypropylene.[2] The method of conformational analysis has also been successfully employed in the interpretation of polymer NMR spectra in solution.[7] We shall apply this type of conformational analysis to the solid state chemical shift data for 1,4-*trans*-polybutadiene.

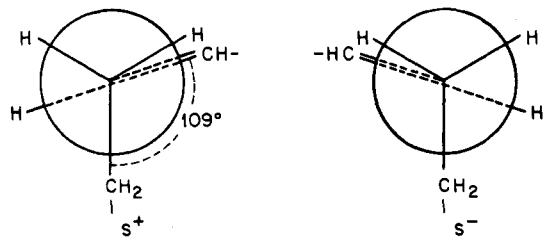
The differences in chemical shifts of the amorphous carbons, relative to the crystalline carbons, are summarized in Table II. The second column indicates the separations observed for sample UH29, as seen in Figure 4. The third column shows the shift difference observed between the resonances of a bulk amorphous polybutadiene[11] and the crystalline carbons of sample UH29. All of the amorphous material in our dilute solution grown crystals is assumed to reside in surface folds (and cilia). The data in Table II indicate that the chemical shifts for carbons in the folds relative to the crystalline chemical shift positions are the same as those of bulk amorphous polybutadiene, despite the special constraints imposed on chain folds.

The chain conformation of crystalline TPBD in the low temperature form[18] (there is a transition at 75 °C to another crystalline form with a different conformation[19,20,21]) is as follows:

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

•••$-CH_2-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-CH_2-$•••

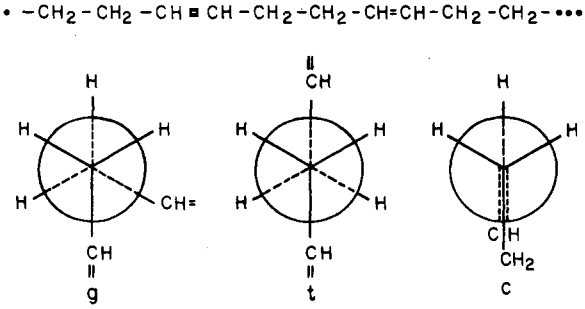
where the double bond is of course trans ("E") and $s^{\pm}$ (or $s^{\mp}$) designate approximate skew conformations:



In the exact skew conformation, the C=C and C–H bonds are eclipsed and the dihedral angle is 120°. A rotational isomeric state (RIS) model of TPBD developed by Mark[22] for the unperturbed randomly coiling chains differs from the crystalline conformation in having the $-CH_2-CH_2-$ bond 53% gauche ($g^{\mp}$) and 47% trans (t), and the $=CH-CH_2-$ bond 79% exact skew ($s^{\pm}$) and 21% cis (c):

E c,$s^{\pm}$ t,$g^{\pm}$ c,$s^{\pm}$ E

•••$-CH_2-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-CH_2-$•••



The methylene carbons of the amorphous fraction would be expected to be shifted upfield from the crystalline position by the introduction of the cis conformation at the $=CH-CH_2-$ bond; the expected shift is ca. −2.8 ppm.[23] As shown in Table II, the observed shift is close to this value. An upfield shift is also expected for the olefinic carbons because of this cis conformation and because of gauche interactions of these carbons with each other. This additional shielding is expected, on the basis of model compounds,[24] to be about −3.4 ppm. The experimental value of −1.2 ppm falls well short of this; the reason is at present not clear (see Conclusion).

Table II
Amorphous Carbon Chemical Shift[a] Relative to Crystalline Carbon Position in 1,4-*trans*-Polybutadiene

carbon	obsd, ppm: UH29	obsd, ppm: bulk amorphous	calcd, ppm: RIS model
—CH=	−1.2	−1.2	−3.4
$—CH_2—$	−2.3	−2.4	−2.8

[a] Negative sign indicates upfield direction or increased shielding.

