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Carbon-13 NMR of Partially Epoxidized 1,4-*trans*-Polybutadiene Crystals

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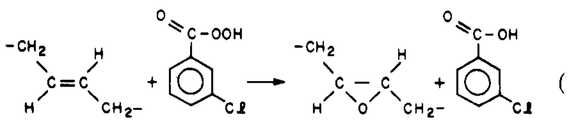
ABSTRACT: Selective epoxidation of double bonds in combination with carbon-13 NMR spectroscopy has been employed to explore the morphology of 1,4-*trans*-polybutadiene crystals grown from dilute heptane solution. The crystals were suspended in toluene and reacted with *m*-chloroperbenzoic acid at 6 °C until the rate of reaction leveled off, which occurred at ca. 12–16% of completion. The reacted crystals were dissolved in $CDCl_3$ and the carbon-13 NMR spectra observed at 50 MHz. It was expected that the surface folds would react completely and that the crystal stems would not react at all, leading to a block structure. The spectra were interpreted with the aid of 1,4-*trans*-polybutadiene reacted in homogeneous solution and a model compound, 3,7-decadiene, reacted to 50% and 100%. From the intensities of "junction" methylene carbon resonances between runs of epoxidized and unreacted monomer units, the fold length and crystalline stem length were calculated for two preparations of crystals. The results for the stem length are in approximate agreement with SAXS measurements. The fold length (corrected for the presence of cilia) was found to be only 2.5–3.0 monomer units, corresponding to the tightest possible fold and (presumably) adjacent reentry.

Introduction

1,4-*trans*-Polybutadiene (TPBD) crystals grown from dilute solution have been found to contain a significant noncrystalline fraction, most if not all of which is at the crystal surfaces. This surface portion is believed to be composed of two components, the chain folds and the noncrystallizing chain ends or cilia. The importance of the chain end component will depend on the molecular weight of the polymer and the crystal thickness. The amorphous fraction can be evaluated by both physical and chemical methods. Broad-line proton NMR,[1] solid-state carbon-13 NMR,[2] X-ray crystallography,[1] infrared spectroscopy,[3] and calorimetry[4] have been applied. With the exception of the NMR methods, these techniques may be regarded as measuring the total noncrystalline content of the sample, whether at the surface or within the crystals.

Chemical methods generally are confined to the surface, although highly reactive agents like ozone and nitric acid will in time penetrate into the crystalline regions of such polymers as polyethylene. For 1,4-*trans*-polybutadiene, a mild, quantitative, but highly selective reagent is needed. To make interpretation of the NMR spectra feasible, it is also highly desirable that the reaction be as simple as possible, uncomplicated by side reactions and alternative routes. The reaction of *m*-chloroperbenzoic acid with double bonds fulfills these requirements.


(1)

This nonradical reaction is believed to be entirely stereospecific; i.e., trans double bonds yield only trans oxirane rings.[5,6] This assumption is rigorously tested in the present work and found to be quantitatively valid.

The epoxidation reaction has been applied to suspensions of dilute-solution-grown crystals of 1,4-*trans*-polybutadiene by Woodward[7-10] to evaluate the fraction of surface folds and cilia. In this work, the principal concern was the extent of reaction, which was evaluated from the depletion of the peracid or from the proton NMR spectrum of the epoxidized polymer. From this information and from the lamellar thickness of crystal aggregates, measured by small-angle X-ray diffraction, the number of butadiene units per surface fold can be calculated. Values of 2.5–6.5 units, with a decrease occurring with decreasing molecular weight, have been reported.[10]

In the present study, a different approach has been taken. Carbon-13 NMR spectra have been obtained for the products of 1,4-*trans*-polybutadiene epoxidation carried out (a) in homogeneous solutions in chloroform and (b) on suspensions of solution-grown crystals in toluene. The reaction in (a) was allowed to proceed only part way toward completion; it was anticipated that the epoxidation of the double bonds would take place at random. In (b), on the other hand, the reaction was allowed to proceed until the rate had decreased to zero or nearly so, which occurs at only ca. 12–16% completion, and it was assumed that only the butadiene units in the fold surface would react, the crystalline stems remaining impervious to the reagent. The reacted chains should now assume a block character. By use of resonance assignments obtained from the product of (a) (and from a model diene), the lengths of the epoxidized blocks, corresponding to the original folds, should then be independently determinable without reference to X-ray results or any other measurements. The crystal thickness and stem length should also be determinable in a similar manner.

These expectations have been largely realized, and we believe the results represent a significant contribution to a solution of the problem of fold length and of adjacent reentry vs. a "random switchboard" arrangement in the fold surface.

Experimental Section

Preparation of Samples. Two polymer preparations, designated UH45 and F1H55, were used.[10] Crystallization was carried out from 0.01% (w/v) heptane solution by using the following procedure: dissolution, precipitation at room temperature, redissolution at the minimum temperature (55 °C for UH45 and 67 °C for F1H55), and isothermal crystallization at 45 °C for UH45 and 55 °C for F1H55. Uniform sized lamellae with some screw dislocation overgrowths resulted. Some other characteristics of these preparations are given in Table I.

Following precipitation and washing of the crystals with heptane at the crystallization temperature, samples were resuspended in toluene at 6 °C; these crystals were reacted for a 5–7-day period with *m*-chloroperbenzoic acid, present in excess.[8-10] The ep-

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Table I
Characteristics of 1,4-*trans*-Polybutadiene (TPBD) Crystal Preparations

designation	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	L,[a] nm	ρ (25 °C), g cm^{-3}	cryst,[b] %	f_e[c]
F1H55	4.4	1.5	23.6	1.005	84	0.117
UH45[d]	1.7	1.7	11.0	0.987	74	0.162

[a] Lamellar thickness, from small-angle X-ray scattering (SAXS). [b] Percent crystallinity, estimated from the density. [c] Fractional extent of epoxidation, estimated from ^{13}C NMR spectrum; vide infra. [d] Trans content is 99.5% as measured by ^{13}C NMR.

oxidized crystals were filtered, washed with toluene at 6 °C and in the case of F1H55 with ether as well, and then freeze-dried prior to ^{13}C NMR measurements.

For epoxidation in homogeneous solution in chloroform two samples were used. A sample of UH45 was reacted to the extent of 30% at room temperature. A second preparation, designated UH48 and having a number-average molecular weight between that for UH45 and F1H55, was epoxidized to an extent of 78%. The epoxidized polymer was recovered by precipitation in methanol and in the case of UH48 the precipitate was washed with ether. Both samples were dried under vacuum at room temperature.

Molecular weights were obtained from GPC, the lamellar thicknesses L from low-angle X-ray, and the densities ρ from density gradient flotation, as described previously.[10] The crystallinity values (column 6 in Table I) were obtained from ρ; a two-component system was assumed and literature values of ρ_A and ρ_C[6,11] were used.

