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Quantitative Investigation of the Amorphous and Crystalline Components in *trans*-1,4-Polybutadiene from Solution. 2. Statistical Treatment

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ABSTRACT: A statistical model based on the assumption of adjacent reentry in lamellas of *trans*-1,4-polybutadiene chains, containing randomly placed cis units, is developed for the calculation of crystallinity and of a NMR tetrad ratio in surface reacted specimens. In this treatment the chain ends and cis units appear at the lamellar surfaces and there are three types of chain folds: (i) those containing only *trans*-polybutadiene units and which have a constant length, (ii) those with interior cis units with the same length as for the all-trans fold, and (iii) those with cis units and accompanying trans units rejected from the crystal core, having a variable length. In this treatment the crystallinity and tetrad ratio are functions of (i) the cis content, (ii) the degree of polymerization, (iii) the crystal traverse length, and (iv) the all-trans-containing fold length, B'. Comparison of calculated with experimental values yields 4 ± 1 for B'.

Introduction

Polydiene lamellas can be quantitatively characterized by both physical and chemical methods. A chemical method that involves epoxidation in suspension followed by carbon-13 nuclear magnetic resonance in solution has been developed.[1] This method was recently used to investigate the effects of crystallization temperature, concentration, and solvent on the average number of monomer units per fold, B, and the average number of monomer units per crystalline stem traverse, A, for low molecular weight fractions of *trans*-1,4-polybutadiene containing 1% cis units.[2] In that and in subsequent work, using a 90/10 *trans*/*cis*-1,4-polybutadiene,[3] the NMR spectra showed that most of the cis units are epoxidized and therefore are rejected from the crystalline core, causing the average fold length to increase with increasing cis content. Depending on the crystallization solvent and the crystallization temperature the average number of monomer units per fold was found to vary from 5 at a cis content of 1% to 16 at a cis content of 10%. These results showed that with each cis unit rejected from the crystal core trans units are also rejected. This leads to a model for the surface that consists of three components: (1) folds with no cis units, (2) folds with one or more cis units that can vary in length, and (3) chain ends. The average number of monomer units in a fold composed only of trans units was estimated by assuming that for each cis unit rejected from the crystal core, $A/2$ trans units are also rejected. This correction resulted in values of 3–5 for the fold length for samples with a 1% cis content. This correction is not expected to be valid for samples with large cis contents, due to the possible presence of folds with more than one cis unit, or for chains in which the cis units are not randomly placed.

It was believed of interest to explore the use of a statistical treatment to investigate the effects of cis content and other parameters on certain experimentally observed quantites for *trans*-1,4-polybutadiene lamellas. In particular, an adjacent reentry folding model that assumes randomly place cis units in the chain, leading to folds of various lengths mixed with non-cis-containing folds having only a small number of trans units, was used. This model was applied to two problems, one of which is the calculation of the crystallinity as a function of the four variables: the average number of monomer units per crystalline stem traverse, A; an all-trans fold length, B'; the degree of polymerization; and the cis content. The calculated values are compared with measured crystallinities from density and/or surface fraction for samples prepared at various temperatures in order to deduce B' values that fit the experimental results. The second application involves a calculation of the intensity ratio for tetrad sequences in segmented block copolymers prepared by epoxidation in suspension of lamellas of *trans*-1,4-polybutadiene samples containing small amounts of cis units. In these calculations it is seen that the crystallinity is not very sensitive to A but does change significantly with cis content and B′, while [EEEE]/[BEEE] is a strong function of A particularly at small B'. Carbon-13 NMR resonances attributed to CH_2 carbon atoms in sequences of four epoxidized trans units, [EEEE], and to CH_2 carbon atoms in a tetrad sequence of one *trans*-butadiene unit and three epoxidized trans units, [BEEE], were partially separated at 100 MHz and the relative peak areas estimated for two samples with different A values. Comparison of the experimental and calculated tetrad radios is then used to estimate B' values. The B' value best fitting the experimental results from both crystallinity and the tetrad radio is found to be 4.