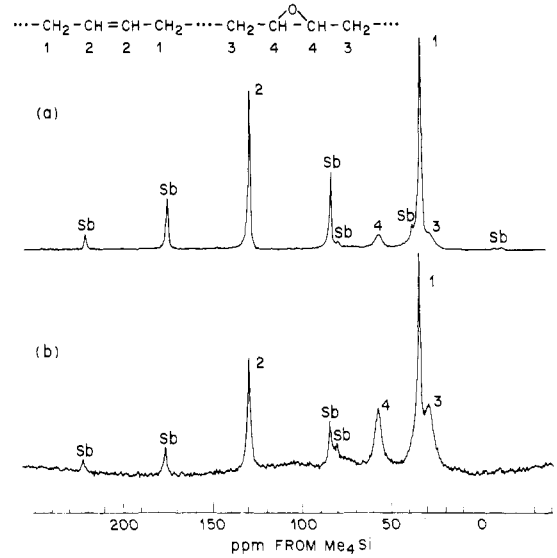
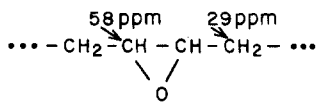


Figure 5. Magic-angle spinning dipolar-decoupled 50.3-MHz carbon-13 spectra of epoxidized 1,4-*trans*-polybutadiene, sample UH-45: (a) with cross polarization; (b) without cross polarization.

Carbon-13 NMR of Epoxidized 1,4-*trans*-Polybutadiene Single Crystals. We have reported[10] a solution carbon-13 NMR study of the epoxidation of solution-grown 1,4-*trans*-polybutadiene single crystals in which it was shown that only the surface folds, and not the crystal stems, are subject to the action of the epoxidation reagent, *m*-chloroperbenzoic acid. We now find that the nonspinning dipolar decoupled spectrum of the epoxidized crystals gives a powder pattern essentially similar to that of Figure 2. Using only scalar decoupling, as in Figure 1, we observe no resonances for the epoxidized crystals. We attribute this finding to an immobilization of the folds, so that the C–H dipolar interactions and the chemical shift anisotropy are no longer averaged. Probably the introduction of oxirane rings has raised the T_g of the fold surface above room temperature.

The MAS/CP/DD spectrum of epoxidized TPBD crystals (sample UH45) is shown in Figure 5a. In contrast to Figure 3, the olefinic and methylene carbon resonances are no longer split. This is a result of complete epoxidation of the folds, the resonances of which now appear at 29 ppm for CH_2 carbons and 58 ppm for the CH carbons of the oxirane rings.



(Fine structure arising from end effects and diastereoisomeric sequences is not resolved.) The fold resonances can be observed more clearly in Figure 5b, in which cross polarization was not employed and a delay of 5.1 s was used between pulses. Although the folds are much less mobile after epoxidation, their carbons apparently have T_1 values considerably shorter than those of the crystalline stems, as indicated by the increased intensity of the fold resonance relative to the crystalline resonance in Figure 5b. Quantitative results as to the percent epoxidation are not available from our solid-state spectra.[25] The line width observed for the oxirane carbons is ca. 5.5 ppm (ca. 275 Hz), a value typical of glassy polymers.[14]

Conclusions

The carbon-13 NMR study of TPBD single crystals demonstrates the feasibility of independent observation of the carbons in the crystalline and amorphous regions of semicrystalline polymers. Under proper experimental conditions, such observations yield a direct quantitative measure of the crystalline fraction and can provide a measure of the mobility of the chain folds (and cilia). This motion is sufficiently rapid to average the direct C–H dipolar interactions and chemical shift anisotropies, provided the folds are not epoxidized. The presence of oxirane rings retards this motion greatly, although it remains more rapid than that of the crystal stems.

As judged by the chemical shifts of the olefinic and methylene carbons in the MAS/CP/DD and MAS/DD spectra, the folds have essentially the same average conformation as the 1,4-trans sequences in amorphous bulk polybutadiene, despite the constraints imposed on them by the requirement of adjacent reentry.[10] The observed chemical shift of the methylene carbons of the folds (and of the amorphous bulk polymer) can be rationalized on the basis of the accepted RIS model for unperturbed 1,4-*trans*-polybutadiene chains, but, as indicated above, the upfield shift observed for the olefinic carbons is less than expected. This discrepancy may arise from packing effects, which result in a specific additional shielding of the olefinic carbons in the crystalline stems. Such differential shielding effects are not unprecedented. For example, in the carbon-13 spectrum of isotactic polypropylene (which is highly crystalline) the methyl and methylene carbon resonances show a marked splitting, apparently arising from crystalline packing effects, while the methine carbon does not.[4] However, the explanation in the present case is speculative.