The model diene, 3,7-decadiene, was obtained from Wiley Organics Co., Columbus, OH. The sample was found to contain trans and cis double bonds in an 85:15 ratio. More detailed analysis of the ^{13}C spectra shows the trans,trans:cis,trans:cis,cis ratio to be 72.5:24.4:3.1. The epoxidation was carried out to the extent of 50% and 100% by using a modification of the procedure for squalene[12] and cyclohexene[13] epoxidations. A chloroform solution of *m*-chloroperbenzoic acid was added dropwise over a 20-min period to a chloroform solution of the 3,7-decadiene (3 parts by volume to 100 parts by volume of chloroform). After 12 h of reaction with continuous stirring the solution was extracted with 5% NaOH solution several times until it tested basic; the water was removed by addition of anhydrous sodium sulfate; and the chloroform was removed by vacuum distillation at room temperature.

NMR Measurements. The 50.31-MHz ^{13}C spectra of the model diene, 3,7-decadiene, and of the polymers were recorded on a Varian XL-200 NMR spectrometer using 17–30% (w/v) solutions in CDCl$_3$ with hexamethyldisiloxane (HMDS) as internal reference, taken as 2.00 on the Me$_4$Si scale. The observing temperature was 40 °C. Five hundred scans were collected for each sample, using a sweep width of 8000 Hz in 32K of memory and a pulse repetition time of 10.0 s. The 90° pulse width was 13 μs. Broad-band noise decoupling was used for all measurements. Quantitative measurements of peaks were made by computer integration and by use of a planimeter.

In order to obtain quantitative information from the spectra of the epoxidized *trans*-polybutadiene samples, it is necessary to establish proper conditions for data collection. These conditions were determined by measurement of ^{13}C spin–lattice relaxation and nuclear Overhauser enhancement (NOE). These were made at 40 °C with the 30% epoxidized UH45 polymer solution (17.7% w/v) in chloroform. The T_1 measurements were carried out by using a standard 180°–τ–90° inversion recovery sequence employing a composite 180° pulse,[14] the delay between 90° sampling pulses being always greater than $5T_1$. NOE determinations were made by using the gated decoupling technique, with the delay between each accumulation of data being greater than 10 times the T_1 for each carbon nucleus. The results of these measurements are summarized in Table II. Relaxation data for the less populated sequences did not appear to differ by more than ±10% from values reported for the primary sequences. The methylene and oxirane ring carbons receive a full Overhauser enhancement while the olefinic carbons exhibit 84% of the maximum enhancement.

In order to calculate the extent of epoxidation we compare the areas of the methylene resonances of the oxirane and olefinic units. Alternatively, one can use the resonances of the epoxide ring carbons and olefinic carbons with the appropriate NOE factor. Excellent agreement was obtained between the results of both methods.

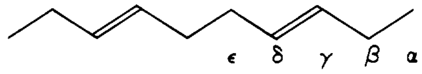
Table II
^{13}C T_1 and NOE Data for Partially Epoxidized 1,4-*trans*-Polybutadiene (TPBD) at 40 °C in CDCl$_3$

carbon	sequence[a]	chemical shift	T_1, s	NOE (η + 1)
—CH=CH—	DDDD	130.06	1.89	2.6$_7$
$-\overset{\text{O}}{\text{CH—CH}}-$	DOD	58.34	1.15	2.9$_6$
—CH=CHCH$_2$—	DDDD	32.79	0.86	2.9$_5$
$-\overset{\text{O}}{\text{CH—CH}}\text{CH}_2-$	DDOD	29.11	0.76	2.9$_8$

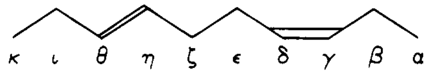
[a] D is double bond (butadiene unit) and O is oxirane ring (epoxy unit).

Results

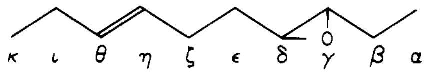
NMR Spectra of 3,7-Decadiene and Its Epoxidation Products. The primary basis of ^{13}C resonance assignments in the polymer spectra are the spectra of the model 3,7-decadiene and its 50% and 100% epoxidation products (see Experimental Section). Since the diene contains approximately 15% cis (*Z*) double bonds, one must recognize the existence of seven isomers, ignoring the cis,cis (*Z*,*Z*) diene and its epoxidation products since they occur only in negligible proportions; the designations shown are based on D for double bond, O for oxirane ring (epoxy unit), *Z*



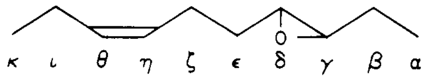
(i) DD-EE



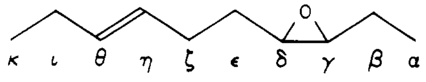
(ii) DD-ZE



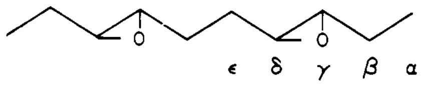
(iii) OD-tE



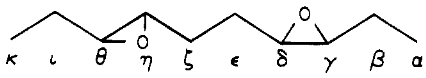
(iv) OD-tZ



(v) OD-cE



(vi) OO-tt



(vii) OO-ct

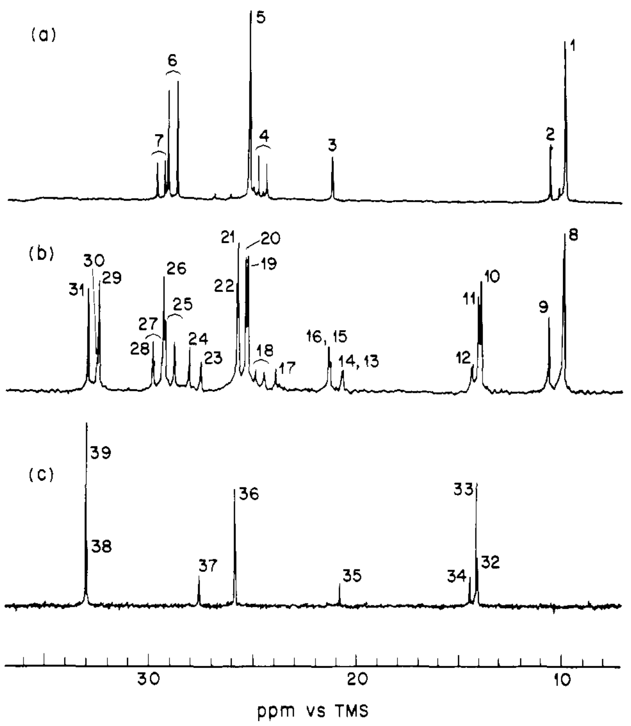
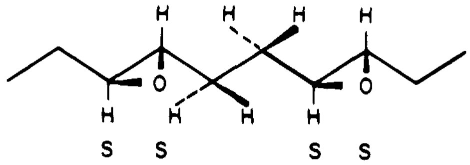


Figure 1. Methylene and methyl carbon region of 50.3-MHz ^{13}C spectra of (a) 100% and (b) 50% epoxidized 3,7-decadiene and (c) the unreacted diene. Observed in $CDCl_3$ at 40 °C.