Statistical Treatment

The treatment to be described is a statistical one and involves the following assumptions: (1) all cis units and chain ends reside at the lamellar surfaces, (2) the cis units are randomly placed in the chain, (3) the folding involves adjacent reentry, and (4) the fold length is constant if the fold does not contain a cis unit rejected from the crystal core during the crystallization process. A segment is defined in this treatment as a sequence of *trans*-1,4-polybutadiene units between an end group and a cis unit or between two cis units. The probability that a trans unit appears in a segment is p, the trans unit fraction; the probability that a segment contains i trans units is $p^i(1 - p)$; and the average segment length is given by $1/(1 - p)$.[4] The trans unit fraction, p, is equal to $1 - q - (1/X_n)$ where q is the fraction of cis units and X_n is the number average degree of polymerization.[4] Three types of folds are considered as possible: (i) folds containing trans units only; (2) folds containing an interior cis unit preceded and/or followed by trans units and having the same length as that containing trans units only; and (3) folds containing one or more rejected cis units, rejected trans units, and the trans units associated with an all-trans fold. These three types of folds are depicted in Figure 1, where (●) signifies a cis unit or a chain end and x-x-x represents rejected trans units. Single cis units rejected from the crystal core are expected to occupy the first position in the fold preceding the pertinent crystal traverse with no additional trans unit rejection. Two types of complete segments are shown in Figure 1, one starting with an end group (a) and ending

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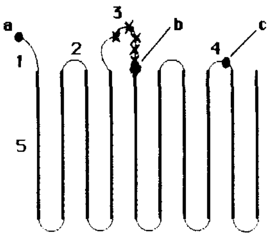

Figure 1. Adjacent reentry model for a polymer chain in a lamella containing (1) chain end, (2) folds with trans units only, (3) a fold with a rejected cis unit, (4) a fold with an interior cis unit, and (5) crystal traverses containing only trans units. Two full segments are shown: one starting at an end group (a) and ending in a rejected cis unit (b) and one starting at the rejected cis unit (b) and ending in an interior cis unit (c).

with a rejected cis unit (b) and the second starting with the rejected cis unit (b) and ending with an interior cis unit (c). The calculations allow for more than one cis unit to reside in a fold.

1. Crystallinity Calculation. The crystallinity of a polymer can be given by the number of monomer units in all the crystal traverses divided by the total number of units. In this paper the average number of monomer units that appear in crystal traverses per segment will be calculated. To obtain the crystallinity the average number of monomer units in a segment must also be obtained.

Segments starting with a rejected cis unit and ending in another rejected cis unit, in an interior cis unit, or in a chain end are considered first. For this type of segment nA monomer units will be found in n crystal traverses if the number of monomer units in the segment is between $n(A + B') - B'$ and $(n + 1)(A + B') - B' - 1$. The total number of crystal traverses possible per chain is the whole number, m, found from $X_n/(A + B)$. Therefore, the average number of units present in the crystal traverses per segment starting with a rejected cis unit is given by

$$S_{01} = \sum_{n=1}^{m} nA \sum_{j=0}^{A+B'-1} p^{[n(A+B')-B'+j]}(1 - p) \qquad (1)$$

For segments starting with an interior cis unit and ending in another cis unit or in a chain end, the average number of units in the crystal traverses is represented by

$$S_{02} = \frac{1}{B' - 1}\sum_{g=1}^{B'-1} \sum_{n=1}^{m} nA \sum_{j=0}^{A+B'-1} p^{[n(A+B')-B'+g+j]}(1 - p) \qquad (2)$$

where g represents the number of trans units between the interior cis unit and the first crystal traverse and $1/(B' - 1)$ is a normalization factor.

