Sequence Distribution Determination of Deuterated Polybutadiene by {^{2}H}^{13}C INEPT Triple Resonance NMR Experiments

Lan Li,† Darlene R. Hensley,† H. James Harwood,‡ Lewis J. Fetters,§ and Peter L. Rinaldi*,†

Knight Chemical Laboratory, Department of Chemistry, and Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, and Corporate Research, Science Laboratories, Exxon Research and Engineering, Annandale, New Jersey 08809

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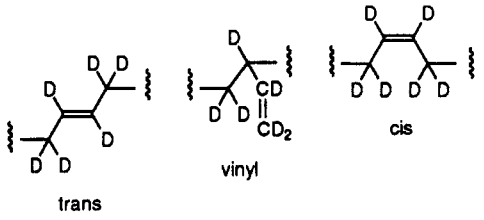
Deuterated polymers such as butadiene have been used in studies on the structure and properties of polymer blends via small-angle neutron scattering (SANS).[1,2] Previous efforts to characterize this polymer using its olefinic carbon resonance pattern were unsuccessful, and a determination based on the aliphatic carbon resonances appeared to yield a high value for the trans content of the polymer.[3] These difficulties were encountered because scalar deuterium–carbon coupling produced a spectrum with a complex group of overlapping multiplets which could not be interpreted. In previous papers[3–5] we have reported applications of {^{2}H}^{13}C INEPT[7,8] NMR experiments for characterizing the structures of organic and polymeric molecules. Such experiments have the advantage of enabling the resonances of deuterium-substituted carbons to be examined without interference from those of nondeuterated carbons. In addition, the resonances of deuterated carbons are observed as narrow lines that are well-defined and easily measured. In this paper we demonstrate that {^{2}H}^{13}C INEPT NMR measurements with simultaneous ^{1}H and ^{2}H decoupling during data acquisition can be used to characterize the composition and microstructure of poly(hexadeuteriobutadiene) (PB-d_6). The relative areas of the olefinic main-chain carbon resonances were obtained from a quantitative one-pulse ^{13}C NMR experiment with ^{1}H- and ^{2}H-gated decoupling to suppress NOE's.



PB-d_6

Figure 1a shows the normal ^{13}C NMR spectrum, obtained with ^{1}H decoupling, of the PB-d_6 sample described in ref 6, which was polymerized in cyclohexane at 20 °C by initiation with t-BuLi. An expansion of the olefinic region is shown in Figure 2a. Due to coupling with ^{2}H, both the olefinic and aliphatic resonances are poorly resolved. This problem can be overcome by applying simultaneous ^{1}H and ^{2}H decoupling (gated to suppress NOE's) to provide the simplified spectra in Figures 1b and 2b. The olefinic carbon resonance assignments, summarized in Table I, are similar to those obtained from PB-h_6,[9] except that they are observed approximately 0.70 ppm upfield from the resonances of corresponding protonated carbons. The vinyl resonances at 142.0 and 113.5 ppm are clearly observed; the methylene peaks in the aliphatic region of this spectrum are better resolved than in spectrum a in Figure 1; and the peak areas can be easily integrated.