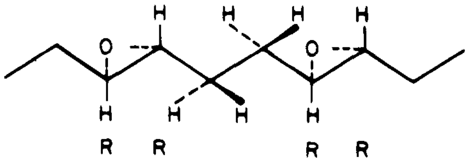
or *E* for cis and trans double bonds, and *c* or *t* for cis and trans oxirane rings. In Figure 1 are shown the alkyl carbon spectra of the decadiene at 100% epoxidation (a) and at 50% epoxidation (b) and unreacted (c). In (c) the ϵ and ζ resonances of compounds i and ii are assigned by comparison to known diene spectra, 2,6-*cis,trans*-octadiene and 2,6-*trans,trans*-octadiene.[15,16] The ϵ-carbon resonance of compound ii is about 5.5 ppm upfield from that of the ζ-carbon resonance, as expected from extensive data on the mutual shielding effect of cis carbons at a double bond.[17] Comparison with (*Z*)-3-decene and (*E*)-3-decene permits the assignment of the remaining alkyl carbons.[18] Again, the β-carbon in ii is about 5 ppm more shielded than the β-carbon in i. The assignments are summarized in Table III, peaks 32–39. It is to be noted that the internal methylene carbons (ϵ, ζ) next to *E* double bonds are nearly insensitive to whether the neighboring double bond is *Z* or *E*.

When two trans oxirane rings are present in the same molecule (compound vi), questions of chirality arise. (We do not consider the compounds with cis rings, as these are not models for the polymer chains.) Thus, compound vi is composed of the isomers vi-a to vi-d.

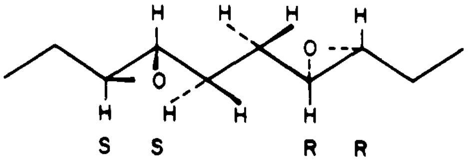
Compounds vi-a and vi-b form a pair of enantiomers as do vi-c and vi-d. Such mirror image pairs cannot normally be distinguished by NMR (in the absence of a chiral environment), but each pair is spectroscopically distinct from the other because they are diastereoisomers. This discrimination is manifested as an equal splitting of the ϵ-methylene carbon resonance (peaks labeled 6 in Figure 1) by 0.44 ppm. The establishment of the magnitude of this splitting in the trans,trans compound vi is the most important information provided by the 3,7-decadiene model and confirms the interpretation of a corresponding splitting in the polymer spectra (next section). Equal splittings occur in the ϵ-carbon and ζ-carbon resonances of the cis,trans dioxirane (OO-*ct*, compound vii) spectrum (doublets 4 and 7, respectively, in Figure 1a).



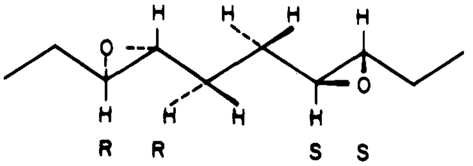
(vi-a)



(vi-b)



(vi-c)



(vi-d)

The ^{13}C spectrum of the 50% epoxidized 3,7-decadiene is shown in Figure 1b. It has all the resonances of (a) and (c) and new resonances of the monoepoxy diene, principally compound iii, OD-*tE*. These are of particular importance since they represent the junction of reacted and unreacted units in the polymer chain. The assignments of the junction methylene resonances were confirmed by an analysis of chemical shifts in *trans*-2-pentene and *trans*-2-pentene 1,2-epoxide.[19] Of the "junction" resonances, that of the ζ-carbon of OD-*tE*, peak 26 in Figure 1b (29.28 ppm) is of particular significance. The corresponding resonance in the polymer spectrum (see next section) is slightly more shielded (29.12 ppm) and provides a direct measure of the fold length.

A question of some interest is whether the presence of an oxirane ring influences the reactivity of the neighboring double bond. If the epoxidation is random, then at 50% reaction the DD, OD, and OO products should be present in a 1:2:1 ratio. A convenient test of this conclusion with regard to the *trans,trans*-diene is furnished by a comparison of resonances 25 (doublet), 29, and 31 in Figure 1b, corresponding to the ϵ-carbons of OO-*tt* (compound vi), OD-*tE* (compound iii), and DD-*EE* (compound i); all should be of equal intensity if the epoxidation is random, and this indeed appears to be the case within experimental error. In a similar manner, we have also determined that the epoxidation of 1,4-*trans*-polybutadiene in solution is random.

In Figure 2 are shown the oxirane ring carbon region of the 50% epoxidized product (a), containing OD and OO compounds, and the 100% epoxidized product (b), containing OO compounds. Assignments of resonances are summarized in Table IV. Chirality splittings are evident but are of somewhat smaller magnitude than for ϵ-carbons.

In Figure 3 and Table V are the olefinic resonances and their assignments. Spectrum b is that of the unreacted dienes. Six olefinic carbon peaks are expected and observed, but the sensitivity of the *E* double bond chemical shifts to the isomerism of the neighboring double bond is so small that the resonances (14,15; 17,18) are just observably split. We have seen that the internal methylene

Table III
^{13}C Chemical Shifts of CH_2 and CH_3 Groups in 3,7-Decadiene and Its 50% and 100% Epoxidation Products (See Figure 1)

peak designation	assignment	chemical shift
1	OO-*tt*-α OO-*ct*-κ	9.97
2	OO-*ct*-α	10.68
3	OO-*ct*-β[a]	21.18, 21.21
4	OO-*ct*-ε[a]	24.37, 24.75
5	OO-*tt*-β OO-*ct*-ι	25.20
6	OO-*tt*-ε[a]	28.67, 29.11
7	OO-*ct*-ζ[a]	29.27, 29.64
8	OD-*tE*-α OD-*tZ*-α OO-*tt*-α OO-*ct*-κ	10.00
9	OD-*cE*-α OO-*ct*-α	10.71
10	OD-*tE*-κ OD-*cE*-κ DD-*ZE*-κ	13.98
11	DD-*EE*-α	14.10
12	OD-*tZ*-κ DD-*ZE*-α	14.46
13	OD-*tZ*-ι	20.66
14	DD-*ZE*-β	20.70
15	OO-*ct*-β[a]	21.25, 21.35
16	OD-*cE*-β	21.35
17	OD-*tZ*-ζ	23.88
18	OO-*ct*-ε[a]	24.44, 24.83
19	OO-*tt*-β OO-*ct*-ι	25.27
20	OD-*tE*-β OD-*tZ*-β	25.36
21	OD-*tE*-ι OD-*cE*-ι	25.72
22	DD-*EE*-β DD-*ZE*-ι	25.77
23	DD-*ZE*-ε	27.45
24	OD-*cE*-ε	27.99
25	OO-*tt*-ε[a]	28.73, 29.21
26	OD-*tE*-ζ	29.28
27	OO-*ct*-ζ[a]	29.38, 29.81
28	OD-*cE*-ζ	29.81
29	OD-*tE*-ε	32.37
30	OD-*tZ*-ε	32.47
31	DD-*EE*-ε DD-*ZE*-ζ	32.91
32	DD-*ZE*-κ	14.05
33	DD-*EE*-α	14.11
34	DD-*ZE*-α	14.44
35	DD-*ZE*-β	20.74
36	DD-*EE*-β DD-*ZE*-ι	25.82
37	DD-*ZE*-ε	27.51
38	DD-*ZE*-ζ	32.93
39	DD-*EE*-ε	32.95

[a] Diastereoisomers.

resonances also exhibit little sensitivity.