Segments starting with an end group can have from 1 to A monomer units remaining outside the crystal core and will contribute an average number of units to the crystal traverses of

$$S_{03} = \frac{1}{A}\sum_{g=0}^{A-1} \sum_{n=1}^{m} nA \sum_{j=0}^{A+B'-1} p^{[n(A+B')-B'+j+g]}(1 - p) \qquad (3)$$

To obtain the average number of repeat units in the crystal traverses per chain, each of the three terms above must be weighted according to the relative probability of their occurrence. There are qX_n cis units and $qX_n + 1$ segments per polymer chain on the average; the probability that a segment starts with a chain end will be $1/(qX_n + 1)$. The probability that a segment starts with a cis unit is $1 - [1/(qX_n + 1)]$; the relative probability that this cis unit is a rejected one is $A/(A + B)$ and an interior one is $B/(A + B)$. Therefore, the average number of monomer units per segment in crystal traverses is

$$S_0 = S_{03}/(1 + qX_n) + [1 - 1/(1 + qX_n)](S_{01}A + S_{02}B)/(A + B) \qquad (4)$$

The average number of monomer units per segment is

$$S = \sum_{i=1}^{X_n} ip^{i-1}(1 - p) \qquad (5)$$

and the crystalline fraction, χ, is given by S_0/S.

2. Calculation of Tetrad Intensity Ratio. The epoxidation in suspension of lamellas grown from *trans*-1,4-polybutadiene containing some randomly placed cis units rejected from the crystal core would give the following tetrad sequences where B represents a *trans*-butadiene unit, E an epoxidized *trans*-butadiene unit, and C an epoxidized cis unit: BBBB, BBBE, BBEE, EBBB, EEBB, BEEE, EEEB, EEEE, BCEE, BECE, BEEC, EECB, ECEB, CEEB, CEEE, EEEC, ECEE, and EECE. The carbon-13 NMR intensity ratio to be calculated by statistical means is [EEEE]/[BEEE]. Calculations of the average number of EEEE and BEEE sequences per polymer segment are carried out separately. The equations applicable to these calculations depend on the choice of B'; the case of $B' = 3$ will be developed first.

Calculation of the average number of BEEE sequences per segment is split into three parts. The first part is for segments starting with a rejected cis unit. For $B' = 3$ there will be $(S_{01}/A) - 1$ folds with three trans units only which contain two BEEE sequences and one fold with one or more consecutive trans units which contain 0 or 1 BEEE sequences depending on the ending cis unit location. The average number of BEEE sequences per segment will be given by

$$S_{31} = 2\left(\frac{S_{01}}{A} - 1\right) + \sum_{n=1}^{m} \sum_{j=3}^{A+B'-1} p^{n(A+B')-B'+j}(1 - p) \qquad (6)$$

Similar consideration for a segment starting with an interior cis unit gives for the average number of BEEE sequences per segment

$$S_{32} = 2\left(\frac{S_{02}}{A} - 1\right) + \frac{1}{(B' - 1)}\sum_{g=1}^{B'-1} \sum_{n=1}^{m} \sum_{j=3}^{A+B'-1} p^{n(A+B')+g+j-B'}(1 - p) \qquad (7)$$

For segments starting with a chain end the average number of BEEE sequences per segment is given by

$$S_{33} = 2\left(\frac{S_{03}}{A} - 1\right) + \frac{1}{A}\sum_{g=0}^{A-1} \sum_{n=1}^{m} \sum_{j=3}^{A+B'-1} p^{n(A+B')+g+j-B'}(1 - p) \qquad (8)$$

When $B' = 3$ the average number of EEEE sequences in a segment will be a function only of the lengths of the chain ends and the folds containing rejected cis units. This can be split into three terms. The first of these accounts for segments starting with a rejected cis unit:

$$S_{41} = \sum_{n=1}^{m} \sum_{j=4}^{A+B'-1} (j - 3)p^{n(A+B')-B'+j}(1- p) \qquad (9)$$

