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$$\frac{\partial Q_{\mathrm{nn}^0}(t)}{\partial t} = A\frac{\partial Q_{\mathrm{nn}^0}(t)}{\partial n^2} - BQ_{\mathrm{nn}^0}(t)$$

where $A = 3.16W_3 - 9.61W_4$, $B = 4.74W_4$, and W_3 and W_4 are respectively the jump rates of three and four bond rearrangements.

New Method for the Microstructure Determination of Polybutadiene with Cis-1,4, Trans-1,4, and Vinyl-1,2 Units by ^{13}C NMR

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ABSTRACT: The assignment of the olefinic resonances in the ^{13}C NMR spectra of various polybutadienes has been tested by comparing experimentally determined and theoretically calculated peak areas. On the basis of a good agreement between the two results, an elegant numerical and graphical method has been outlined for the rapid determination of the cis-1,4, trans-1,4, and vinyl-1,2 ratio of these polymers.

Introduction

Infrared and Raman spectra of polybutadienes have been used for the determination of the microstructure of polybutadienes consisting of sequences of cis-1,4 (c), trans-1,4 (t), and vinyl-1,2 (v) units.[1,2] Both methods rely more or less on isomerically pure polymers, each containing relatively high concentrations of one of the three kind of base units.

Another method not requiring pure polymers is ^{1}H NMR. Direct information about the ratio v/(c + t) can be obtained from the ^{1}H NMR spectrum.[3] However, except for polymers that contain only two base units, i.e., v and c or t, it is not possible to extract information about the amounts of the three base units that are present in polybutadienes containing significant fractions of all three parts.[3-5] Even at 400 MHz, the resolution of the olefinic resonances is insufficient to resolve c and t signals.[6]

^{13}C NMR spectroscopy, on the other hand, offers more information because detailed assignments have been described for the aliphatic[7-10] and olefinic carbons.[8,11] Therefore, a quantitative analysis, excluding the necessity of using model polymers, has been attempted by measuring the v/(c + t) ratio by ^{1}H NMR[6] and the ratio c/t via ^{13}C NMR[6] (aliphatic carbon resonances). The combination of these two techniques results in a c, t, and v ratio for polybutadienes. Alternatively the aliphatic ^{13}C resonances[7,9] have been used (assuming Bernoullian statistics) to give indirect information on the relative abundance of the three base units.

The first method necessitates two independent measurements (^{1}H/^{13}C NMR); the second (^{13}C NMR) is severely hampered by questionable assignments[6,10] and different compositionally induced diads for the methylene carbons and triads for the methine carbons.[9] Furthermore T_1 and NOE effects are not necessarily equal for these different signals.

A similar ^{13}C NMR analysis has not been employed for the olefinic resonances, although general agreement exists about the assignments.[8,11] This might be due to the decreasing chemical shift dispersion going from the aliphatic carbon resonances to the olefinic resonances, leading to complex, partially overlapping signals. With the above mentioned assignments of Elgert et al.[11] a simple method is outlined for measuring the isomeric distribution along the polybutadiene (PB) chains. Sequence analysis therefore is used to quantify the microstructure of PB.

Experimental Section

A series of five PB rubbers (unfilled, uncured) is examined here. The commercially available polymers, arranged in succession of increasing v content are from Hüls (all cis) (A), Goodyear (liquid

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Table I
Assignments for the ^{13}C NMR Signals of the Olefinic Main-Chain Cis-1,4 and Trans-1,4 Carbons in Polybutadiene[11] (Polymer E)

carbon atom	resonance	triad assignt	chem shift, ppm
—C=C*—	1	vtv	131.79
	2	ctv, ttv	131.35
	3	vcv	130.69
	4	vtt, vtc	130.56
	5	ccv, tcv	130.24
	6	ctc, ctt	
	7	vcc, vct	130.08
	8	ttc, ttt	
—*C=C—	9	ctv, ttv	129.88
	10	ccc, tcc	129.67
	11	cct, tct	129.48
	12	ccv, tcv	129.34
	13	vtc	128.51
	14	vtt	128.37
	15	vtv	128.23
	16	vcc	128.08
	17	vct	127.90
	18	vcv	127.75

