Microstructure Determination of Nondeuterated, Partially Deuterated, and Perdeuterated Polybutadienes with Cis-1,4, Trans-1,4, and Vinyl-1,2 Units by ^{13}C NMR

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ABSTRACT: The microstructure of anionically prepared polybutadiene (PB-h_6) has been determined via ^{13}C NMR using two spectral regions. Sequence distributions of cis-1,4, trans-1,4, and vinyl-1,2 units were determined for the olefinic main-chain carbon resonances and the aliphatic methylene carbons by using relative area intensities. Assuming Bernoullian statistics to hold, the cis-1,4, trans-1,4, and vinyl-1,2 ratio can be determined. Good mutual agreement between both methods exists. A similar analysis has been performed for PB-d_4,h_2, deuterated at the methylene carbons, and PB-d_6. The microstructure of the last two polymers was significantly higher in trans content (using an analysis of the aliphatic region only). However, in a comparison of the measured cis-1,4, trans-1,4, and vinyl-1,2 ratio determined via an analysis of the olefinic carbons (PB-d_4,h_2), it could be shown that a lower value for trans content should be obtained. For PB-d_6 only the aliphatic part is amenable for a quantitative analysis.

Introduction

Isotopic substitution leads to numerous alterations in the physical and chemical properties of polymers. Considerable efforts have been devoted in the past especially to the synthesis of deuterated polymers, exemplified by perdeuterated polyethylene, polystyrene, polyamide 66, and polybutadiene. These perdeuterated polymers have been used to obtain information by deuteron NMR about local ordering phenomena in elastomers,[1] by isotopic effects in compatible polymer mixtures,[2,3] and in studies by cross-polarization dynamics via ^{13}C cross-polarization–magic angle spinning experiments dealing with intimate mixing phenomena in polymer mixtures.[4,5]

From an NMR point of view the primary advantage of selectively deuterated polymers is to provide a rigorous test of the chemical shift assignments for nondeuterated polymers. An elegant example can be found in the case of polyamide 66.[6] In the case of polybutadiene (PB), as compared to homopolymers such as polyethylene or polystyrene, complications arise in the *quantitative* determination of the microstructure of the parent polymer. Formally this polymer has to be considered as a terpolymer, consisting of three base units, cis-1,4 (*c*), trans-1,4 (*t*), and vinyl-1,2 (*v*). ^{13}C NMR has recently been employed by one of us[7] in a study of nondeuterated polybutadienes using the sequence-induced splitting of the main-chain *olefinic* methine carbons in central *c* or *t* units to quantify the microstructure of PB.

Shortly afterward Sato et al.[8] published a complementary study on the sequence-induced splittings of the main-chain methine and methylene *aliphatic* signals, also to quantify the microstructure of PB. In this work we present methods to determine the microstructure of deuterated polybutadienes using as model compounds nondeuterated PB (PB-h_6), 1,1′,4,4′-tetradeuteriopolybutadiene (PB-d_4,h_2), and perdeuterated polybutadiene (PB-d_6) and comparing the quantitative results of an independent analysis of the olefinic and aliphatic regions of the ^{13}C NMR spectrum.

Experimental Section

The preparation of PB-d_4,h_2 and PB-d_6 was carried out using the general procedures outlined elsewhere.[9]

The monomers were obtained from Merck, Sharp and Dohme, Ltd., Montreal, Canada (≥98.8 atom % deuterium labeled). The initiator *sec*-butyllithium was purified, and benzene was the polymerization solvent for the *anionic* polymerization of butadiene. The active center concentration was chosen[10] in such a way as to yield a microstructure (in base units, *c*, *t*, and *v*) close to that of liquid polybutadiene CDS-B-3 (PB-h_6) (Goodyear Tire and Rubber Co., Akron, OH), being the same sample as analyzed in a recent publication[7] (sample A).

The polybutadienes were characterized via size-exclusion chromatography (SEC). A Waters 150C GPC was used with tetrahydrofuran as the carrier solvent. The instrument was equipped with six μ-Styragel columns having a continuous range of porosity from 10^6 to 10^2 Å. A flow rate of 1 mL min^{-1} was maintained. The columns were calibrated using both near-monodisperse polybutadienes prepared and characterized in the laboratory of L.F. and samples available from the Goodyear Tire and Rubber Co. The M_w of PB-h_6 (A), PB-d_4,h_2 (B), and PB-d_6 (C)[11,12] are 2.6, 3.0, and 3.2 kg mol^{-1}, respectively, and the polydispersity indexes (M_w/M_n) are 1.1, 1.2, and 1.0. Thus the polybutadienes used in this work do not differ much in average molar mass and possess relatively narrow molar mass distributions.