For segments starting with an interior cis unit the contribution is given by

$$S_{42} = \frac{1}{B' - 1}\sum_{g=1}^{B'-1} \sum_{n=1}^{m} \sum_{j=4}^{A+B'-1} (j - 3)p^{n(A+B')-B'+j+g}(1 - p) \qquad (10)$$

For segments starting with a chain end

$$S_{43} = \frac{1}{A}\sum_{n=0}^{m}\left[\sum_{g=4}^{A-1} \sum_{j=0}^{A+B'-1} (g - 3) + \sum_{g=0}^{A-1} \sum_{j=4}^{A+B'-1} (j - 3)\right]p^{n(A+B')-B'+g+j}(1 - p) \qquad (11)$$

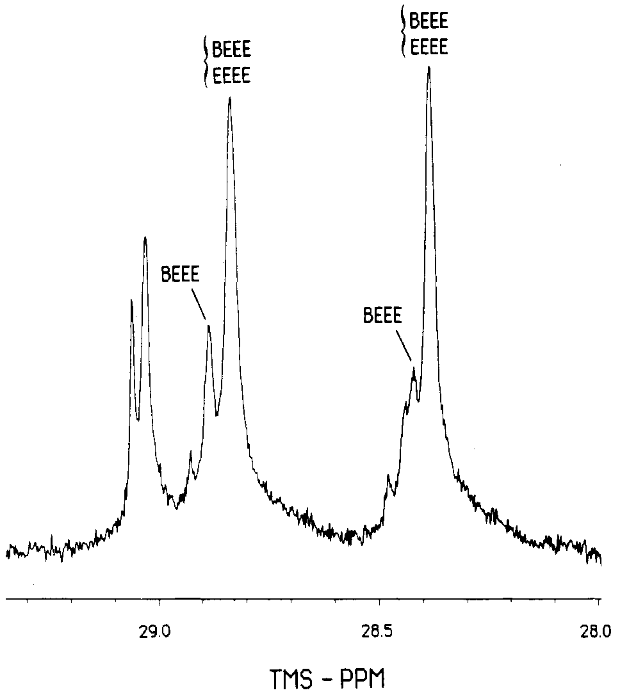

Figure 2. Carbon-13 NMR spectrum at 100 MHz for methylene carbon atoms in the reacted portions of *trans*-1,4-polybutadiene epoxidized in suspension. Crystallized from 0.05% cyclohexane solution at 10 °C.

The three terms for the EEEE and the BEEE sequences are combined separately with the same weighting as given in the section Crystallinity Calculation and the ratio is taken to obtain [EEEE]/[BEEE].

When B' is greater than 3, changes must be made in S_{32}, S_{41}, S_{42}, and S_{43}. To the term representing the EEEE sequences $(B' - 3)(S_0/A - 1)$ is added. For the term representing BEEE and $B' = 4$, S_{32} becomes

$$S_{32}' = S_{32} + \frac{1}{B' - 1}\sum_{g=3}^{B'-1}\sum_{n=1}^{m}\sum_{j=3}^{A+B'-1} p^{n(A+B')+g+j-B'}(1 - p) \quad (12)$$

For $B' = 5$ the additional summation in eq 12 becomes two summations, corresponding to the two possible positions of the cis unit.