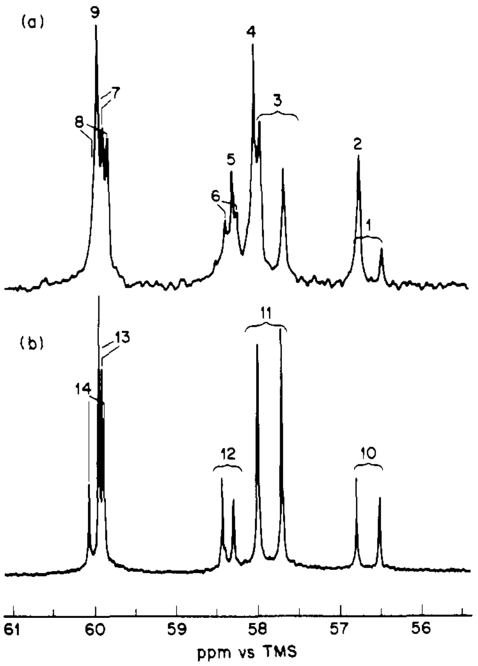


Figure 2. Oxirane ring carbon region of 50.3-MHz ^{13}C spectra of (a) 50% and (b) 100% epoxidized 3,7-decadiene; same conditions as in Figure 1.

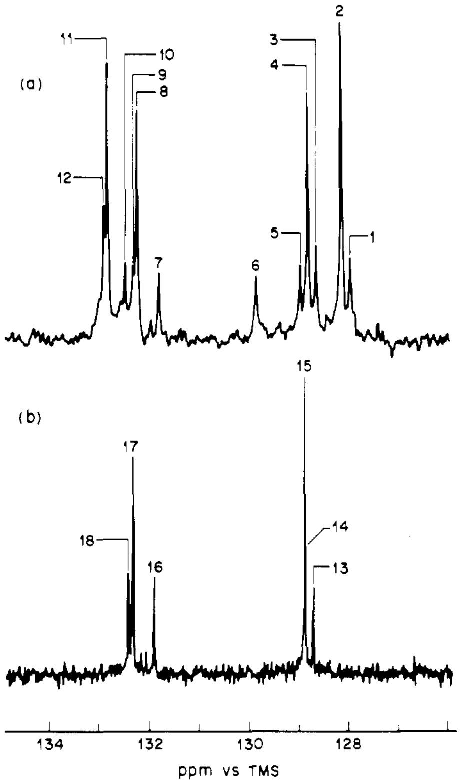


Figure 3. Olefinic carbon region of 50.3-MHz ^{13}C spectra of (a) 50% and (b) unreacted 3,7-decadiene; same conditions as in Figure 1.

NMR Spectra of Epoxidized *trans*-Polybutadienes. The carbon-13 spectra of epoxidized 1,4-*trans*-polybutadiene UH45 and UH48 (see Experimental Section) are shown in Figures 4–6, which represent four spectral regions: CH_2 of oxirane units, CH_2 of butadiene units, oxirane ring CH, and double bond CH. Spectrum a in each region is that of the polymer epoxidized as crystals suspended in toluene at 6 °C. Spectra b and c in each region represent the polymer epoxidized in homogeneous solution in chloroform to levels of 30% and 78% of completion, respectively. The assignments and structural formulas are summarized in Tables VI–VIII, corresponding to Figures 4–6, respectively. The chemical shifts are in good agreement with those observed for the corresponding carbons in the model compounds discussed in the previous section.

The assignments of carbons c and d (see structure ii in Table VI) correspond to those for the model compounds, particularly the ε and ζ carbons in OD-*tE*. The assignment is in agreement with that proposed by Gemmer and Golub,[5] which was based on the differential effect of a lanthanide shift reagent on the methylene carbons between a double bond and an oxirane ring. The resonances of the ζ and ε junction carbons must always be of equal intensity,

Table IV
^{13}C Chemical Shifts of the Oxirane Ring CH Groups in 50% and 100% Epoxidized 3,7-Decadiene (See Figure 2)

peak designation	assignment	chemical shift
1	OO-ct-δ [a]	56.49, 56.78
2	OD-c*E*-δ	56.78
3	OO-tt-δ [a] OO-ct-η [a]	57.71, 58.00
4	OD-t*E*-δ OD-t*Z*-δ	58.08
5	OD-c*E*-γ	58.33
6	OO-ct-γ [a]	58.28, 58.41
7	OO-tt-γ [a]	59.92, 59.99
8	OO-ct-θ [a]	59.87, 60.04
9	OD-t*E*-γ OD-t*Z*-γ	59.99
10	OO-ct-δ [a]	56.53, 56.82
11	OO-tt-δ [a] OO-ct-η [a]	57.74, 58.02
12	OO-ct-γ [a]	58.32, 58.45
13	OO-tt-γ [a]	59.90, 59.95
14	OO-ct-θ [a]	59.88, 60.07

[a] Diastereoisomers.

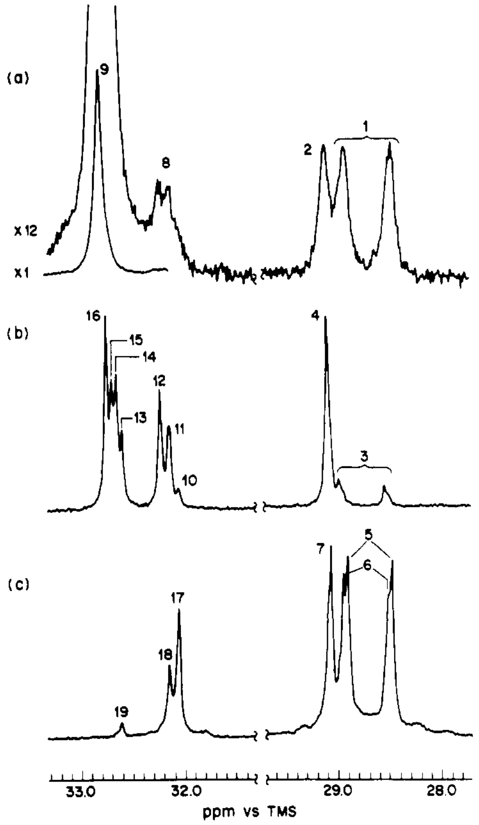


Figure 4. Methylene carbon region of 50.3-MHz ^{13}C spectra of 1,4-*trans*-polybutadiene. (a) UH45 suspended crystals epoxidized to 16.2%, and polymer epoxidized in homogeneous solution to extent of (b) 30% and (c) 78%; same conditions as in Figure 1.

