References and Notes

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^{13}C Nuclear Magnetic Resonance Spectroscopy of Polydienes, Microstructure of Polybutadiene

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ABSTRACT: ^{13}C nmr spectra have been recorded of several polybutadienes and their hydrogenated analogs, with various amounts of 1,2 structure, but with a roughly constant ratio of cis-1,4 to trans-1,4 structures. From an assignment of these spectra a detailed picture has emerged of the sequence distribution of the cis- and trans-1,4 and the 1,2 units in the polybutadiene chain. It is shown that these units are distributed in an essentially random manner and that 1,2 units are head to tail incorporated.

The use of ^{13}C nmr as a tool for investigating the microstructure of polybutadiene was first reported by Duch and Grant.[1] Their initial observation was that *cis*- and *trans*-1,4-butadiene incorporation could be distinguished from the spectra since there is a difference of 5.4 ppm between cis and trans oriented methylene carbons and a difference of 0.7 ppm between the olefinic carbons. More recently Mochel[2] observed that 1,2-polybutadiene displays a set of chemical shifts completely different from that of 1,4-polybutadiene. This indicates the sensitivity of the ^{13}C chemical shift to differences in the polymer microstructure.

We have studied a number of polybutadienes with varied 1,2-butadiene contents in order to obtain more detailed information on the microstructure.

I. Experimental Section

Polybutadiene samples with various amounts of 1,2 structure were prepared by polymerization in hydrocarbon solvents or ethers (for a higher 1,2 content) with *sec*-butyllithium as initiator. Three of these polymers were completely hydrogenated.

For nmr purposes the polybutadienes were dissolved in CCl_4 and the hydrogenated products in a 1:1 mixture of $CHCl_3$ and CCl_4. ^1H nmr spectra were recorded on a Varian XL-100 and an HR-220 spectrometer. The ^{13}C measurements were carried out in part in a Varian HA-100 equipped with a Fourier transform accessory and in part on a Varian XL-100, using a CAT for spectrum accumulation. ^{13}C-enriched CS_2 was employed as an external ^{13}C lock for the HA-100 and deuterated methylene chloride provided the internal ^2H lock for the XL-100. The carbon spectra were all noise decoupled except when spectral analysis required partial decoupling of the protons.

II. Experimental Results and Analysis

A. Experimental Results. First of all the constitution of the polymers in terms of percentages of cis, trans, and vinyl structures was established with the aid of nmr. The vinyl content was readily calculated from 100-MHz ^1H nmr spectra; the cis and trans contents could be determined with 220-MHz ^1H nmr, ir, or ^{13}C nmr. The results of these measurements are summarized in Table I.

For the analysis of the microstructure both pulsed FT ^{13}C spectra and CW ^{13}C spectra were recorded. Although FT spectra have the advantage of a high signal-to-noise ratio (see *e.g.*, Figure 3), we often recorded CAT spectra to obtain the best possible spectral resolution, avoiding at the same time the dependence of the signal intensity on the pulse repetition rate (Figures 1, 2, and 4).

B. Spectral Analysis. In view of the complexity of the spectra at high vinyl content and the need for an unambiguous interpretation we carried out the analysis in three phases.

First, we eliminated the distinction between cis and trans structures by completely hydrogenating the polybutadienes. This resulted in a substantial reduction in the number of ^{13}C nmr lines to be identified (see Figure 1). Besides the fact that the resultant polymers were alkanes, for which abundant models studies and shift prediction formulae[3,4] are available, elucidation of their structure led to an understanding of the incorporation of 1,2 and 1,4 units in the original polybutadiene. To obtain a clear picture of cis-trans ordering in alkyllithium-based polybutadienes without interfering vinyl features, we reduced the vinyl content as far as possible. For this purpose we synthesized two polymers having a very low vinyl content (*ca.* 4%) and different cis:trans ratios (samples F and G in Table I). Their ^{13}C nmr spectra (Figure 2) could readily be interpreted in terms of cis-trans polyads.

Making use of the experience thus gained we attacked the more complicated problem of analysing the spectra shown in Figures 3 and 4. This analysis should throw some light on the cis-trans vinyl ordering in alkyllithium-based polybutadienes.