Experimental Section

The procedures for the preparation, fractionation, and crystallization of *trans*-1,4-polybutadiene were presented in the preceding paper.[2] The lamellar structures obtained on crystallization from amyl acetate or cyclohexane were reacted in suspension at 0 °C with dissolved *m*-chloroperbenzoic acid. All of the epoxidized samples were quantitatively characterized in $CDCl_3$ solution by carbon-13 NMR at 50 MHz.[2] One of the preparations from cyclohexane, crystallized at 10 °C from 0.05% solution, and one from amyl acetate, crystallized at 30 °C from 0.05% solution, with both being epoxidized in amyl acetate for 14 days by using [MCPBA]/[DB] of 1.5, were analyzed by carbon-13 NMR at 100 MHz, by using a JEOLCO instrument. The conditions used were a 16-KHz spectral width, 64K memory, 10-s relaxation delay, and 4000 scans with proton decoupling. Intensities were measured by separation of overlapping resonances and graphical determination of areas by cutting and weighing. A representative spectrum taken at 100 MHz is shown in Figure 2. In the assignments given earlier for lamellas epoxidized in suspension, each of the two equal resonances at 28.9 and 28.4 ppm evident at 50 MHz were attributed to CH_2 carbons in both EEEE and BEEE sequences, the splitting being caused by the presence of diastereoisomers.[1] Further splitting of each of these was reported for a 78% solution epoxidized TPBD; this is more apparent in the 100-MHz spectrum given in Figure 2 for lamellas epoxidized in suspension. According to the previous assignments one set of BEEE resonances appear in the present spectrum at 28.83 and 28.88 ppm while one of the EEEE resonances occurs at 28.83 ppm. Therefore, [EEEE]/[BEEE] is given by $(R - 1)/2$ where R is the ratio of the area of the 28.83 ppm resonance to that of the 28.88 ppm resonance.

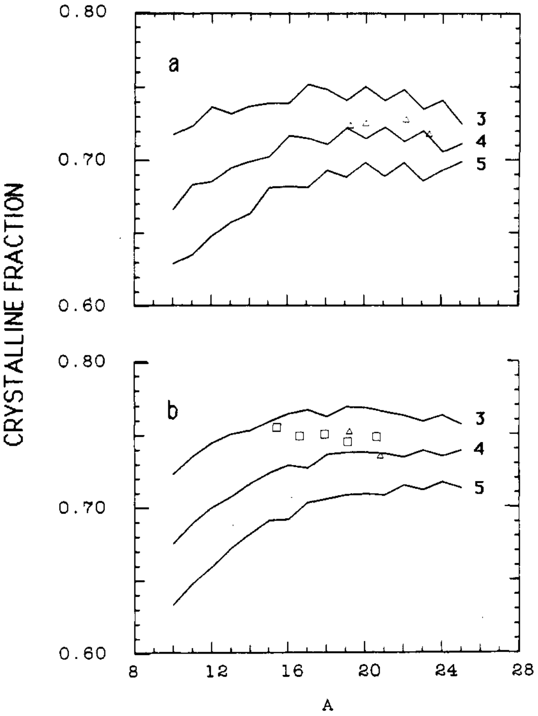

Figure 3. Crystallinity vs. the number of monomer units per crystal traverse, A, for 99% *trans*-1% *cis*-1,4-polybutadiene: (—) Calculated, the numbers are B' values; (□) crystallized from cyclohexane; (△) crystallized from amyl acetate; (a) X_n = 300; (b) X_n = 440.

Comparison of Calculated and Experimental Results

The crystallinity, calculated by using eq 1–5, is plotted in Figure 3 as a function of A and is represented by a set of solid lines for three values of B' (3, 4, and 5). A single value for the cis content, 1%, and two values of the number average degree of polymerization, 300 and 440, commensurate with experiment, were employed in these calculations. For X_n of 300 the lines are jagged; they become smooth with an increase in X_n or in q. They also become smooth when A and X_n are treated as average quantities. Three sets of experimentally determined crystallinity values plotted vs. the corresponding experimentally determined A values, shown as points, are also included on Figure 3. The variations in A, seen for a given fraction crystallized from a particular solvent, arise due to the use of different crystallization temperatures which were in the range 10–40 °C. Both the calculated and experimental crystallinities show only a small variation with A value. The fraction of monomer units not reacting is given by $A/(A + B)$, where B is the average number of monomer units per fold. It was shown experimentally that for these samples the fraction not reacting, obtained from carbon-13 NMR measurements, can be equated to the crystalline fraction from density.[2] From experiment, as A increases, B is found to increase. In terms of the model used in this paper, this is due to an increase in the number of trans units being rejected along with each cis unit rejected. Therefore, the crystallinity shows only a 4% change when B' is taken as 3 and A is changed from 10 to 25 and an 8% change when B' is 4 or 5. Comparison of the experimental crystallinities with the curves calculated assuming adjacent folding suggests that the all-trans fold contains 3–4 monomer units.