The 50-MHz ^{13}C NMR spectra were obtained with a Varian XL-200 spectrometer. The sample concentration was 9% (w/v) in deuteriochloroform. Spectra were obtained at 25 °C, using broad-band ^{1}H decoupling, a pulse width of 60°, and a pulse delay of 5 s and accumulating 2000 scans with a digital resolution of 0.79 Hz/point, corresponding to a spectral width of 11 000 Hz and a data size of 16K. Monomer sequence distributions were determined by comparing the relative peak areas of the carbons involved. In performing quantitative NMR measurements via sequence distributions, one must take into account differences in nuclear Overhauser effects (NOE) and spin–lattice relaxation times (T_1). T_1 values have not been measured. No differential NOEs have been determined, but two additional experiments have been performed on sample A using a larger delay (20 s), the first without gating off the NOE and the

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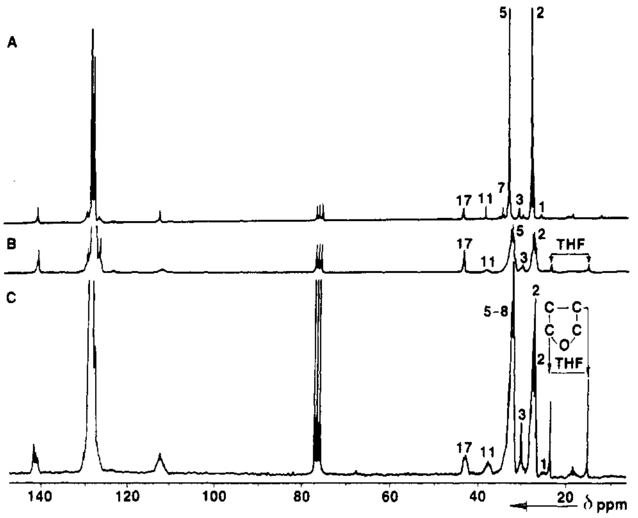

Figure 1. ^{13}C NMR spectra of PB-h_6 (A), PB-d_4,h_2 (B), and PB-d_6 (C), recorded in $CDCl_3$. Assignments are identical as presented recently by Sato et al.[8] for the aliphatic part and have been discussed in text.

second gating off the NOE, looking both at the olefinic and aliphatic carbon atoms.

Results and Discussion

Assignments. Olefinic Region. In Figures 1 and 2 are depicted the ^{13}C NMR spectra of the three polymers PB-h_6 (A), PB-d_4,h_2 (B), and PB-d_6 (C), showing either the total spectrum (Figure 1) or the olefinic main-chain cis-1,4 and trans-1,4 carbon resonances (Figure 2). The olefinic region can be subdivided into two parts:

(a) The resonances at approximately 114 and 143 ppm have been assigned[7] to the vinyl-1,2 carbons, respectively, the methylene and methine carbons, surrounded by neighboring *c*, *t*, or *v* units. As is clearly shown in Figure 1, the methine olefinic carbon resonance has been split by the ^{13}C–D scalar coupling, leading for a CD group to a distorted triplet (combination of sequence and tacticity effects) with a coupling constant of ~20 Hz and a 1:1:1 intensity ratio. A quintet with intensity ratio 1:2:3:2:1 should be observed for the CD_2 group. Hardly any deuterium isotope effects have been observed on the ^{13}C chemical shifts. If one assumes the experimentally observed additivity increments, valid for the substitution of a CH_2 group by a CD_2 in an aliphatic carbon chain[13] (respectively, $\alpha = -0.84$, $\beta = -0.20$, and $\gamma = -0.05$ ppm), to hold also for olefinic carbons, maximum high-field shifts of 1–2 ppm were anticipated. Apparently these increments are different for olefinic carbons, being zero or almost zero.

(b) The complex resonance pattern between 127–133 ppm depicted in Figure 2 (polymer A) is due to sequence-dependent splitting of the two olefinic carbons in central *c* or *t* units, present in different combinations of homotriads (*ccc* and *ttt*), heterotriads (*ccv*, *ttv*, etc.), and symmetric and nonsymmetric isolated triads (*tct*, *vcv*, *tcv*, *vct*, etc.). For a detailed discussion regarding the spectral assignments, the reader is referred to ref 7, where we have also used the assignments of Elgert et al.[15] in combination with their notation. The striking similarity between the olefinic resonances in the spectrum of polymer B (PB-d_4,h_2) and polymer A (PB-h_6) (Figure 2) shows that the effect of deuteration on the nondeuterated main-chain olefinic signals is very slight. For all carbons identical high-field shifts, estimated to be much smaller than 0.3 ppm ($\beta + 2\gamma$, relying on the values presented by Cheng and Dziemianowicz[13]), were observed. Therefore, this effect hardly deteriorates the resolution in this region.