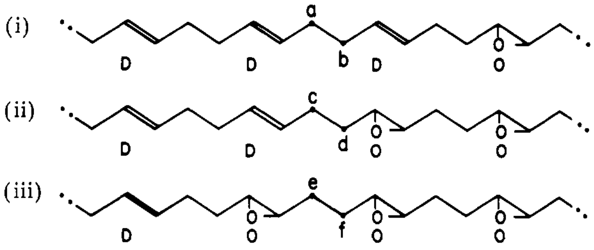
and either may be used as a measure of junction units. The resonances in Figure 4, particularly 1 through 7, are the most useful analytically and will be interpreted in detail in the next section.

The oxirane ring carbon resonances are shown in Figure 5 and assigned in Table VII. There is both positional splitting (in DOO) for carbons g and h and chirality splitting of each in OOO (where they are equivalent). It appears from the model compounds that each ring carbon is sensitive to the chirality only of the nearest neighboring ring. Chirality splitting is particularly evident in spectrum c of Figure 5, in which the sequence OOO is dominant.

Table V
^{13}C Chemical Shifts of Olefinic Carbons in 3,7-Decadiene and Its 50% Epoxidation Product (See Figure 3)

peak designation	assignment	chemical shift
1	OD-c*E*-η	127.99
2	OD-t*E*-η	128.15
3	DD-*ZE*-δ	128.66
4	DD-*EE*-δ	128.84
5	DD-*ZE*-η	128.98
6	OD-t*Z*-η	129.86
7	DD-*ZE*-γ	131.83
8	DD-*EE*-γ	132.27
9	DD-*ZE*-θ	132.36
10	OD-t*Z*-θ	132.51
11	OD-t*E*-θ	132.87
12	OD-c*E*-θ	132.95
13	DD-*ZE*-δ	128.70
14	DD-*ZE*-η	128.86
15	DD-*EE*-δ	128.89
16	DD-*ZE*-γ	131.89
17	DD-*EE*-γ	132.33
18	DD-*ZE*-θ	132.41

Table VI
^{13}C Chemical Shifts of CH$_2$ Groups in Epoxidized 1,4-*trans*-Polybutadiene (See Figure 4)[a]



peak designation	assignment	chemical shift
1	OOOO-e,[b] f[b] DOOO-e,[b] f[b]	28.47, 28.94
2	DDOO-c	29.12
3	DOOD-e,[b] f[b] DOOO-e,[b] f[b] OOOO-e,[b] f[b]	28.56, 29.00
4	DDOD-c ODOD-c DDOO-c ODOO-c	29.11
5	OOOO-e,[b] f[b] DOOO-f[b]	28.46, 28.90
6	DOOO-e[b] DOOD-e,[b] f[b]	28.50, 28.95
7	ODOD-c DDOO-c ODOO-c	29.07
8	DDOO-d	32.21
9	DDDO-a, b DDDD-a, b	32.79
10	ODOO-d	32.07
11	DDOO-d ODOD-d	32.15
12	DDOD-d	32.24
13	ODDO-a, b	32.61
14	DDDO-a (or b)	32.66
15	DDDO-b (or a)	32.71
16	DDDD-a, b	32.76
17	ODOO-d	32.06
18	DDOO-d ODOD-d	32.15
19	ODDO-a, b	32.61

[a] Structural formulas of three representative sequences are shown. [b] Diastereoisomers.

The olefinic carbon spectra are shown in Figure 6 and the assignments are presented in Table VIII. These res-

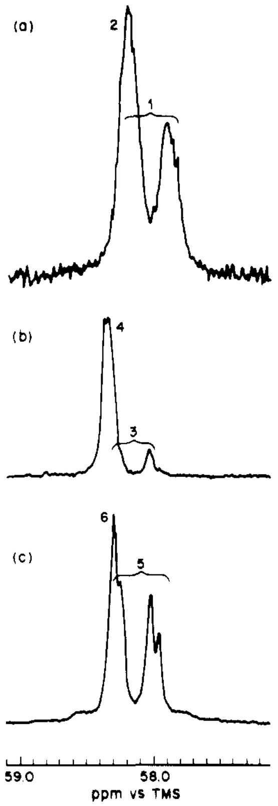
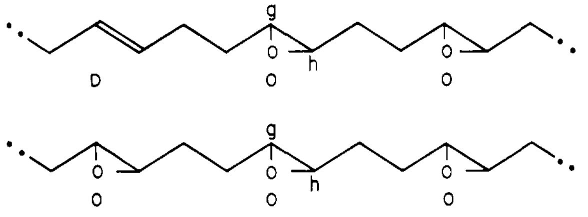


Figure 5. Oxirane ring carbon region of 50.3-MHz ^{13}C spectra of 1,4-*trans*-polybutadiene. (a) UH45 suspended crystals epoxidized to 16.2%, and polymer epoxidized in homogeneous solution to extent of (b) 30% and (c) 78%; same conditions as in Figure 1.

Table VII
^{13}C Chemical Shifts of Oxirane Ring CH Groups in Epoxidized 1,4-*trans*-Polybutadiene (See Figure 5)[a]



peak designation	assignment	chemical shift
1	OOO-g,[b] h[b] DOO-h[b]	57.90, 58.22
2	DOO-g	58.22
3	DOO-h[b] OOO-g,[b] h[b]	58.04, 58.34
4	DOD-g, h DOO-g	58.34
5	OOO-g,[b] h[b] DOO-h[b]	58.05, 58.33 57.98, 58.28
6	DOO-g	58.33

[a] Structural formulas of two representative sequences are shown. [b] Diastereoisomers.

onances are complex and the diene is not an adequate model because the chemical shifts exhibit sensitivity to pentad sequences of O and D units, two of which are represented in Table VIII. The symmetrical appearance of the spectra (particularly Figure 6b) is believed to arise from nearly equal upfield and downfield shifts of the resonances of carbon i and j in nonpalindromic sequences, e.g., DDDDO or DDDOD. The spectra can further be consistently interpreted on the basis that whereas the presence of one epoxy unit as the immediate neighbor of a diene unit, as in DDDOD, shifts the olefin carbon resonances to the maximum extent (compare peaks 6 and 12), the presence of two epoxy neighbors, as in DODOD, produces a much smaller shift (peak 8), equivalent to that produced by one next-nearest-neighbor DDDDO; in the latter the other olefinic carbon is equally shifted downfield (peak 10). In spectrum c, Figure 6, the sequence OODOO predominates strongly and is in nearly the same position as DDDDD. Carbons a (or b) in sequences DDDOD and ODDOO also show nearly equal resonance positions.