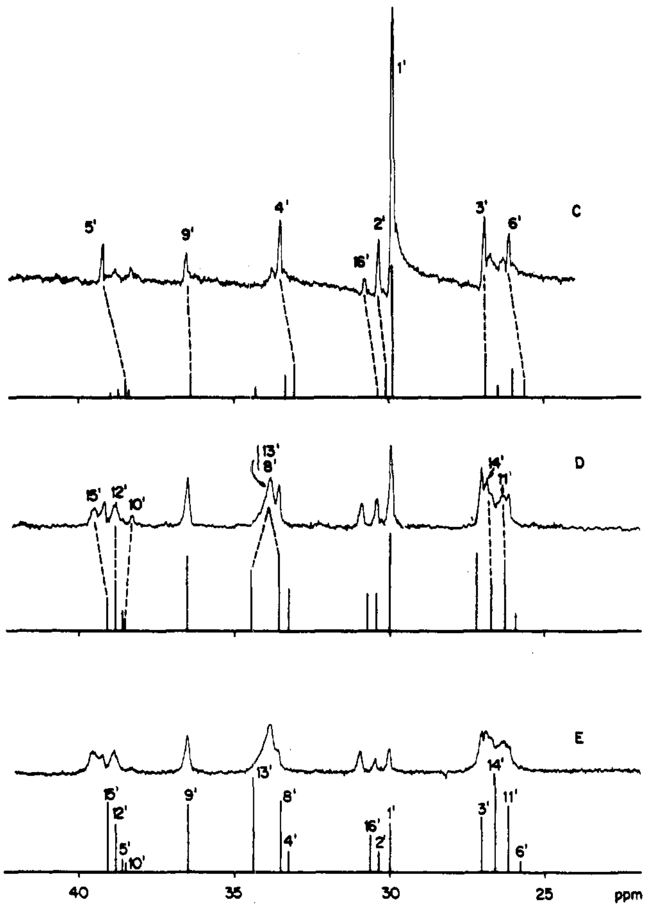


Figure 1. ^{13}C nmr spectra (CW) of hydrogenated polybutadienes. Shifts are in ppm relative to Me_4Si. The numbering C, D, E refers to Table I. Stick spectra are explained in the text.

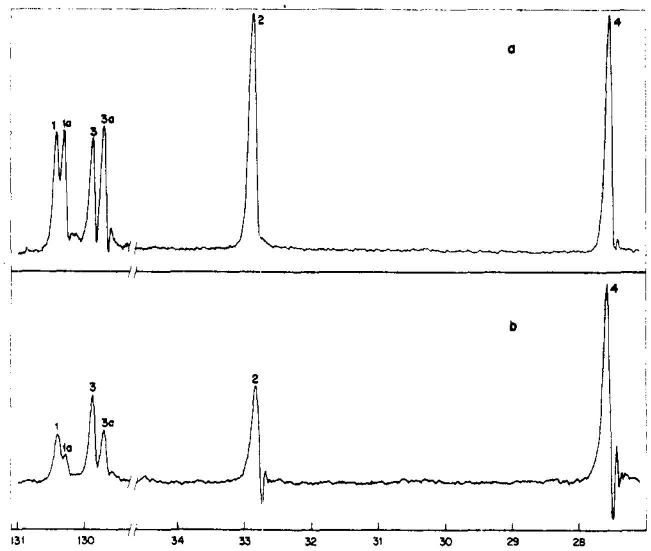


Figure 2. ^{13}C nmr spectra (CW) of two polybutadienes with a very low vinyl content. Note the splitting of the olefinic resonance lines. The numbering refers to structures in the text: (a) 50:50 cis:trans; (b) 64:36 cis:trans.

Table I
Compositions of the Polybutadienes under Study

Sample	% 1,2	% Trans-1,4	% Cis-1,4
A	14	49	37
B	34	42	24
C	43	37	20
D	64	23	13
E	75	13	12
F	4	48	48
G	4	35	61

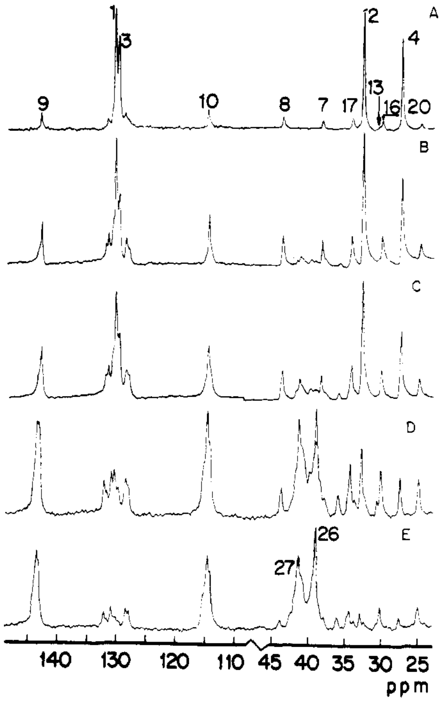
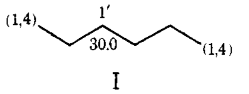


Figure 3. ^{13}C FT nmr spectra of polybutadienes with various vinyl contents (see Table I). Shifts are relative to Me_4Si. The numbering of the carbon lines refers to structures in the text.