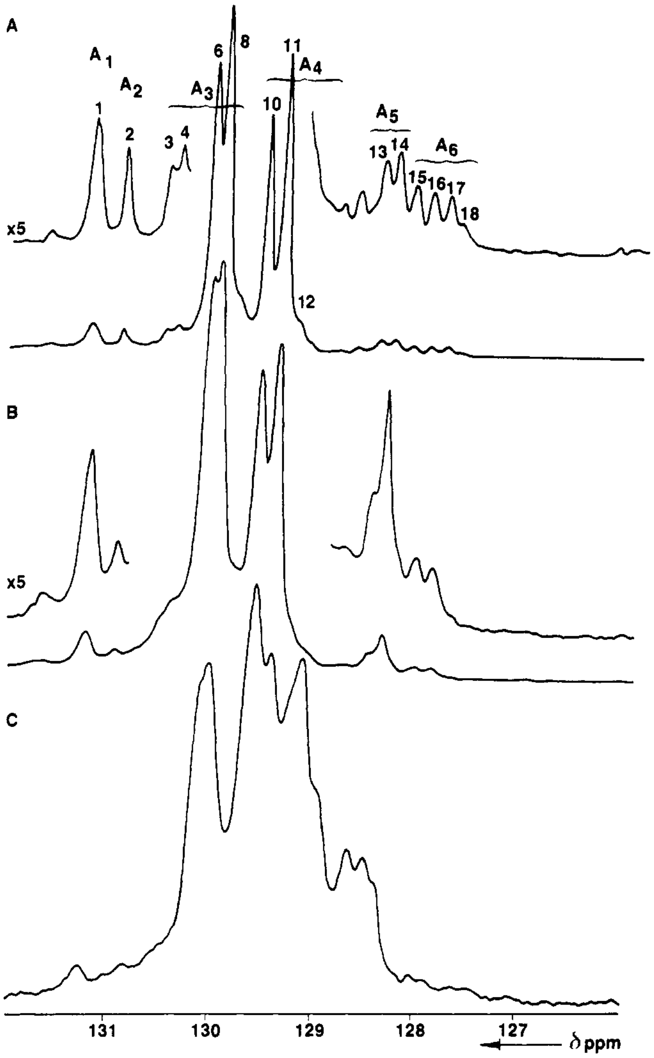

Figure 2. Expanded ^{13}C NMR spectra of the olefinic main-chain cis-1,4 and trans-1,4 resonances for PB-h_6 (A), PB-d_4,h_2 (B), and PB-d_6 (C). Assignments have been discussed in text.

However, the spectrum of polymer C (PB-d_6) shows a strong decrease of resolution in this part of the spectrum. This can be entirely ascribed to the scalar ^{13}C–^{2}H (=^{13}C–D) coupling of ~20 Hz leading to a severe overlapping of triplets and a spread of each single observed resonance to a 3-fold set of resonances with an averaged spectral width of 60 Hz (~1.2 ppm) (see Figure 2). As a result no information regarding sequence assignments can be obtained from this region for polymer C.

Aliphatic Region. The signal assignment for PB-h_6 is the same as reported by Sato et al.,[8] Bywater,[16] and Kanakavel.[17] For a detailed discussion regarding the spectral assignments the reader is referred to the recent work of Sato et al.[8] We have used the assignments of Sato et al.[8] in combination with their notation. Therefore, in Figure 1 the signals 1–17 reflect the same diad (CH_2) and triad (CH) sequences as observed and assigned by Sato et al.[8] By visual inspection of the corresponding spectra of PB-h_4,d_2 (B) and PB-d_6 (C), similar assignments can be made, although appreciable line broadening occurs due to C–D interactions. Isotopically induced high-field shifts occur ($\alpha = -0.84$, $\beta = -0.20$) as can be observed in a comparison of parts A–C of Figure 1 in accordance with the results obtained for polyethylene-d_4.[13]

Quantitative Analysis. Experimentally, *v* can be determined, from the olefinic main-chain carbons, using eq 1 where A_{114}, etc., denote the peak areas of the resonances indicated by their respective chemical shifts.