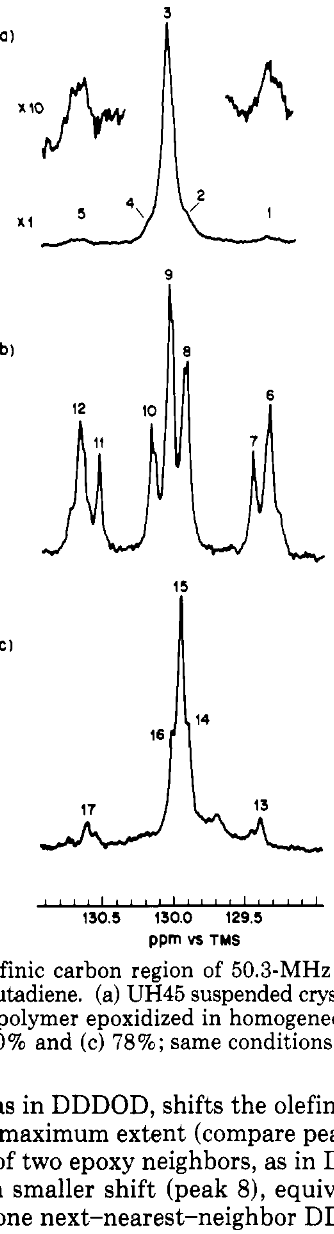
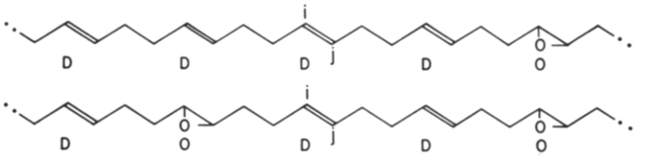


Figure 6. Olefinic carbon region of 50.3-MHz ^{13}C spectra of 1,4-*trans*-polybutadiene. (a) UH45 suspended crystals epoxidized to 16.2%, and polymer epoxidized in homogeneous solution to extend of (b) 30% and (c) 78%; same conditions as in Figure 1.

Calculation of Fold Length, Stem Length, and Crystal Thickness. The principal objective of this study is the determination of the lengths of the surface folds, the crystal thickness, and the stem length (expressed in terms of numbers of butadiene units). In order to make this determination, we must be sure that the folds react completely and that the crystal stems do not react at all with the *m*-chloroperbenzoic acid, resulting in ‥-OOO-‥ and ‥-DDD-‥ block sequences, with no measurable proportions of -ODO- or -DOD- sequences. Spectra a in Figures 4, 5, and 6 are entirely consistent with this assumption. The olefinic carbon spectrum (Figure 6), which is the most sensitive in this regard, provides a particularly satisfying test. For example, the absence of resonances corresponding to -ODO- sequences in the spectra of the epoxidized crystals can be demonstrated by comparison of Figure 6a-c. The presence of an -ODO- sequence causes an intensity difference for peak 8 relative to peak 10 in the solution epoxidized sample. The absence of an intensity difference between peaks 2 and 4 for epoxidized crystals

Table VIII
^{13}C Chemical Shifts of Olefinic Carbons in Epoxidized 1,4-*trans*-Polybutadiene (See Figure 6)[a]

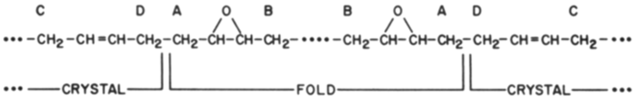


peak designation	assignment	chemical shift
1	DDDOO-j	129.34
2	DDDDO-i (or j)	ca. 129.90
3	DDDDD-i, j	130.06
4	DDDDO-j (or i)	ca. 130.20
5	DDDOO-i	130.68
6	DDDOD-j	129.34
7	DDDOO-j ODDOD-j	129.46
8	DDDDO-i (or j) DODOD-i, j	129.92
9	DDDDD-i, j ODDDO-i, j	130.05
10	DDDDO-j (or i)	130.18
11	ODDOD-i DDDOO-i	130.54
12	DDDOD-i	130.67
13	ODDOO-j	129.43
14	DODOO-j	129.94
15	OODOO-i, j	129.99
16	DODOO-i	130.04
17	ODDOO-i	130.65

[a] Structural formulas of two representative sequences are shown.

demonstrates the absence of the –ODO– sequence in this sample and confirms the complete epoxidation of the folds.

The crystal stem and fold of the epoxidized polymer may be represented as follows:



Let [B] represent the total resonance area of the B methylene carbons as defined above; this corresponds to resonances e and f in Table VI (peak 1 in Figure 4a), i.e., the two diastereoisomeric OO sequences. Let [D] represent the total resonance area of the "junction" methylene carbons of epoxidized units, designated D (c in Table VI and peak 2 in Figure 4a). Let the fold length in monomer units be represented by U' (see ref 10). The number of D carbons per fold is then 2 and the number of B carbons per fold is $2(U' - 2) + 2$ or $2U' - 2$. Therefore

$$[\mathrm{B}]/[\mathrm{D}] = (2U' - 2)/2 = U' - 1 \qquad (2)$$

or

$$U' = ([\mathrm{B}]/[\mathrm{D}]) + 1 \qquad (3)$$

We find from spectrum a in Figure 4 a value of 3.0 monomer units for sample UH45 and from similar data for sample F1H55 a value of 5.0 monomer units. Some corrections must be applied to these values; this is discussed below.

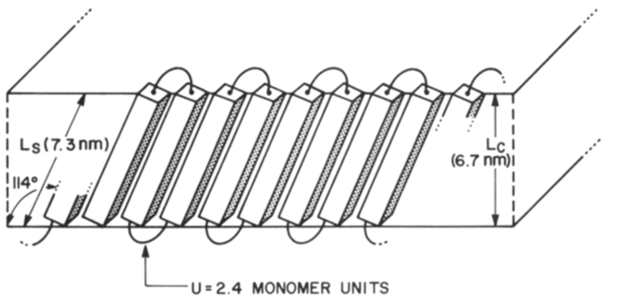


Figure 7. Schematic representation of 1,4-*trans*-polybutadiene UH45 crystals with surface folds. L_s is stem length; L_c is crystal thickness; U is fold length in number of monomer units (see text).

The stem length, L_s (see Figure 7), may be determined from the following expression, based on the assumption that none of the crystalline phase has reacted:

$$L_{\mathrm{s(nm)}} = [([\mathrm{C}]/[\mathrm{D}]) + 1]R \qquad (4)$$

where [C] represents the resonance area of the C methylene carbons defined above (resonance a and b in Table VI), [D] represents the resonance area of the junction methylene carbons (resonance c in Table VI), and R is 0.483 nm, the repeat distance of the butadiene unit along the crystalline stem. Values of 7.3 and 19.7 nm are calculated from samples UH45 and F1H55, respectively. This is equivalent to 15.2 and 40.8 monomer units per stem, respectively.

The stem length may also be estimated from the following expression, again based on the assumption that the folds react fully, that the crystalline phase does not react, and that $\bar{M}_n$ is large:

$$L_{\mathrm{s(nm)}} = [(U'/f_e) - U']R \qquad (5)$$

The quantity f_e is the fractional extent of epoxidation; it was found in this work to be 0.162 for UH45 and 0.117 for F1H55. Values of 7.5 and 20.6 nm for L_s are calculated for samples UH45 and F1H55, respectively, from eq 5.

One could also estimate the stem length from Figure 6a by comparison of peak 3 vs. the sum of peaks 1 and 5. An L_s value of 7.6 nm is obtained from UH45, in good agreement with the results calculated above.