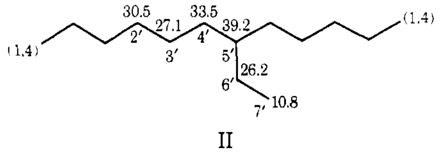
i. 1,2-1,4 Linkages (Hydrogenated Polybutadiene). The spectra of the hydrogenated polybutadienes are shown in Figure 1. In making the assignments we started with the simplest structures, *i.e.*, those with a low vinyl content, and gradually proceeded to the more complex structures. We employed a combination of available techniques for ^{13}C assignments, namely, model alkanes, partial decoupling, and shift prediction formulae.[3,4] An impression of the sort of agreement between predicted and observed shifts can be obtained from Table II and the stick spectra in Figure 1.

The first structure to be discussed is that derived from 1,4 blocks, structure I. The assignment of carbon type 1'



I

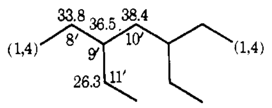
is simply that of the methylene carbons in polyethylene. The introduction of a single vinyl group into the chain, however, gives rise to structure II, following hydrogenation.



II

The pendent ethyl group generates six spectroscopically distinguishable carbon types, 2' to 7'. The observed shifts are indicated in II. These assignments agree closely with those reported for the same structural ensemble in a copolymer of ethylene and 1-butene[5] and also in a low-density polyethylene where isolated ethyl branches are known to occur.[6]

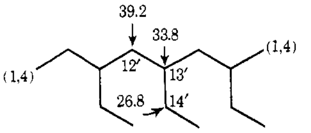
At increasing 1,2 contents there is a higher probability of finding sequences of more than one 1,2 unit, as in structure III.



III

This results in the creation of four new carbon types 8′–11′, the assignments for which were made with the help of the chemical shift parameters of Lindeman and Adams[3] and Grant and Paul.[4] For example, $C_{11'}$ and $C_{8'}$ each have an extra δ carbon compared to $C_{6'}$ and $C_{4'}$, respectively. They are therefore predicted to be deshielded by between 0.1 and 0.3 ppm. Actually, $C_{11'}$ and $C_{8'}$ were observed 0.1 and 0.3 ppm, to low field, respectively. Carbons 9′ and 10′ experience, respectively, a $\gamma + \delta$ and a $\beta + \gamma$ effect, relative to 5′ and 4′, which explains the 2.9-ppm shift upfield for 9′ and the 4.9-ppm downfield shift for 10′.

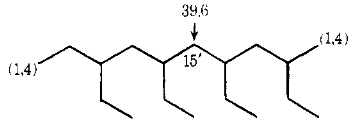
The following ensemble is that of three 1,2 units (IV).



IV

Three new carbon types are generated, 12′, 13′, 14′ having, respectively, δ, $\gamma + \delta$, and δ carbons extra compared to 10′, 9′, and 11′. The assignment of the observed shifts in IV is considered unambiguous. Unfortunately, the effects of tacticity become increasingly evident. In these blocks of 1,2 units, iso-, hetero-, and syndiotactic triads can occur and have been seen for many polymers, *e.g.*, in spectra of polypropylene multiple signals can be observed for different triads.[7] In our case, however, the effects of tacticity are such that only signal broadening occurs, so that at present it is impossible to analyse this aspect any further.

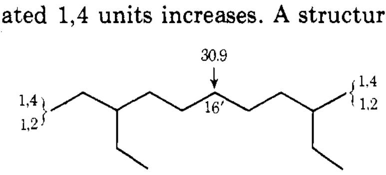
The only new structure ensemble consisting of nothing but 1,2 units which gives rise to spectroscopically distinguishable carbons is that containing four 1,2 units (V).



V

Carbon-15′ has an extra δ carbon compared to 12′ and hence its assignment as the lowest field signal. Sequences of more than four 1,2 units give no new carbon types with the present resolution.

At very high 1,2 contents, however, the probability of finding isolated 1,4 units increases. A structure such as VI



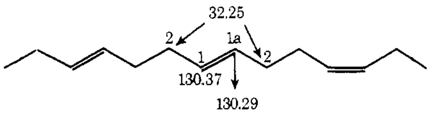
VI

gives rise to one new signal, 16′, having an extra δ effect compared to 2′, hence its assignment at 30.9 ppm. Table II summarizes the calculated and observed chemical shifts for these polymers. Calculated ^{13}C chemical shifts and calculated intensities are also shown in Figure 1 in the form of stick spectra. ^{13}C intensities were calculated from Bernouilli statistics, that is, we assumed a random placement of 1,2 and 1,4 structural elements in the polymer chain. Carbon atoms 1′, 2′, 3′, 4′, 5′, 6′, 9′, and 16′ are the most suitable for intensity comparison since they do not suffer the effects of tacticity and the corresponding nmr lines are therefore quite narrow. Lines numbered 8′, 10′, 11′, 12′, 13′, 14′, and 15′ are broadened since they originate from atoms in 1,2 polyads, where isotactic, heterotactic, and syndiotactic triad sequences give rise to slightly different chemical shifts.