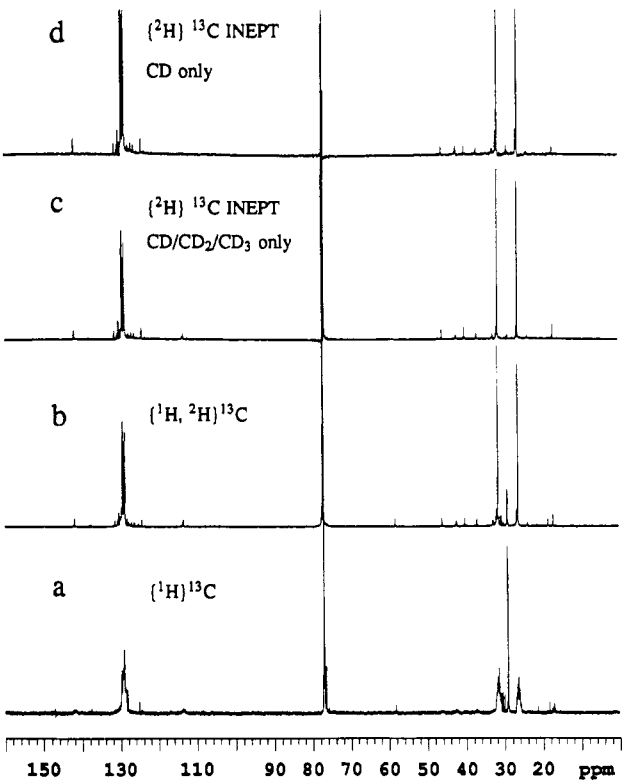


Figure 1. 300-MHz NMR spectra of PB-d_6 (MW ca. 1150) in a 1:1 mixture of $CHCl_3$ and $CDCl_3$ (v/v): (a) one-pulse ^{13}C NMR spectrum (with continuous ^{1}H decoupling; the spectrum was acquired with a 1.815-s acquisition time, a 16 502-Hz spectral window, a 40° pulse, and 1024 transients); (b) one-pulse ^{13}C NMR spectrum with simultaneous ^{1}H and ^{2}H waltz-16 decoupling during the acquisition time, a 16 502-Hz spectral window, a 4.5-s relaxation delay, a 0.908-s acquisition time, a 60° pulse, and 8192 transients); (c and d) {^{2}H}^{13}C INEPT spectra (with continuous ^{1}H decoupling and ^{2}H decoupling during the acquisition period). The spectra in c and d were acquired with a 0.2-s relaxation delay, a 20-ms polarization transfer delay, a 5-ms refocusing delay for (c) and a 14-ms refocusing delay for (d), a 0.599-s acquisition time, a 16 502-Hz spectral window, and 20 480 transients. The 90° pulse widths were 21.0, 230, and 12.5 μs for the ^{1}H, ^{2}H, and ^{13}C channels, respectively.

Because the ^{2}H isotopic labeling is less than 100%, some of the resonances in Figure 2b arise from nondeuterated carbons. These signals are shifted due to isotope shift and result in numerous small signals and shoulders on large peaks. {^{2}H}^{13}C INEPT provides a useful means of filtering resonances of unlabeled carbons from the spectrum. This experiment can be run with different delays to produce spectra with CD, CD_2, and CD_3 signals (Figures 1c and 2c), and spectra with only CD signals (Figures 1d and 2d). For example, a signal at 29.20 ppm in Figure 1a has a considerably lower relative intensity in Figure 1b, because the CD_n multiplets are decoupled, and is missing from parts c and d of Figure 1. Signals from CH carbons at 125.23, 128.14, and 128.50 ppm in Figure 2a are absent from parts c and d of Figure 2; and the vinyl CD_2 signal in Figure 2c is absent from Figure 2d.

† Knight Chemical Laboratory, Department of Chemistry, The University of Akron.
‡ Maurice Morton Institute of Polymer Science, The University of Akron.
§ Exxon Research and Engineering.

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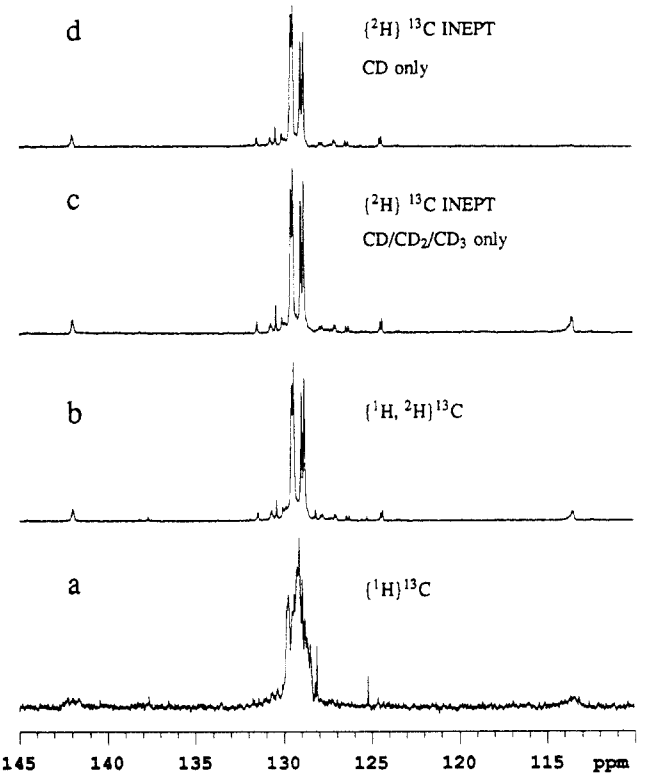

Figure 2. Expansions of the olefinic carbon resonances of PB-d_6 depicted in Figure 1: (a) one-pulse ^{13}C NMR spectrum with ^1H waltz-16 decoupling; (b) one-pulse ^{13}C NMR spectrum with ^1H and ^2H decoupling; (c) $\{^2H\}^{13}C$ INEPT spectrum showing CD, CD_2, and CD_3 resonances; (d) $\{^2H\}^{13}C$ INEPT spectrum showing only CD resonances.