The crystal thickness, L_c (see Figure 7), is calculated from the stem length, L_s (from eq 4), by multiplication by the sine of the angle of inclination, 114°.[11] The results are shown in column 6 in Table IX. These can be compared with L_c values given in column 7 which were calculated from lamellar thickness measurements by using

$$L_c = \rho_A(1 - f_e)L/[\rho_A(1 - f_e) + \rho_C f_e] \qquad (6)$$

where ρ_A and ρ_C are amorphous and crystalline densities, respectively, from the literature,[11,20] L is the lamellar thickness as given in Table I and obtained by SAXS measurements,[10] and f_e is as defined above.

Table IX
Fold Lengths, Stem Lengths, and Crystal Thicknesses for 1,4-*trans*-Polybutadiene Lamellae

polymer	L_s,[a] nm	U',[b] monomer units	U,[c] monomer units		L_c,[e] nm	
			^{13}C NMR	SAXS[d]	^{13}C NMR	SAXS[f]
UH45	7.3	3.0	2.4	2.7	6.7	9.0
F1H55	19.7	5.0	3.0	4.0	18.0	20.7

[a] Stem length, nm, from ^{13}C NMR. [b] Fold length without cilia correction in monomer units, from ^{13}C NMR. [c] Fold length with cilia correction in monomer units. [d] By use of eq 14, using eq 6 for L_c (crystal thickness) and value of f_e (extent of epoxidation) from ^{13}C NMR. [e] Crystal thickness, nm. [f] From eq 6.

A correction must be made to the fold length calculation in eq 2 to take into account the noncrystallizing ends or cilia, which are not involved in chain folding but nevertheless contribute to the C-13 resonances employed in calculating U'. Let C represent the average length of two cilia, expressed in monomer units.[10] It has been shown[10] for 1,4-*trans*-polybutadiene lamellae that

$$C = 0.79L_c/R \quad (7)$$

For our purposes, two units are subtracted from C since the chemical shifts of the carbon nuclei in the two terminal units of each chain can be reliably demonstrated to fall outside the resonances employed in eq 2. Also, since L_s instead of L is the quantity obtained from the ^{13}C NMR measurements we can approximate C by the following:

$$C' = (L_s/R) - 2 \quad (8)$$

Using the values for L_s from eq 4 and a value of 0.483 nm for R, we find C' is 13 and 39 for samples UH45 and F1H55, respectively. The number of folds per number-average chain (F_n) is related to the total number-average chain length, $\bar{M}_n/M_o$, as follows:[10]

$$\bar{M}_n/M_o = (L_s/R)(F_n + 1) + UF_n + C \quad (9)$$

where U is the corrected number of monomer units per fold and M_o is the molecular weight of a butadiene unit. The three terms on the right hand side of eq 9 give the number of units in the $F_n + 1$ crystalline stems, the numbers of units in the F_n folds, and the number in the two chain ends, respectively. F_n can also be expressed in terms of the fraction epoxidized, f_e, by[10]

$$L_s/R(F_n + 1) = (\bar{M}_n/M_o)(1 - f_e) \quad (10)$$

Rearrangement of eq 9 leads to

$$F_n = [(\bar{M}_n/M_c) - (L_s/R) - C]/[(L_s/R) + U] \quad (11)$$

and rearrangement of eq 10 leads to

$$F_n = (R/L_s)[(\bar{M}_n/M_o)(1 - f_e) - 1] \quad (12)$$

The total number of butadiene units per number-average chain at the surface of the crystal is given by $U'(F_n + 1)$, recalling that U' as calculated from eq 3 includes both folds and cilia, and since the two cilia per chain contain two A methylene groups (see diagram above) they will be counted as one fold. The corrected value of monomer units per chain fold is then

$$U = (U'(F_n + 1) - C')/F_n \quad (13)$$

Values of F_n were calculated for UH45 and F1H55 from eq 11 taking as a first approximation $U = U'$, where U' was obtained from eq 3. For UH45 this gave a value of 16, which is the same as that obtained from eq 12. Substitution of this value into eq 13 yields $U = 2.4$ for UH45. Recalculation of F_n from eq 11 with $U = 2.4$ yields $F_n = 16$, as before. For F1H55 eq 11 gives a first approximation value of 16 while eq 12 gives 17. Substitution of these into eq 13 yields values for U of 2.9 and 3.0, respectively. Use of the latter number yielded an F_n value of 17 from eq 11. U can also be computed from the fraction epoxidized, f_e, by using an equation obtained by combining (9) and (10) above.

$$U = (L_s/R)[(\bar{M}_n/M_o)(f_e) - C]/[(\bar{M}_n/M_o)(1 - f_e) - (L_s/R)] \quad (14)$$

L_s was calculated from the lamellar thickness, L, measured by using low-angle X-ray scattering, via eq 6 for L_c with a correction for tilt; in this calculation of U the value of C was taken as $0.79L/R$ (see above). The U values computed using eq 13 and 14 are compared in columns 4 and 5 of table IX.

Discussion

For both the TPBD samples studied in this work the crystal thickness, L_c, as obtained by ^{13}C NMR analysis of junction and nonjunction methylene carbons in surface epoxidized lamellae is lower than that calculated from small-angle X-ray scattering (SAXS) measurements on the crystal mats (see columns 6 and 7, Table IX). However, general agreement in the relative L_c values for the two preparations is found. One possible reason for the consistently higher L_c values calculated from SAXS is that the amorphous density, ρ_A, used in eq 6 is that extrapolated from the melt.[20] Assigning a lower value to ρ_A in eq 6 would result in a lower value for L_c; doing this would also lead to better agreement between f_e, the surface fraction epoxidized as determined by ^{13}C NMR, and $1 - f_c$, where f_c is the crystalline fraction obtained from the density (see Table I), as noted earlier for this polymer.[10] Experimental results[21] and calculations using space filling models for polyethylene[22] also suggest that ρ_A as extrapolated from the melt is larger than the fold surface density. The marked difference in L_s or L_c for the two crystal preparations used is a consequence of the crystallization temperatures employed, 45 °C (UH45) and 55 °C (F1H55), as shown by Finter and Wegner.[23] Above 53–54 °C crystallization of TPBD takes place[10] in the high–melting form[24] with a relatively large lamellar thickness. When this material is cooled to room temperature a transformation[25] to the low-temperature crystal form occurs with little if any change in lamellar thickness. On the other hand, crystallization at 53 °C or below yields the low-melting form[11] with a much smaller lamellar thickness.