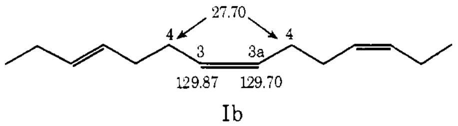
Restricting, therefore, the attention to the narrow lines, one can make a comparison with predicted intensities within one type of polymer and one can also follow the change in intensities on going from one polymer to another. Doing so we conclude that within a margin of 20%[8] there is agreement between experimental and predicted intensities and that therefore 1,4 and 1,2 units in these polymers are randomly distributed.

ii. Cis-Trans Linkages at Low Vinyl Concentration. The spectra of two polymers of low vinyl content (4%) but with different cis:trans ratios are shown in Figure 2. Lines associated with vinyl structures are not observed above the noise. The splitting of the trans and cis olefinic signals (lines 1, 1a and 3, 3a, respectively) into apparent doublets with the aliphatic signals remaining as singlets is of great importance. It implies that the olefinic carbons are sensitive to the configuration of the neighboring butadiene units. As compared with a trans neighbor, a cis neighbor produces a slightly different shielding. In order to assign the olefinic lines it is necessary to consider the signal intensities in Figure 2b. The cis:trans ratio is given by the ratio of the aliphatic signals, from which we see that Figure 2a represents a 50:50 cis:trans polybutadiene and Figure 2b a 64:36 cis:trans polymer. Clearly, the most intense line of each olefinic pair, *viz.*, signals 1 and 3, must originate from carbons having a cis 1,4 neighbor and the lines with the lower intensity, 1a and 3a, from carbons with a trans neighbor. The fact that the relative intensities (3:1 = 1:1a = 3:3a = 3a:1a = 4:2) all equal the cis:trans ratio 64:36 reflects the completely random distribution of cis and trans units.

The question which of the two olefinic cis carbons in, for example, a cis-trans dyad "feels" the configuration of the neighboring trans unit is not answered at this stage. Intuitively perhaps one would conclude that the cis olefinic carbon *nearest* to the trans double bond would "feel" the trans configuration more than the other cis olefinic carbon, which is further separated from the trans neighbor by the cis double bond. In fact this is not the case! As will be shown in subsection iii, the olefinic carbon furthest removed from the neighbor is the one which "feels" the configuration of that neighbor. The lines numbered 1, 1a, 3, and 3a in Figure 2 correspond therefore to the olefinic carbons indicated in the 1,4-triad structures.



Ia



Ib

iii. Cis-Trans Vinyl Ordering. The introduction of increasing amounts of vinyl structures into cis:trans 1,4-polybutadiene results in rather complex spectra. Part of the complexity arises from the generation of new carbon types, as was seen in subsection i, when the number of pendent ethyl groups increases and part is due to the appearance of tacticity effects as the block size of the vinyl

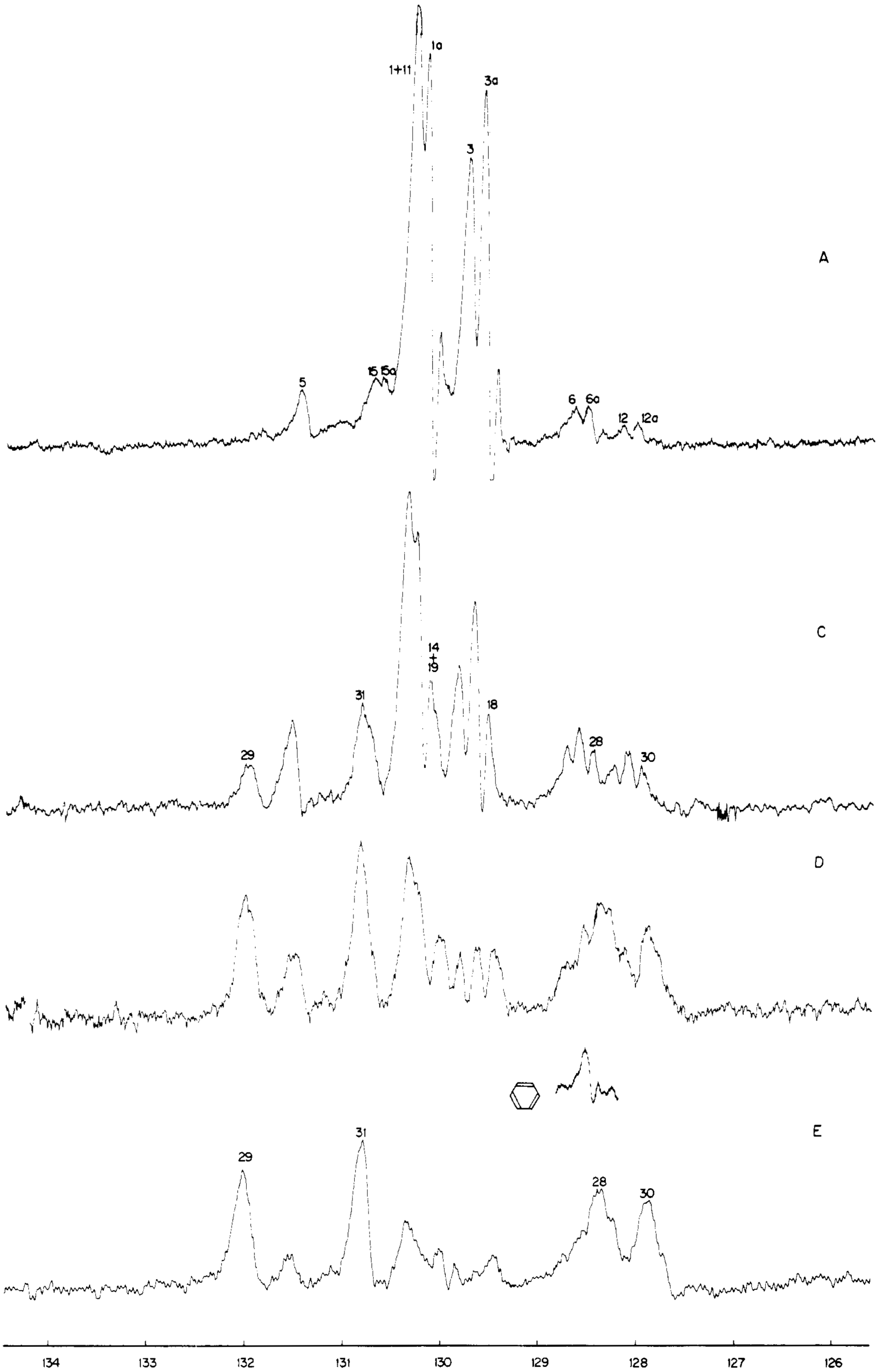
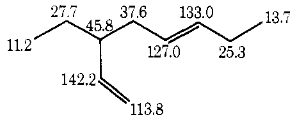