Table I. Chemical Shifts of Carbon Resonances Observed for Polybutadienes PB-h_6 and PB-d_6

		chemical shift (ppm)		
sequence	carbon[a]	PB-h_6[b]	PB-d_6[c]	$\Delta\delta$ (ppm)[d]
C-v	4	24.98–25.00	23.78–23.89	−1.2
C-1,4	1,4	27.42–25.77	26.36 (CD_2)	−1.1
			26.71 (CDH)	−0.8
T-v	4	30.16	29.19	−1.0
T-1,4	1,4	32.75	31.59 (CD_2)	−1.2
			31.96 (CDH)	−0.8
1,4-V-1,4	1	33.99–34.16	32.73–32.89	−1.1 to −1.3
1,4-v-T	1	38.18	37.06	−1.1
v-V	1,2	39.48-41.7	40.21–40.61	−1.1 to −1.3
1,4-V-1,4	2	43.47–43.70	42.32–42.56	−1.2
1,4-V	3	142.75–142.63	141.98–141.94	−0.77 to −0.69
T-v	3	131.35[e]	130.65	−0.70
v-C-v	3	130.69[e]	130.04	−0.65
v-T	3	130.56[e]	129.86	−0.70
v-T	3	129.88[e]	129.17	−0.71
t-T	3	130.08[e]	129.41	−0.67
c-T	3	130.24[e]	129.52	−0.72
C-v	2	129.34[e]	128.62	−0.72
C-t	2	129.48[e]	128.80	−0.68
C-c	2	129.67[e]	128.96	−0.71
v-T	2	128.23–128.51[e]	127.61–127.89	−0.61 to −0.62
v-C-v	2	127.75[e]	127.07	−0.66
v-C-t	2	127.90[e]	127.26	−0.64
v-C-c	2	128.08[e]	127.42	−0.68
1,4-V	4	114.08–114.26	113.45–113.54	−0.63 to −0.72

[a] Carbon: 1,4 unit, $-C(1)H_2C(2)=C(3)HC(4)H_2-$; 1,2 unit, $-C(1)H_2C(2)H(C(3)H=C(4)H_2)-$. [b] Reference 11. [c] Measured from spectrum c in Figure 1. [d] Isotope shift calculated from values in columns 3 and 4. [e] Reference 9.

van der Velden et al.[9] have proposed that the olefinic carbon resonances of polybutadienes be grouped into six areas (A_1–A_6) for use in calculating their cis, trans, and vinyl contents. Table II lists the relative areas observed for these regions and compares them with areas observed previously in the spectra of polybutadiene and poly(1,1,4,4-tetradeuteriobutadiene) that were prepared in the same manner as PB-d_6. Within the limits of experimental error, all three sets of relative areas are equivalent, indicating that the three polymers have the same compositions and microstructures.

Table II. Relative Areas of Olefinic Carbon Resonance Regions Observed for Polybutadienes PB-h_6, PB-d_4, and PB-d_6

resonance range	chem shift range	PB-h_6[a]	PB-d_4[a]	PB-d_6[b]	calc[c]
A_1	131.7–132.3	0.01	0.00	0.00	0.00
A_2	131.3–131.7	0.04	0.03	0.02	0.02
A_3	129.9–130.8	0.53	0.50	0.53	0.53
A_4	129.3–129.9	0.36	0.40	0.40	0.39
A_5	128.2–128.6	0.03	0.04	0.02	0.03
A_6	127.7–128.0	0.03	0.02	0.02	0.02

[a] Reference 9. [b] This work. [c] Calculated for t = 0.465, c = 0.415, and v = 0.120.

The aliphatic carbon resonances observed in the $\{^2H\}^{13}C$ INEPT spectra (c and d of Figure 1) are clearly those expected for a polybutadiene with a low vinyl content. The chemical shifts observed are compared in Table I with those assigned by Sato and others to the aliphatic carbon resonances of similar nondeuterated polymers.[10] In general, carbons containing two deuterium atoms are observed 1.2 ± 0.1 ppm upfield from their nondeuterated counterparts, and singly deuterated carbons are observed upfield 0.8–0.9 ppm from their nondeuterated counterparts.

The $\{^2H\}^{13}C$ INEPT NMR experiment, combined with ^2H labeling, thus provides a useful method for studying the structure of polymers. Application of this experiment combined with one-pulse ^{13}C NMR and simultaneous ^1H- and ^2H-gated decoupling provides considerable spectral simplification, which is valuable for performing quantitative analysis and for developing resonance assignments.

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