$$v = \frac{A_{114} + A_{143}}{A_{114} + (A_{127} - A_{133}) + A_{143}} \qquad (1)$$

In the case of PB-d_4h_2, the numerator has been changed to $2A_{143}$ and the denominator to $2A_{143} + A_{127} - A_{133}$, because differences in NOE effects can occur for CD_2 carbons in regards to CH or CH_2 groups. In all cases v equals 0.10. The cis-1,4, trans-1,4, and vinyl-1,2 ratio of polymers A and B (and not C) can also be obtained (especially the c/t ratio) independently from the experimentally determined peak areas A_i (i = 1–6) for the main-chain *olefinic* carbons (see Figure 2 and ref 7) through a least-squares fitting program. This program estimates, assuming Bernoullian statistics, the c, t, and v ratios by minimizing the summed squared difference D between the six experimental areas and the theoretically calculated areas (see eq 2).

$$A_1 = \frac{1}{2}v^2t(1 - v)^{-1}$$

$$A_2 = \frac{1}{2}vt$$

$$A_3 = \frac{1}{2}cv(1 - v)^{-1} + \frac{1}{2}(cv + 2t)$$

$$A_4 = c\left(1 - \frac{1}{2}v\right)$$

$$A_5 = \frac{1}{2}vt(1 - v)^{-1}$$

$$A_6 = \frac{1}{2}cv(1 - v)^{-1} \qquad (2)$$

As a consequence of the decreased resolution for polymer C (see Figure 2), such an analysis is *not possible* for PB-d_6.

In a similar manner, in the *aliphatic* region, the c, t, and v ratio can be determined by a comparison of theoretically calculated diad sequence distribution of cis-1,4, trans-1,4, and 1,2 units and experimentally observed sequence distribution effects using only the aliphatic methylene carbon signals[8] (see eq 3) (Figure 1).

$$B_1 = c\text{-}v = A_1/A_t$$

$$B_2 = t\text{-}v = A_3/A_t$$

$$B_3 = v\text{-}c = (c\text{-}v + t\text{-}v) - v\text{-}t$$

$$B_4 = v\text{-}t = (A_{10} + A_{11} + A_{13})/A_t$$

$$B_5 = \text{cis-1,4} = \frac{1}{2}A_2/A_t$$

$$B_6 = \text{trans-1,4} = \frac{1}{2}[(A_4 + A_5 + A_6)/A_t - v\text{-}c]$$

$$B_7 = v\text{-}v = A_{14}/A_t$$

$$A_t = 1.5(A_1 + A_3) + 0.5(A_2 + A_{4\text{-}6} + A_{10} + A_{11} + A_{13}) + A_{14} \qquad (3)$$

Theoretically the sequence diads can be determined, assuming Bernoullian statistics to hold as is indicated in eq 4.

$$B_1 = B_3 = cv$$

$$B_2 = B_4 = tv$$

$$B_5 = c(c + t) = c(1 - v) \qquad (4)$$

$$B_6 = t(c + t) = t(1 - v)$$

$$B_7 = v^2$$

The validity of eqs 3 and 4 can be verified, realizing that the total area (B_i (i = 1–7)) necessarily equals 1, because peak areas are normalized to unity. Such an analysis can now be performed for all three polymers, because all methylene carbons either bear protons (polymer A) or deuterons (polymers B and C).

In Table I have been listed the experimental results for polymers A–C, obtained *without* suppression of NOE effects, using a pulse delay of 5 s. As is evident from NOE and T_1 measurements on the aliphatic carbons of polybutadienes[8] and T_1 measurements on the olefinic carbons,[7] it can be safely concluded that the pulse repetition time of 5 s (a pulse width of 60°) is long enough to recover all magnetization. The NOEs for the aliphatic carbons are almost equal for all signals (2.7–3.0).[8] Therefore, these results already indicate quantitative conditions to be valid under our experimental setup, at least for PB-h_6. Moreover, our results obtained for measurements with and without suppression of the NOE effects (polymer A) are identical within accuracy limits.