Figure 4. Expansion of the 125–135-ppm region of Figure 3 (CW spectra), showing the olefinic cis and trans carbon resonances. Notice the large number of lines for these two carbon types. Benzene reference is at 128.53 ppm.

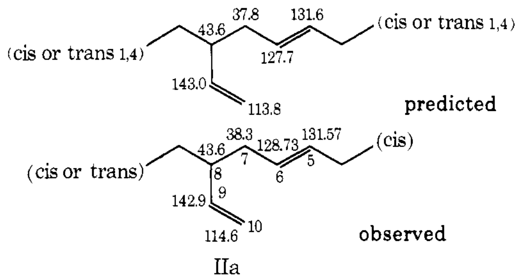
sequences increases. Figure 3 gives an overall picture of how the spectral pattern changes with increasing vinyl content; Figure 4 shows an expansion of the olefinic region from 125 to 135 ppm (cis and trans olefinic carbons) obtained with a higher resolution. At least 15 lines are observed for these *two* carbons. Most of the subsequent discussion concerns the assignments of these olefinic carbons since they provide us with all the information we need regarding the juxtaposition of 1,4 and 1,2 units without the interfering influence of tacticity effects. An assignment is also presented for the aliphatic carbons but some ambiguities occur here at high vinyl content due to extensive signal overlap.

For identification and assignment of the spectra the effect of pendent ethenyl groups on the in-chain carbons must be estimated. There are several procedures whereby chemical shifts can be predicted and these will be used here. For example, the *aliphatic in-chain carbons* are affected in very much the same way by the hanging groups as in the hydrogenated product discussed in subsection i, that is, β, γ, and δ effects may be additively applied. The effect of a double bond on an α carbon depends on the degree of substitution of the double bond: a vinyl group produces a downfield shift of 2.0 ppm,[10] a cis-disubstituted olefin gives an upfield shift of 2.6 ppm and a trans-disubstituted olefin a downfield shift of 2.9 ppm. The *olefinic in-chain carbons* are slightly differently affected particularly with regard to the influence of substitutents *across* the double bond (α', β', γ', and δ' effects). From data on model olefins,[11] we extracted the following pertinent parameters for predicting in-chain olefinic carbon shifts: $\gamma = -1.74 \pm 0.05$ ppm, $\gamma' = 0.84 \pm 0.10$ ppm, $\delta = 0.30 \pm 0.03$ ppm, $\delta' = -0.15 \pm 0.03$ ppm.

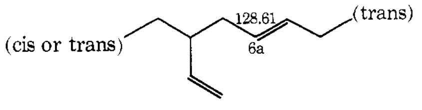
Following the same procedure as in subsection i, the first structure element we consider is that corresponding to isolated vinyl groups. Whereas the hydrogenated species (structure II, subsection i) gives one set of lines only, we now have the additional effect of cis and trans isomerism of 1,4 units. In principle, there are eight possible structures that have to be considered. To simplify the discussion of the assignments these eight structures are divided into two series, one with the vinyl group preceding cis and trans (IIa, b, c, d) and the other with the vinyl group following cis and trans (IIIa, b, c, d). The model compound 3-ethyl-1-*trans*-5-octadiene is a convenient starting point for considering structures in which the vinyl group precedes a 1,4 unit.