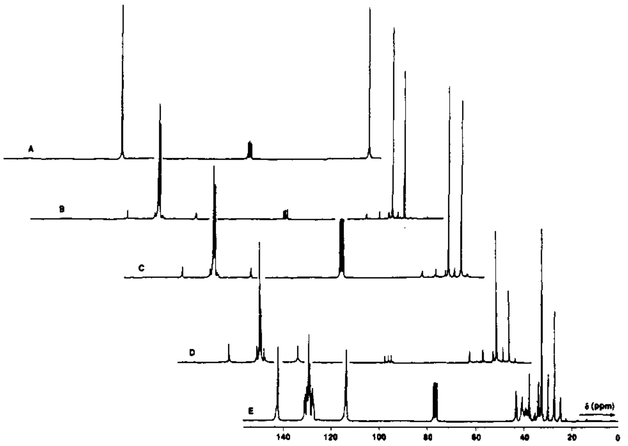

Figure 1. ^{13}C NMR spectra of five polybutadienes, recorded in $CDCl_3$, arranged in order of increasing v content. The spectra have been shifted with a horizontal offset with respect to each other: A, B, C, and E at 50 MHz; D at 25 MHz.

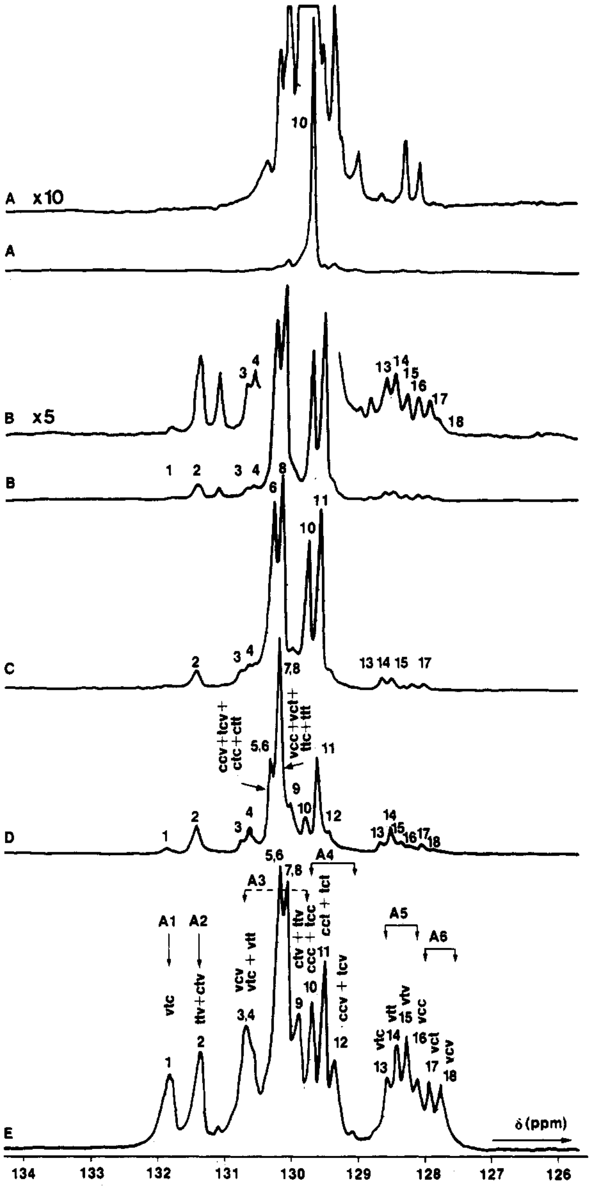

Figure 2. Expanded ^{13}C NMR spectra of the olefinic main-chain cis-1,4 and trans-1,4 carbon resonances, arranged in increasing vinyl-1,2 content. Assignments have been discussed in the text.

polybutadiene) (B) and Aldrich (lot no. 18, 138-2) (C) (anionically made polymers), DSM (D) (emulsion polymer), and Aldrich (lot no. 20, 050-6) (E).

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 generally obtained at 25 °C, using broadband decoupling 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 length 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 been measured with the use of the standard 180° $-\tau-$90° inversion recovery pulse sequence, using six values of τ of 0.07, 0.26, 0.93, 3.27, 11.43, and 40 s. The T_1s were determined from a three-parameter fit to the peak intensities with the use of the program supplied with the spectrometer. No differential NOEs have been determined, but two additional experiments have been performed on sample C using a larger delay (20 s), the first without gating off the NOE and the second gating off the NOE, looking mainly at the olefinic carbon atoms.