Possibly the 60° pulse and a delay of 5 s are not sufficient for carbons bearing deuterons CD and CD_2. However, only differences in NOEs or T_1 values for aliphatic CD_2 (polymers B and C, see eq 3) or olefinic CD resonances (polymer C) are essential. Implicitly we have assumed that no *differential* spin–lattice relaxation times are present for different compositional triads (ctv, ttv, vvv, etc.) or analogous diad sequences in the olefinic methine (CD) and methylene (CD_2) resonances in the ^{13}C NMR spectra. Moreover no differential NOEs have been considered to occur. Therefore, we also assume (see e.g. ref 13 for copolymers of ethylene and perdeuterioethylene) that no differential sequence-dependent T_1 effects occur for sequence split CD_2 (aliphatic) or CD (olefinic) carbons. Of course, differences in T_1 relaxation times are expected to occur if one compares area intensities between aliphatic and olefinic carbons. Within these limits also for polymers B and C relative peak areas are proportional to the number of carbon atoms involved.

The experimental results obtained for polymer A nicely confirm an independent analysis to be possible either in the aliphatic or in the olefinic region. The calculated amounts, using either eq 2 or 4, are within ±0.03 compared with each other. Similar agreement could be obtained for other polymers, whose spectra have been published in an earlier report (cf., e.g., polymers D and E; ref 7). Therefore, it intrinsically proves that the isomeric content of PBs can be unraveled using two basically independent carbon resonance areas, leading to results that are in agreement.

Due to the broadness of the spectral lines from the deuterated polymers A_{4-6} cannot be measured, only a reliable measurement of A_{4-8} is possible (see Figure 1; compare parts A of Figure 1 with parts B and C). This inevitably makes B_6 (trans-1,4) too high, since additional sig-

Table I
Experimentally Observed and Theoretically Calculated Peak Areas A_i (i = 1–6) (Olefinic Region) and B_i (i = 1–7) (Aliphatic Region)

1. Calculation Using Equation 3

	sequence	A exptl	A calc	B exptl	B calc	C exptl	C calc
olefinic	A_1	0.01	0.00	0.01	0.00		
	A_2	0.04	0.03	0.03	0.03		
	A_3	0.53	0.52	0.50	0.52		
	A_4	0.36	0.39	0.40	0.39		
	A_5	0.03	0.03	0.04	0.03		
	A_6	0.03	0.02	0.02	0.02		
	c		0.415		0.415		
	t		0.465		0.465		
	v		0.120		0.120		

2. Calculation Using a Modified Version of Equation 3

		A exptl[1]	A exptl[2]	A calc	A calc	B exptl[2]	B calc	C exptl[2]	C calc
aliphatic	B_1	0.04	0.04	0.05	0.04	0.02	0.04	0.05	0.04
	B_2	0.07	0.07	0.06	0.065	0.07	0.065	0.07	0.07
	B_3	0.04	0.04	0.05	0.04	0.02	0.04	0.05	0.04
	B_4	0.07	0.07	0.06	0.065	0.10	0.065	0.08	0.07
	B_5	0.33	0.31	0.34	0.31	0.32	0.31	0.30	0.30
	B_6	0.44	0.46	0.43	0.47	0.47	0.47	0.45	0.45
	B_7	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.02
	c			0.39	0.35		0.35		0.35
	t			0.49	0.53		0.53		0.52
	v			0.12	0.12		0.12		0.13

nals from 1,4-v-1,4 and 1,4-vv are added. This is illustrated in Table I, where B_6 for polymer A is evaluated from eq 3 and its modified incorrect version. The modification of eq 3 (A_{4-8} instead of A_{4-6}) inevitably leads to an overestimation of the trans-1,4 content.

Therefore, for PB-d_4,h_2 a discrepancy can be observed in a comparison of the data derived from the olefinic part and the aliphatic part. Therefore, if we use both the olefinic methine resonances and the aliphatic methylene CD_2 resonances, a slight difference occurs (Table I). This can be fully attributed to the overlap of signals 7 and 8 and signals 5–6 in this region. Similar results are obtained for the system PB-d_6. Therefore, the microstructure for all polymers (A–C) is the same, but the results obtained in an analysis of the aliphatic part of PB-d_4,h_2 and PB-d_6 are slightly higher (c/t ratio decreases at the expense of the c content) than obtained via an analysis of the olefinic part (only possible for polymer B). Although an analysis of PB-d_6 is possible and the experimentally determined microstructure of PB-d_6 is in accordance with results obtained by another group (Bates et al.[2]) (t = 0.53, c = 0.36, v = 0.11), we believe that the cis/trans ratio is closer to 0.40/0.47 than 0.35/0.52. Alternatively, small differences in cis/trans ratio between Bates' sample and ours are possible, due to two different polymerization recipes (3/1 mixture anisole/lithium[2] and benzene).

Additional Material. IR and Raman spectra of polymers A–C are available on request at the address of (G.P.M.v.d.V.).

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