Solid-state carbon-13 NMR studies are currently being extended to single crystals of 1,4-*trans*-polyisoprene. The results will be published later.

Since completion of this paper we have learned of a related study on partially crystalline bulk 1,4-*trans*-polybutadiene.[26] The olefinic carbon chemical shift tensor components reported by this author agrees well with our results.

Acknowledgment. We thank Dr. Lynn Jelinski for helpful discussions, particularly of chemical shift anisotropies. The City College portion of this work was supported by National Science Foundation (Polymers Program) Grant No. DMR-8007226 and a PSC–CUNY Research Award.

Registry No. 1,4-*trans*-Polybutadiene, 9003-17-2.

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(23) A comparison of chemical shift data and conformational modeling for the central carbons in 1-pentene and 1,5-hexadiene indicates that the full shift effect on a methylene carbon due to a cis arrangement with an olefinic carbon three bonds removed is 13.5 ppm shielding. As discussed by Mark and by Abe and Flory,[22] the conformational characteristics of the three internal bonds in 1,5-hexadiene should be identical with those of the three single C–C bonds in the TPBD repeat unit. Thus the $-CH_2-CH=$ bonds should be 79% skew and 21% cis in both molecules. Since we observe the methylene carbons in 1,5-hexadiene to resonate 2.8 ppm upfield from the central methylene carbon in 1-pentene, we expect the methylene carbons in amorphous TPBD to also resonate 2.8 ppm upfield from the crystalline methylene carbons in TPBD. Furthermore, if this 2.8-ppm upfield shift is attributed to the 21% cis arrangement of methylene and olefinic carbons, then we expect 2.8/.21 = 13.5 ppm for the full shielding effect of this cis arrangement.
(24) From model compounds and conformational modeling we estimate the gauche arrangement of two olefinic carbons to produce a shielding of 4.15 ppm relative to the trans arrangement. Olefinic carbons are found to be shielded by 5.6 ppm as the result of being cis to a methylene carbon three bonds removed. We observe the C_4 and C_7 olefinic carbons in 3,7-decadiene to resonate 2.2 ppm upfield from the olefinic carbons in 3-hexene. From Mark's[22] RIS model of TPBD, bond 5 in 3,7-decadiene is expected to be 47% trans and 53% gauche ±. We therefore expect the full shielding effect of a gauche arrangement of two olefinic carbons to be 2.2/0.53 = 4.15 ppm. The C_2 olefinic carbon in 2-pentene resonates 1.8 ppm upfield from the olefinic carbons in 2-butene. From Mark's TPBD RIS model we can estimate that the =C–C– bond in 2-pentene is 68% skew and 32% cis. The full shielding effect on an olefinic carbon produced by a methylene carbon in the cis arrangement would be expected to be 1.8/0.32 = 5.6 ppm. The net effect of these gauche arrangements with olefinic carbons and cis arrangements with methylene carbons is to produce an expected upfield shift of (0.53)(4.15) +

(0.21)(5.6) = 3.4 ppm for the amorphous olefinic carbons in TPBD relative to those olefinic carbons in the crystalline regions.

(25) Solution NMR measurements indicate a level of 28% epoxidation for sample UH29, in good agreement with the amorphous content of 26.7% as determined from the solid-state spectrum. The solution spectrum for UH45 shows an epoxidation of 16.2% as compared to an amorphous content of 26.3% from the solid-state results.[10] At present we cannot offer an explanation for the latter discrepancy.

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^{13}C-NMR Studies on Ditactic Poly(α-olefins). 1. Poly(1,2-dimethyltetramethylenes) and Their Tetrad Models†

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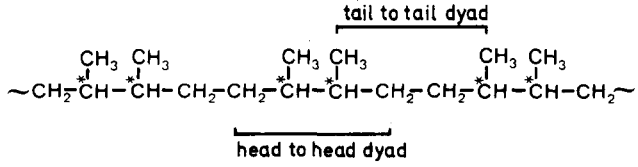
ABSTRACT: Poly(1,2-dimethyltetramethylenes) (head-to-head polypropylenes) were prepared with different tacticities. In addition, low molecular weight compounds representing dyad and tetrad segments of the polymers were synthesized in separate stereoisomeric forms. The 90-MHz ^{13}C-NMR spectra are compared and discussed with respect to their information concerning the stereochemistry. A complete assignment of the signals of atactic poly(1,2-dimethyltetramethylene) is given. The results are analyzed in terms of general aspects of chemical shift effects in aliphatic chain molecules.