The least-squares fitting program (written in Fortran) was run on a HP 1000-A600 minicomputer and calculates within 30 s the desired ratios.

Discussion of the Method

Assignments. In Figure 1 are shown the ^{13}C NMR spectra of the five polymers arranged in order of increasing v contents. The olefinic region can be subdivided into two parts:

a. The resonances at approximately 114 and 143 ppm have been assigned to the two different vinyl 1,2 carbon atoms, the methylene and methine, surrounded by neighboring c, t, or v units. Besides compositional sequence splittings, also configurational splittings (tacticity) occur. This can be seen in Figure 1, especially for polymer E. Up to now, the deceptively simple ^{13}C NMR patterns have not been completely analyzed.[12,13]

b. The complex resonance pattern between 127–133 ppm, depicted in Figure 2, is due to compositional splittings 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.).[8,9,11] When the negligible influence of tacticity effects is ignored, the theoretically expected number of resonances on a triad level is 36, i.e., $2(xcy + xty)$, x, y = c, t, v. However the homotriads and the symmetric isolated triads contain two magnetically equivalent carbons, so the number of resonances to be observed cannot exceed 24. Experimentally,

Table II
Experimentally Observed and Theoretically Calculated Peak Areas A_i (i = 1–6) and Best Fit Values for c, t, and v for Polymer C

	conditions		
parameter	broadband decoupling, 5-s pulse delay	broadband coupling, 20-s pulse delay	gating off NOE, 20-s pulse delay
A_1			
calcd	0.005	0.005	0.005
exptl	0.015	0.005	0.009
A_2			
calcd	0.032	0.031	0.033
exptl	0.038	0.036	0.034
A_3			
calcd	0.527	0.534	0.533
exptl	0.524	0.532	0.532
A_4			
calcd	0.368	0.365	0.358
exptl	0.365	0.364	0.358
A_5			
calcd	0.037	0.036	0.039
exptl	0.033	0.031	0.040
A_6			
calcd	0.031	0.029	0.031
exptl	0.020	0.024	0.028
t	0.470	0.480	0.475
v	0.135	0.130	0.140
c	0.395	0.390	0.385

16–18 different carbon resonances are reasonably well resolved (Figure 2).

No new assignments for this spectral region have been accomplished after 1975,[8,11] therefore we have used the assignments of Elgert et al.[11] in combination with their notation. All assignments have been depicted for polymer E in Figure 2 and have been listed in Table I (polymer E) together with the respective chemical shifts.

Quantitative and Data Analyses. Quantitative analysis is based on a least-squares fitting procedure between the experimentally observed and theoretically calculated areas of the main chain cis-1,4 and trans-1,4 olefinic resonances. Although the v-centered triads (at 114 and 143 ppm) have been excluded, the v ratio indirectly determines also to a certain extent the areas of the carbon resonances, e.g., triads like vtv, ctv, and ttv.

For the olefinic resonances of the central c and t carbons (127–133 ppm) occurring in the different kinds of compositional triads, it is evident that a simple experimental discrimination between the cis- and trans-centered triads is not possible for two reasons: (a) overlapping resonances for the cis-1,4 and trans-1,4-centered triads (peaks 5 and 6, 8, 9, and 10, Figure 2) and (b) the resonance of two different carbon atoms of one triad at very different fields (e.g., peaks 3 and 18 for vcv).

Therefore, a somewhat more elaborate method must be followed which, however, uses all 16–18 experimentally observed peak areas. For practical purposes, we have chosen not to determine all isolated peak areas via curve resolution methods, but we have merely selected six peaks or combinations of peaks, namely 1, 2, 3–9, 10–12, 13–15, and 16–18. In Table II are listed these experimentally observed peak areas, denoted by A_i (i = 1–6), for the five respective polymers (normalized to unity).