A larger value of the uncorrected number of monomer units per fold, U', for F1H55 as compared to that for UH45 was obtained from ^{13}C NMR analysis of the junction and nonjunction methylene carbons by use of eq 3 (see Table IX, column 3); upon correction for noncrystallizing chain ends, however, this difference is considerably narrowed (column 4). This can be attributed principally to the longer noncrystallizing chain ends, which occur as a consequence of the larger stem length, L_s, for the former preparation. From eq 8, 12, and 13, $U - U'$ is found to be approximately proportional to $L_s^2/[(\bar{M}_n)(1 - f_e)]$. Since L_s^2 is in the numerator, the effect of a higher average molecular weight is of less importance than the effect of a larger L_s. For F1H55 the corrected value for the number of monomer units per fold, as obtained directly from the ^{13}C NMR methylene resonances (column 4, Table IX), is significantly lower than that from the measured lamellar thickness (column 5). This is most likely a consequence of the overestimation of L_s in the latter calculation. The apparent reason for this overestimation was discussed in the paragraph above.

The number of monomer units to complete the tightest fold in this polymer has been given[20] as three. Therefore the direct ^{13}C NMR results found in this work strongly favor the model of a tight adjacent reentry fold[26] for TPBD lamellae grown from dilute heptane solution using material with $\bar{M}_n$ of 1.7×10^4 and 4.4×10^4. This conclusion is in agreement with earlier work on some TPBD preparations from heptane solution in which various methods, including epoxidation,[8,27] bromination,[9] broad-line proton NMR in the presence of CS_2,[28] and infrared spectroscopy,[3] were used. Chain folding in TPBD was also studied by Oyama, Shiokawa, and Murata[20] by an analysis of carbonyl infrared bands, and it was concluded that for annealed TPBD lamellae a fold of three monomer units is present.

The method used in this work to determine the fold and the crystalline stem lengths in TPBD lamellae should be applicable to any system for which the monomer units in the folds, the units in the stems, and the "junction" points between folds and crystalline stems can be distinguished. Complete nondestructive chemical transformation of the fold without significant penetration of the crystalline portions should yield block copolymers that can be analyzed by ^{13}C NMR or some other sensitive method. This general type of approach using ^{13}C NMR is currently being applied to the study of folding in 1,4-*trans*-polyisoprene fractions; the results of that work will be reported at a later date.

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Registry No. Polybutadiene, 9003-17-2; 3,7-decadiene, 72015-36-2.

References and Notes

(1) Tatsumi, T.; Fukushima, T.; Imada, K.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1967**, *B1*, 459.
(2) Bovey, F. A.; Schilling, F. C., manuscript in preparation.
(3) Hendrix, C.; Whiting, D. A.; Woodward, A. E. *Macromolecules* **1971**, *4*, 571.
(4) Eng, S. B.; Stellman, J. M.; Woodward, A. E. *J. Macromol. Sci., Phys.* **1973**, *B7*, 533.
(5) Gemmer, R. V.; Golub, M. A. *J. Poly. Sci., Polym. Chem. Ed.* **1978**, *16*, 2985.
(6) Oyama, T.; Shiokawa, K.; Murata, Y. *Kobunshi Ronbunshu* **1980**, *37*, 327.
(7) Stellman, J. M.; Woodward, A. E. *J. Polym. Sci., Part B* **1969**, *7*, 755.
(8) Stellman, J. M.; Woodward, A. E. *J. Polym. Sci., Part A-2* **1971**, *9*, 59.
(9) Wichacheewa, P.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1849.
(10) Tseng, S.; Herman, W.; Woodward, A. E.; Newman, B. A. *Macromolecules* **1982**, *15*, 338.
(11) Iwayanagi, S.; Sakurai, I.; Sakurai, T.; Seto, T. *J. Macromol. Sci., Phys.* **1968**, *B2*, 163.
(12) Van Duuren, B. L.; Schmitt, F. L. *J. Org. Chem.* **1960**, *25*, 1761.
(13) Carlson, R. G.; Behn, N. S.; Cowles, C. *J. Org. Chem.* 1971, *36*, 3832.
(14) Levitt, M. H.; Freeman, R. *J. Magn. Reson.* **1979**, *33*, 473.
(15) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757, referenced in 16.
(16) Breitmaier, E.; Haas, G.; Voelter, W. "Atlas of Carbon-13 NMR Data"; Heyden & Son, Inc.; Philadelphia, 1979.
(17) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.
(18) De Haan, J. W.; Van de Ven, L. J. M., *Org. Magn. Reson.* **1973**, *5*, 147, referenced in 16.
(19) Schilling, F. C., unpublished observations. Assignments of the junction methylene resonances of OD-t*Z* and OD-c*E* were made by assuming shift effects similar to those observed in the OD-t*E* compound.
(20) Oyama, T.; Shiokawa, K.; Murata, Y., *Polym. J.* **1974**, *6*, 549.
(21) Harrison, I. R.; Runt, J. *J. Macromol. Sci., Phys.* **1980**, *B17*, 83.
(22) Harrison, I. R.; Juska, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *17*, 491.
(23) Finter, J.; Wegner, G. *Makromol. Chem.* 1981, *182*, 1859.
(24) Suehiro, I.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1970**, *4*, 39.
(25) Moraglio, G.; Polizotti, G.; Danusso, F. *Eur. Polym. J.* **1975**, *1*, 183.
(26) Keller, A. *Philos. Mag.* 1957, *2*, 1171.
(27) Newman, B.; Stellman, J. M.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 2311.
(28) Eng. S.-B.; Woodward, A. E. *J. Macromol. Sci., Phys.* **1974**, *B10*, 627.

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^{1}H and ^{13}C NMR Investigation of Xanthan Gum

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ABSTRACT: ^{1}H NMR spectroscopy was used to determine the ratio of pyruvate/acetate groups in a sample of xanthan. In addition, a quantitative measurement of both substituents is given by the integral of the ^{1}H signals compared to the signal of H-1 α of the mannopyranosic unit. The results allowed us to conclude that in the xanthan investigated each side chain is substituted with one acetate and one pyruvate group. ^{1}H NMR spectroscopy is also used to investigate the chemical stability of the substituents. It is shown that the thermal stability is lower when the polymer is in the random coil state. The ^{13}C NMR spectra of initial and modified xanthans are given. Partial assignment of the carbon signals is proposed. The spectrum obtained for xanthan free of acetate and pyruvate groups confirms the regular chemical structure corresponding to five monomers per repeating unit. The NMR analysis was favored by partial enzymatic depolymerization of the xanthan to decrease the solution viscosity and the conformational melting temperature of the polymer.

Introduction

Xanthan gum solutions have been widely studied in recent years because of their commerical importance,[1,2] but also to establish the conformation and conditions of conformational transition of xanthan that can be driven by changes in temperature, ionic strength, pH, and polymer concentrations.[3-7] The ordered polymer chain conformation[8-11] and the molecular weight[12-15] remain a matter of discussion. However, some rheological investigations are consistent with a stiff conformation[11,14,16] that leads to a liquid crystalline solution.[17] The primary structure of the xanthan has been shown[18] (Figure 1) to consist of a (1→4)-β-D-glucose chain with a trisaccharide substituent on alternate glucose residues. This side chain is β-D-mannopyranosyl (1→4)-α-D-glucuropyranosyl-(1→2)-β-D-mannopyranoside 6-*O*-acetate. The terminal D-mannose residue of the side chain may have a pyruvic acid residue linked to the 4 and 6 positions. But the acetate and py-