The stereochemistry of polymers and the mechanisms of their growth reactions have been studied extensively because of the influence of structural variations on polymeric properties. The addition of a monomer to a growing chain often leads to a variety of stereoisomeric segments in the polymer. Conjugated dienes can react by 1,4 or 1,2 addition, the 1,4 unit may be either cis or trans, and the placement of the residue in the monomeric unit can lead to different relative configurations. In addition to these structural variations some monomeric units can be arranged in a head-to-head:tail-to-tail fashion (HH), in contrast to the "normal" head-to-tail addition (HT). In some polymers HH placements can be found in rather high proportions. Poly(vinyl fluoride) typically can have up to 10% inversions.[1] The polymerization of propylene with specific Ziegler–Natta catalysts can yield head-to-head: tail-to-tail linkages up to 11% as has been shown by ^{13}C-NMR studies.[2,3]

A number of polymers have been reported consisting exclusively of HH placements. The properties often differ significantly from those of the corresponding HT polymers.[4–15] The inverted incorporation of the consecutive monomer units in a HH polymer leads to a broader structural variety than found in HT polymers. HH polymers are ditactic. Generally, inverted asymmetrically substituted polyolefins show NMR spectra different from those of HT polymers. The atoms and bonds adjacent to a nucleus whose signal is observed either are different in structure or are located at different distances.



Because of this peculiar symmetry of HH polymers, the chemical shift effects of the molecular segments which are adjacent to an atom whose resonance is observed can be distinguished by distance and direction.[16]

The present study is concerned with the preparation and ^{13}C-NMR characterization of HH-polypropylenes [poly(1,2-dimethyltetramethylenes)] of different tacticities. ^{1}H-NMR and ^{13}C-NMR spectra have been previously reported. They do not give evidence of sequence structures more extended than the threo and erythro HH placements.[12–15,17] High-resolution ^{13}C-NMR spectra can give more information for the characterization of the stereochemistry of HH-polypropylenes. The spectra are more complicated than those of HT-polypropylene, but they are also of principal interest for the investigation of chemical shift effects in chain molecules. Because interpretation of the complex ^{13}C-NMR spectra is only possible by comparison with the more distinctive spectra of suitable models, additional stereoregular molecules have been prepared which represent dyad and tetrad segments of the polymers.

Experimental Section

Poly(1,2-dimethyltetramethylenes) (PDTM). All polymerizations were carried out with carefully purified monomers and solvents using high-vacuum line techniques.

(a) Erythrodiisotactic PDTM was prepared according to Natta[18] by the copolymerization of 0.36 mol of *cis*-2-butene with ethylene over a period of 10 h in 70 mL of *n*-heptane at −30 °C. The ethylene was fed continuously to the reactor in a nitrogen stream at a partial pressure of 80 mmHg. The catalyst was prepared from 7.1 mmol of VCl_4 and 17.8 mmol of $Al(n\text{-}C_8H_{17})_3$ in 10 mL of *n*-heptane. The polymer was precipitated in methanol and extracted from the polyethylene fraction with boiling *n*-hexane. The hexane fraction had a butene proportion of 45%, was partially crystalline, and consisted mainly of alternating butene–ethylene sequences. The molecular weight was 12 500 (vapor pressure osmometry), T_m was 338 K, and T_g was 235 K (DSC).

(b) Erythrodiatactic PDTM. *cis*-1,4-Poly(2,3-dimethyl-1,3-butadiene) was prepared as described by Teh Fu Yen[19] from 0.244 mol of 2,3-dimethyl-1,3-butadiene in 150 mL of *n*-hexane at room temperature over a period of 48 h with 14.6 mmol of $Al(i\text{-}C_4H_9)_3$ and 14.6 mmol of $TiCl_4$ in 30 mL of *n*-hexane. The polymer was precipitated in a methanolic HCl solution and reprecipitated from toluene. Complete hydrogenation could be

† Dedicated to Professor W. H. Stockmayer in honor of his 70th birthday.

0024-9297/84/2217-0733$01.50/0