Making use of these shifts, we arrive at the following *predicted* shifts for structures IIa and IIb.



IIa



IIb

With the help of structures IIa and IIb, we can settle the problem raised in subsection ii, *viz.*, which of the two olefinic carbons in 1,4 polyads feels the neighboring cis:trans effect. By replacing one cis or trans neighbor in structures Ia or Ib by a vinyl unit the cis:trans effect is caused to come from one side only (the right-hand side in structures IIa and IIb). It is easy to show that the more remote carbon (6, 6a) gives rise to the split carbon resonance at about 128.7 ppm while the nearby carbon-5 produces only a single line at 131.6 ppm. Carbons-6 and -6a feel a $\gamma + \delta$ effect relative to 1 and 1a and are therefore shifted about 1.4 ppm *upfield*, while carbon-5 feels a $\gamma' + \delta'$ effect, resulting in a *downfield* shift relative to 1 and 1a of 0.7 ppm (see Figure 4A).

Table II
Predicted and Observed Chemical Shifts[a] for the Hydrogenated Polybutadienes

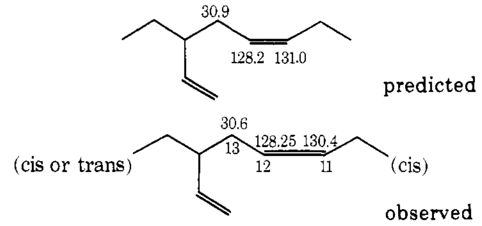
Carbon Type	Predicted	Obsd	Carbon Type	Predicted	Obsd
1′	30.0	30.0	9′	36.5	36.5
2′	30.3	30.5	10′	38.5	38.4
3′	27.1	27.1	11′	26.2	26.3
4′	33.2	33.5	12′	38.8	39.2
5′	38.6	39.4	13′	34.4	33.8
6′	25.8	26.2	14′	26.7	26.8
7′	11.1	10.8	15′	39.1	39.6
8′	33.5	33.8	16′	30.6	30.9

[a] Shifts in ppm relative to Me_4Si.

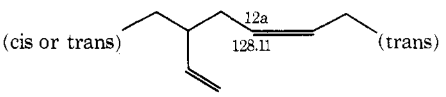
The apparent reversal in the assignment of 6 and 6a is justified by the fact that the intensity ratio 6:6a should equal 1:1a, this is best evident in Figure 4C.

The assignments made for structures Ia and Ib are now justified. It was already clear that, *e.g.*, the line at 130.37 ppm was due to a trans olefinic carbon with a cis neighbor. Apparently, the line must be assigned to carbon-1 in structure Ia (*i.e.*, the carbon in the far end of the double bond). The second trans line at 130.29 ppm is therefore assigned to carbon-1a. The assignments for 3 and 3a can be justified in a similar way, following the discussion of the vinyl-cis structures (see below).

The different shifts for 6 and 6a being accounted for, the remaining assignments in structures IIa and IIb fall close enough to the predicted shifts to be considered satisfactory. We can use a similar procedure as an aid to the assignments of structures IIc and IId, where a vinyl group



IIc

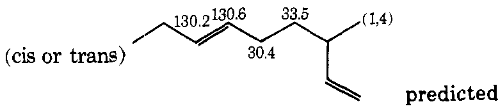


IId

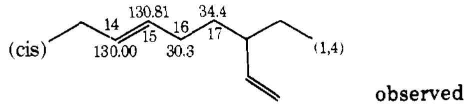
precedes a cis group. The predicted shift for C_{13} of 30.9 is arrived at from the shift of $C_{4'}$ in II, subsection i (33.5) modified by a cis double bond, generally -2.6 ± 0.3.[10] Although no signal is observed at this position there is clear evidence for a signal at 30.6 ppm in polymers A, D, and E in Figure 3. The predicted olefinic shifts were obtained by assuming that the difference between the cis and trans lines of the parent 1,4 structures, being about 0.5 ppm (structures Ia and Ib), also extends to the vinyl-cis and vinyl-trans structures (structures IIa and IIc and also IIb and IId.

Again two lines are observed (12 and 12a) for the olefinic carbon farthest removed from the cis or trans neighbor. Carbon-11 is not actually observed and it is therefore assumed that its signal falls under the strong trans-cis line at 130.37 (carbon-1). This is a reasonable assumption since the intensity of this line is not seen to diminish as much as is expected in high vinyl polymers, where the occurrence of carbon-1 becomes negligible. The ratio of the intensities for 12 and 12a is similar to that for the "parent" intensities 3a and 3. This is further support for our assignments.