The theoretically calculated peak areas denoted by a_1–a_6 can now be evaluated, taking into account Bernoullian statistics.[14] For matters of convenience, we define the parameters c, t, and v now also as the molar fractions of cis-1,4, trans-1,4, and vinyl-1,2 units present in the polymer chain. In such a description the homotriad ccc indicates three sequential cis-1,4 units, and the relative abundance in such a model will be given by c^3 and the abundance of other triads like ttv or tvt by vt^2. This Bernoullian model has been applied to polybutadienes[7,11,15] and only very slight deviations have been reported for hydrogenated polybutadienes.[15] The six peak areas should fulfill the following relations:

$$\begin{aligned} a_1 &= v^2t \quad \text{peak 1} \\ a_2 &= tv(1 - v) \quad \text{peak 2} \\ a_3 &= cv + (cv + 2t)(c + t) \quad \text{peaks 3–9} \\ a_4 &= (2c - cv)(c + t) \quad \text{peaks 10–12} \\ a_5 &= vt \quad \text{peaks 13–15} \\ a_6 &= cv \quad \text{peaks 16–18} \end{aligned} \tag{1}$$

The validity of eq 1 can be verified, realizing that the total area a_i (i = 1–6) necessarily equals two main-chain cis or trans olefinic carbon atoms, in other words

$$\sum_{i=1}^{6} a_i = 2(c + t) = 2(1 - v) \tag{2}$$

Peak areas, normalized to unity, can be calculated as

$$A_i = a_i / \sum_{i=1}^{6} a_i \tag{3}$$

This leads to the following set of equations:

$$\begin{aligned} A_1 &= \tfrac{1}{2}v^2t(1 - v)^{-1} \\ A_2 &= \tfrac{1}{2}vt \\ A_3 &= \tfrac{1}{2}cv(1 - v)^{-1} + \tfrac{1}{2}(cv + 2t) \\ A_4 &= c(1 - \tfrac{1}{2}v) \\ A_5 &= \tfrac{1}{2}vt(1 - v)^{-1} \\ A_6 &= \tfrac{1}{2}cv(1 - v)^{-1} \end{aligned} \tag{4}$$

The cis-1,4, trans-1,4 and vinyl-1,2 ratio of these polybutadienes can now be obtained from the experimentally determined areas A_i through a least-squares fitting program.[16] This program estimates the c, t, and v ratios by minimizing the summed squared difference D between the six experimental areas and the calculated six areas obtained using eq 4

$$D = \sum_{i=1}^{6} (A_i(\text{calcd}) - A_i(\text{exptl}))^2 \tag{5}$$

According to eq 4 this is a complicated nonlinear minimization problem. Fortunately, there are two constraints that simplify the problem:

$$\begin{aligned} c, t, v &\geq 0 \\ c + t + v &= 1 \end{aligned} \tag{6}$$

From these constraints, it can deduced that the solution of this problem can be found in a small well known part of the infinite set of all possible solutions.

In Figure 3, this small part has been drawn in 3-dimensional solution space. It is evident that solutions of eq 4 have to be found in the triangle spanned by c = 1, t = 1, and v = 1. Because of the limited set of solutions and the availability of only six measured areas, the fitting program uses a direct-search method to find the minimum value of D. In Table II have been listed the experimentally observed results and the results of the least-squares fitting program applied to polymer C, under three different measuring conditions, i.e., using pulse delays of 5 and 20 s without suppression of NOE effects and using a pulse

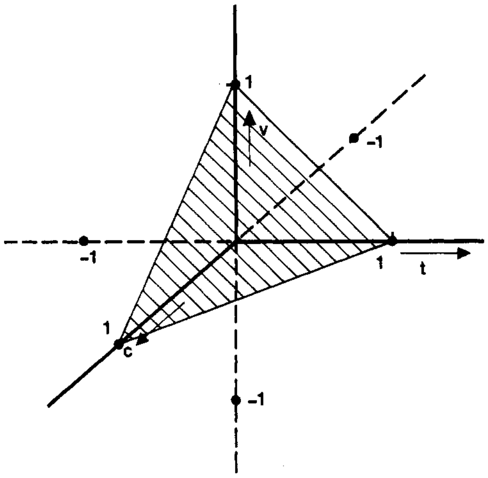

Figure 3. The surface of the triangle visualizes the allowable solutions of the minimization problem, according to the constraints of eq 6.