Table I
Tetrad Ratios for Epoxidized *trans*-1,4-Polybutadiene Lamellas

			[EEEE]/[BEEE]			
				calcd		
cryst solvent	T_c, °C	A	exptl[a]	$B' = 3$	$B' = 4$	$B' = 5$
cyclohexane	10	15	1.3 ± 0.2	0.7	1.1	1.5
amyl acetate	30	20	1.5 ± 0.2	1.0	1.5	1.8

[a] Crystallized from 0.05% solution by using material with X_n = 350 and a cis content of 1%; epoxidized in amyl acetate at 0 °C for 14 days with [MCPBA]/[DB] = 1.5.

Experimental values for the tetrad intensity ratio, [EEEE]/[BEEE], from carbon-13 NMR at 100 MHz, as obtained from the areas under the resonances at 28.83 and 28.88 ppm following curve separation, are given in Table I, column 4. Considerable uncertainty is evident due to the presence of a small resonance at 28.93 ppm, with the values shown being averages of those with and without the area under this resonance. Values for [EEEE]/[BEEE], calculated from the adjacent fold model, are given for B' equal to 3, 4, and 5 in columns 5, 6, and 7, Table I. Comparison of the experimental and calculated ratios suggests that the number of monomer units in the all-trans fold is 4–5. This is in approximate agreement with the results given above for the crystallinity of TPBD preparations.

The calculated values for the tetrad ratio show a 5-fold increase when B' is taken as 3 and about a 2-fold increase for B' of 4 and 5, when A is changed from 10 to 25. As discussed above when A is increased, the average number of monomer units per fold, B, increases due to trans unit rejection. This causes an increase in [EEEE] but has a much smaller effect on [BEEE], especially for $B' = 3$.

The experimentally determined average number of monomer units per fold for lamellas of *trans*-1,4-polybutadiene containing small quantities (1%) of cis units was found to vary from 5.6 to 9.2 with rejection of all cis units from the crystal core.[2] According to the present study, in which a statistical approach is used, the folds without cis units contain 4 ± 1 trans units; the folds with cis units can vary in size from four to a maximum number of $A + B' - 1$ (18–28), the latter depending on the crystallite thickness, as determined by the crystallization conditions. For a cis content of 1% and $A + B$ of 20–33, as found experimentally, there will be 3–5 folds without cis units to every one with such a unit. The more monomer units per crystal traverse, the larger the maximum number of monomer units in a fold, as given by $A + B'$. The *trans*-1,4-polybutadiene samples discussed in this paper are relatively low in molecular weight and cis content. A sample with a cis content of 10% and X_n of 3700 has also been investigated.[3] A crystallinity calculated from the statistical theory developed above for a B' of 3–4 was found to agree with the experimentally determined value for that sample, suggesting that adjacent reentry folding occurs. Details of that work will be given in a separate publication.

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Registry No. 1,4-Polybutadiene, 9003-17-2.

References and Notes

(1) Schilling, F. C.; Bovey, F. A.; Tseng, S.; Woodward, A. E. *Macromolecules* **1983**, *16*, 808.

(2) Wang, P.; Woodward, A. E. *Macromolecules*, preceding paper in this issue.

(3) Wang, P.; Woodward, A. E., submitted for publication.

(4) The average segment length is given by $\sum_{i=1}^{X_n} p^{i-1} i (1 - p)$ which for x large is $1/(1 - p)$. A chain with qX_n cis units contains $qX + 1$ segments and the average segment length is $X_n/(qX_n + 1)$; therefore, $1 - p = q + 1/X_n$.