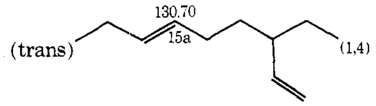
The next series of structures are those where the vinyl unit follows a 1,4 unit: cis-trans-vinyl, trans-trans-vinyl, cis-cis-vinyl and trans-cis-vinyl. The following structure shows the predicted shifts for trans-trans-vinyl and cis-trans-vinyl.



These shifts were derived from pure trans with application of the appropriate shift parameter. The following are the observed shifts. The aliphatic carbon assignments agree satisfactorily and need no further discussion. Again the effect of the configuration of the unit on the left-hand side is to produce splitting of the signal from the olefinic carbon (15, 15a) on the right-hand side of the double bond.

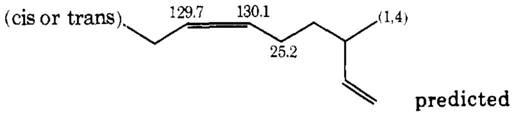


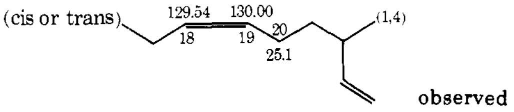
IIIa



IIIb

The cis unit can be treated similarly.

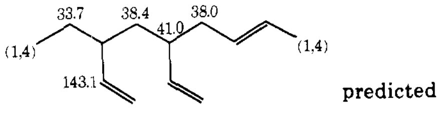




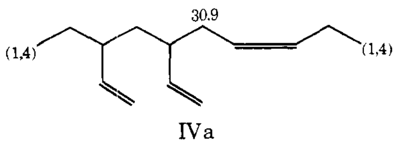
IIIc, d

The olefinic signals fall in a congested spectral region and any additional splitting is probably obscured.

Nearly all the signals observed in the low-vinyl polymers have now been assigned. The remaining signals, which increase in intensity at higher vinyl contents, come from structures comprising vinyl sequences of more than two units. The first to be considered is the block of two units.



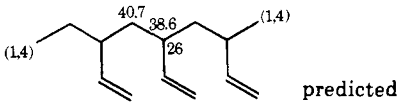
IV



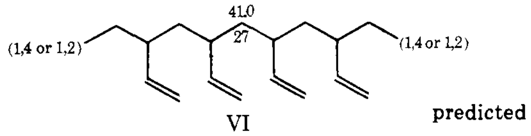
IVa

It is evident from the predicted shifts that as the size of the vinyl sequences increases the backbone-CH$_2$ signal shifts to low field (increasing β effect), whereas the backbone-CH signal shifts to high field (increasing γ effect). Hence, there will be a crossover at two vinyl units. This, combined with the effects of tacticity, adds to the complexity of the spectral picture. Rather than attempt to make assignments and run the risk of ambiguity for structures IV and IVa we present only the predicted shifts.

At high-vinyl contents the presence of larger vinyl blocks is clearly evident and lines associated with these structures can be assigned.



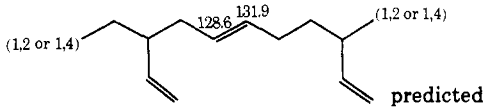
V

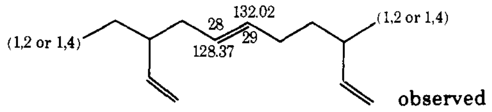


VI

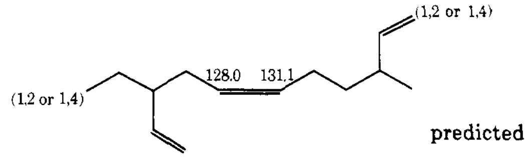
Carbon atoms 26 and 27 are observed at 39.0 and 41.5 ppm, respectively. Both lines show the effects of tacticity and this has been described previously.[2]

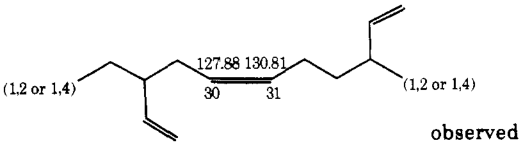
Isolated 1,4 cis or trans units are the last structures to be considered.





VII





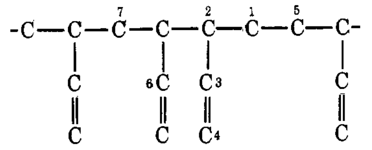
VIIa

The predicted shifts were derived from structures IIa to d by considering the effect of an additional δ or δ' where this was appropriate.

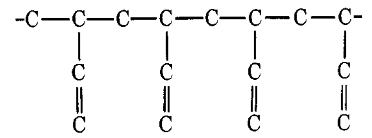
Although all of the short polyad sequences in polybutadienes were indeed observed and assigned, the frequency of their occurrence could only be roughly estimated, because of the limited spectral resolution that can be attained in 23-kG magnetic fields. From the intensity changes in Figures 3 and 4 it can at any rate be concluded that the cis-trans-vinyl ordering must be random within a margin of some 30%.