Table III
Experimentally Observed and Theoretically Calculated Peak Areas A_i (i = 1-6) and the Best Fit Values for c, t, and v for Five Polybutadienes A-E

parameter	polymer A	B	C	D	E
A_1					
calcd	0.000	0.004	0.005	0.017	0.061
exptl	0.000	0.010	0.015	0.017	0.059
A_2					
calcd	0.000	0.028	0.032	0.061	0.064
exptl	0.000	0.038	0.038	0.061	0.071
A_3					
calcd	0.010	0.518	0.527	0.611	0.443
exptl	0.000	0.516	0.524	0.610	0.440
A_4					
calcd	0.985	0.390	0.368	0.200	0.189
exptl	0.973	0.388	0.365	0.203	0.191
A_5					
calcd	0.000	0.032	0.037	0.078	0.125
exptl	0.027	0.032	0.033	0.078	0.121
A_6					
calcd	0.005	0.028	0.031	0.032	0.118
exptl	0.000	0.016	0.020	0.031	0.118
t	0.000	0.465	0.470	0.555	0.265
v	0.010	0.120	0.135	0.220	0.485
c	0.990	0.415	0.395	0.225	0.250

delay of 20 s, gating off the NOE. In Table III are summarized the results for the five polymers, using the standard conditions, i.e., broadband decoupling and a pulse delay of 5 s.

Table IV
Experimentally Determined Values for the Microstructure of Cis-1,4, Trans-1,4, and Vinyl-1,2 Units of Polybutadiene Using ^{13}C NMR (Olefinic) and IR Spectroscopy[17,18]

	polymer A	B	C	D	E
	^{13}C Olefinic Resonances				
c	0.99	0.42	0.40	0.22	0.25
t	0.00	0.46	0.47	0.56	0.26
v	0.01	0.12	0.13	0.22	0.49
	IR				
c		0.41	0.41	0.20	0.23
t		0.51	0.48	0.58	0.37
v		0.08	0.11	0.22	0.40

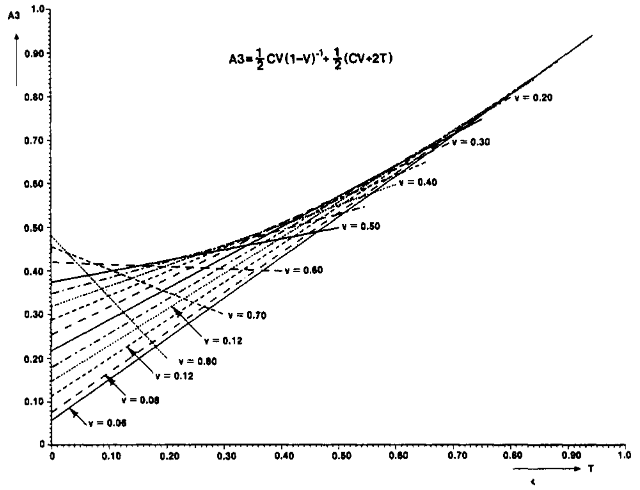

Figure 4. Universal calibration curve relating the theoretically calculated peak area A_3 and t. Each curve holds for only one fractional value of v.

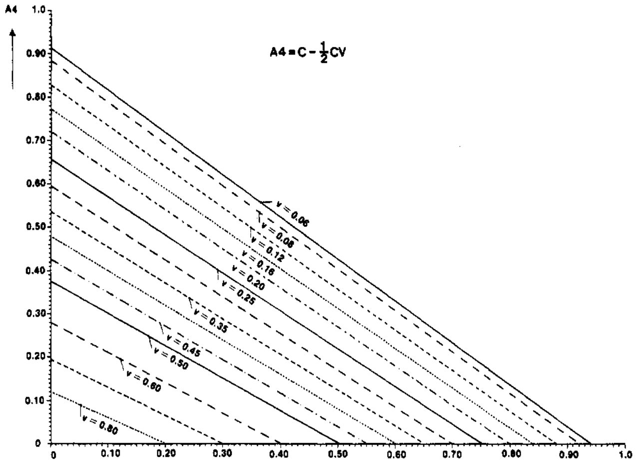

Figure 5. Universal calibration curve of the calculated peak area A_4 (peaks 10-12; see text) as a function of the t ratio. Each curve applies to only one value for the v ratio.

Results and Discussion

T_1 values have been measured for the main-chain olefinic carbon resonances 6, 8, 10, and 11 (polymer C), being 3.5, 2.9, 2.9, and 2.2 s, respectively, and for the two side-chain olefinic carbon atoms, resonating at 114 (0.9 s) and 143 ppm (3.6 s). With the assumption that these values are representative for the other olefinic carbon resonances, an experiment with a longer delay (20 s, exceeding $5T_1$) shows good agreement with the results obtained with a shorter delay (5 s). Finally the good agreement of the results for the experiment, gating off the NOE, with the previously discussed experimental data convincingly demonstrates the quantitative validity of the results. Thus it is evident from Table II that a close correspondence exists between calculated and observed values, implicitly proving the assumed Bernoullian model. The results obtained for all polymers (see Table III), calculated with 4 and 5 are found (see Table IV) to be in reasonable agreement with the results obtained by IR spectroscopy.[1,17] Moreover, the theoretically calculated values for v can also be compared with experimentally determined values, bearing in mind the similar T_1 values for the vinyl carbons (3.6 and 0.9 s) and the olefinic main-chain carbons, using eq 7

$$v = \frac{A_{114} + A_{143}}{A_{114} + A_{127-133} + A_{143}} \tag{7}$$

where A_{114}, etc., denote the peak areas of the resonances indicated by their respective chemical shifts. The calculated amounts, using eq (7), are within ±0.02 compared with the results using eq (5). Provided that the value of

v has been determined (either via ^{1}H NMR[6] or eq 7), a graph of the theoretically calculated (eq 4) major peak areas A_3 and/or A_4 vs. t, using the experimentally determined values for A_3 and/or A_4 and the experimental value of v as input, easily shows that $t = 0.47$ (polymer B, $v = 0.12$)

The results on several polybutadienes will be briefly discussed. For high cis-1,4 polybutadienes, it is difficult (or even impossible) to estimate the contents of the small fractions of v and/or t via IR spectroscopy.[1,17] Via ^{13}C NMR it is possible to quantify the small amounts of vinyl present (Table II, Figure 1) and the absence of t units (Figure 1) (polymer A). The experimentally observed ^{13}C NMR spectra of polymers B and C are nearly identical with and very similar to real 1,4-polybutadienes. The observed resonances at 131.1 and 128.8 ppm, being present in polymer B and presumably also in polymer E, have been assigned tentatively to the combined resonance of the ctv and ttv (see Table II, peak area A_2) and vtc triads (peak area A_5). The six different olefinic triads that remain for real cis-1,4/trans-1,4 polybutadienes, i.e., ccc, cct, tct, ctt, ttc, and ctc lead to only four peaks (see Table I), occurring at 130.24, 130.08, 129.67, and 129.48 ppm. They therefore contribute only to areas A_3 (all trans olefinic atoms) and A_4 (all cis-centered olefinic carbon atoms), in full agreement with eq 1 and 4. The experimentally observed ^{13}C NMR spectra of polymers B and C are nearly identical with real 1,4 polybutadienes,[18] showing four major peaks. The contribute only to areas A_3 (all trans olefinic carbon atoms) and A_4 (all cis-centered olefinic carbon atoms), in full agreement with eq 1 and 4. The experimental results (Table II) nicely confirm the approximately equibinary (equal molar ratios) behavior. Moreover it is promising that subtle differences in the olefinic spectral region (especially peaks 13–18) exist, which apparently lead to slightly different ratios. For emulsion polybutadienes, exemplified by polymer D, the fraction v is approximately constant over a large range of polymerization temperatures[19] and in fact equal to $v \simeq 0.20$. The experimentally observed value of $v = 0.22$ is in good agreement with the estimated value of $v = 0.20$, as is the value of $v = 0.555$, expected for a polymerization temperature between 40 and 80 °C.[19] The above outlined procedure has several advantages: (a) it is independent of the degree of conversion, (b) it takes into account only main-chain olefinic carbon atoms, displaying no differential NOE or T_1 effects, (c) it has the possibility of an experimental cross-check of the v ratio. The method however cannot be applied to mixtures of polybutadienes with different c, t, and v ratios (polymer blends), due to the breakdown of eq 1. Therefore it is also impossible to estimate the c, t, and v contents of emulsion polybutadienes, synthesized with a temperature gradient during the polymerization procedure, because the polymerization temperature determines to a major extent the c, t, and v ratios of these polymers.[19]

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