III. Discussion

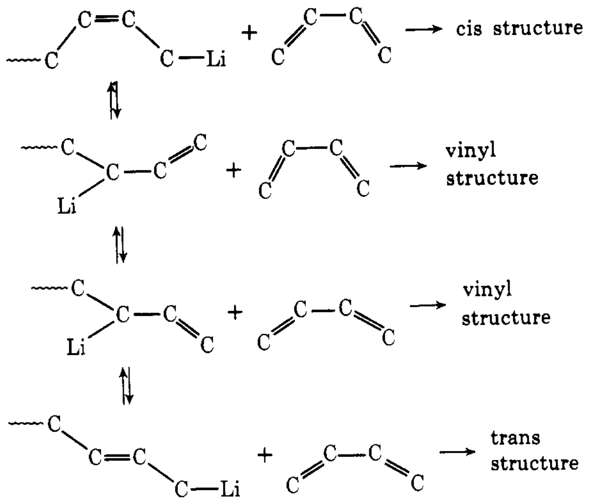
The assignments of the spectra and the agreement between predicted and observed intensities provide strong evidence for the proposed model for polybutadiene in which cis-trans and vinyl units are randomly incorporated into the structure. The question whether head-to-head or tail-to-tail incorporation occurs has not been discussed. The mere fact that all spectral lines have been assigned with the exception of one line at 35.2 ppm suggests that addition proceeds only in a head-to-tail manner. If the incorporation were irregular, giving, for instance



instead of



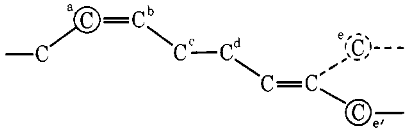
seven new ^{13}C lines would be expected for the *hydrogenated* species, with predicted shifts of 29.3, 41.6, 24.7, 11.8, 32.0, 25.0, and 35.7 ppm for carbons atoms 1 to 7, respectively. These shifts have not been observed (see Table II) and we conclude that no measurable concentration of head-to-head or tail-to-tail units is present. This finding is in accordance with an isomerization-propagation mechanism for alkyllithium-initiated butadiene polymerization, as suggested by Gebert *et al.*[12] According to these authors the vinyl structure is generated after isomerization of the living polymer end.



Clearly, a vinyl structure generated by this mechanism cannot lead to head-to-head or tail-to-tail linkages within vinyl blocks.

The random polymer structure we arrived at sharply contrasts with reports of other authors,[2,13,14] who claimed a blocky structure for polybutadienes prepared in various ways. The arguments put forward in the first article[2] concerning the absence of cis-trans linkages in alkyllithium-based polybutadiene are in our opinion[15] unjustified. The polymers reported in the other two papers[13,14] were prepared with a nickel catalyst and, therefore, strictly speaking one cannot *a priori* be certain that they will have the same structure as the alkyllithium-based polymers. The authors were, however, completely led by the arguments advanced in the first paper.[2] We feel very confident that if the spectra of the polymers were recorded with a higher resolution (or in stronger magnetic fields), the ^{13}C nmr spectra would reveal their random character.

One of the most remarkable points to be discussed is perhaps the splitting of the olefinic carbon resonances from cis and trans elements having a cis or trans neighbor. At first sight it seems very strange that in the cis-trans dyad shown below, carbon atom C_a should "feel" whether carbon C_e is in a cis (e) or a trans (e′) configuration, the two carbons being separated from each other by six bonds!



A steric model shows, however, that carbons a and e can come quite close by rotation about the three inner single bonds and we therefore conclude that the effect is a spatial one. This then explains why carbon atoms C_b and C_c are insensitive to the position of C_e. Carbon atom C_d is, of course, the most affected of all, the cis-trans effect on its chemical shifts being 5.4 ppm.

IV. Conclusion

The structures of polybutadiene with low and medium vinyl contents have been determined with the help of ^{13}C nmr spectroscopy. Since the spectra were too complicated for a direct analysis, we first concentrated on the ^{13}C spectra of closely related polymers with a much simpler structure, *viz.*, hydrogenated polybutadienes, and polymers having almost exclusively the 1,4 structure. All polymers proved to have a random distribution of cis-1,4, trans-1,4, and 1,2 (vinyl) structural elements. Besides, we established that (within vinyl blocks) butadiene is incorporated only in a head-to-tail manner.

Acknowledgment. The authors thank Dr. A. D. Vreugdenhil, who provided many of the polymer samples.

Addendum

Similar conclusions to our own concerning the structure of 1,4-polybutadiene have appeared in the recent literature. Santee and coworkers[16] concluded from a study of the proton nmr spectra that cis- and trans-1,4 units were randomly distributed, while Elgert and co-workers[17] reached the same conclusion from a study of the ^{13}C nmr spectrum.

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