Quantitative Investigation of the Amorphous and Crystalline Components in a 89% *trans*-Polybutadiene Copolymer from Solution

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ABSTRACT: *trans*-Polybutadiene containing 10% cis, 88.5% trans, and 1.5% 1,2 units was crystallized from solution and the resulting preparations studied by surface epoxidation coupled with carbon-13 NMR, differential scanning calorimetry, transmission electron microscopy, and X-ray scattering methods. It was found that lamellas grown from two different solvents and at different temperatures in the same solvent have an average crystalline stem length, A, of 11 ± 1 monomer units, an average number of monomer units per fold, B, of 16 ± 1, and a crystallinity of 41%. The crystallinity observed is in agreement with that calculated by using a statistical treatment developed previously which assumes adjacent reentry with folds having three repeat units mixed with longer folds containing rejected cis and adjacent trans units. A three-dimensional gel structure containing lamellas was observed when this polymer was crystallized from 0.7 or 1% amyl acetate solution at 10 °C. A "fold entanglement" mechanism of gelation is proposed for this polymer.

Introduction

In paper 1 in this series[1] an investigation of various *trans*-1,4-polybutadiene fractions containing 1% cis units and having molecular weights (M_v) in the range of 7000–36 000 was reported. In that study the polymers were crystallized from solution and the lamellas obtained subjected to reaction in suspension with *m*-chloroperbenzoic acid (MCPBA). The resulting segmented block copolymers, containing *trans*-1,4-polybutadiene sequences alternating with epoxidized 1,4-polybutadiene sequences, were characterized in solution by carbon-13 NMR spectroscopy. With use of earlier assignments,[2] the spectroscopic analysis showed that within the detection limits all the cis units were rejected to the lamellar surfaces and were available for epoxidation. It was found also that the fraction of double bonds reacted was in agreement with the amorphous fraction of the lamellas as obtained from density measurements; this suggests that the reaction at the surface was complete without significant penetration of the crystalline core occurring. From the NMR analysis,[2] the average number of monomer units per fold, B, and the average number of monomer units per crystalline stem, A, were obtained. Values of B of 5–9, increasing with increasing A, resulted. Assuming that the rejection of cis units from the crystalline core would also cause the rejection of trans units and that a fold contains one or no cis units, an approximate expression for the fixed minimum fold length (B'), which represents the fold length for a 100% pure *trans*-1,4-polybutadiene, was obtained

$$B' = B - qA(A + B)/2 \quad (1)$$

where q is the fraction of cis units in the polymer. Use of eq 1 yielded B' values of 4 ± 1 monomer units.

In paper 2 in this series a statistical treatment for calculation of parameters such as crystallinity and a tetrad ratio for the block copolymer from A, B, q, and average degree of polymerization X_n was presented;[3] the calculated and experimental crystallinity and tetrad ratios were found to be in agreement for B' values of 4 ± 1.

In this paper, the results of a crystallization study carried out for a polybutadiene sample containing 88.5% trans, 10% cis, and 1.5% 1,2 units and having a M_n of 200 000 will be presented and discussed. The partially crystalline material was characterized by DSC, X-ray, electron microscopy, and surface epoxidation/carbon-13 NMR analysis methods. In this study crystallization was carried out at concentrations from 0.05 to 1% in amyl acetate at 10 °C with gelation occurring at 0.7% concentration. Evidence is given also for the presence of small amounts of cis units which enter the crystalline core.

Experimental Section

Samples. Two high *trans*-polybutadiene samples were used. One of these, employed in all parts of this study, was kindly provided by GEN Corp. The basic characteristics of this sample are as follows: $M_n = 2.0 \times 10^5$, $M_w/M_n = 2.3$, cis fraction = 0.10, 1,2 fraction = 0.015. This sample will be referred to below as 89% *trans*-PBD. Another sample prepared by using $RdCl_3$ as catalyst in aqueous emulsion[1] has $M_n = 2 \times 10^4$ and a cis fraction of 0.01. This sample was used as a comparison to the 89% *trans*-PBD sample and will be referred to as 99% *trans*-PBD.

Crystallization Procedures. Crystallization of 89% *trans*-PBD was carried out in 0.05% (w/v) solutions of amyl acetate at 10 °C and diethyl ketone at 10 and 20 °C by a self-seeding procedure.[1] Samples were crystallized at additional concentrations in amyl acetate solution at 10 °C (0.1, 0.3, 0.7, and 1%). The same self-seeding procedure was used for the 99% *trans*-PBD crystallized at 30 °C from 0.05% amyl acetate solution and at 10 °C from 1 and 5% amyl acetate solutions.

DSC Measurements. Completely dried crystalline samples of both polybutadienes were subjected to DSC measurement with a Du Pont 1090 instrument at a 10 °C/min heating rate. The melting point, heat of fusion, transition temperature, and heat of transition were calculated by using the instrument computer.

X-ray Scattering. X-ray scattering was carried out on the dried crystalline mats made from lamellas of 89% *trans*-PBD prepared from 0.05 and 1% amyl acetate solutions at 10 °C and the mats of 99% *trans*-PBD grown from 0.05 and 1% amyl acetate solutions. A Cu target, 32 mA, 40 kV, and 1-h exposure were used.

Surface Epoxidation and Carbon-13 NMR Analysis. Epoxidation of solution crystallized lamellas was carried out in amyl acetate at 0 °C at a *m*-chloroperbenzoic acid/double bond mole ratio of 3 for 89% *trans*-PBD and 1.2 for the 99% *trans*-PBD. Reaction times of 9–20 days were used.

Quantitative carbon-13 NMR spectra were obtained at 50.32 MHz by using gated decoupling, a 90° pulse, an 8333 kHz spectral width, 32 K memory, and a 10-second relaxation delay.[2] TMS was used as an internal reference. Intensities were measured by computer integration in all copolymer analyses.

Results

Morphology. The 89% *trans*-PBD can be crystallized only as irregular overgrown lamellas in dilute amyl acetate, as shown in Figure 1. These lamellas are elongated with pointed ends and have about a 10-μm length and a 4-μm width. With crystallization from 0.05% diethyl ketone solution, single layers are obtained, as shown in Figure 2. The total lamellar thickness of that preparation was es-

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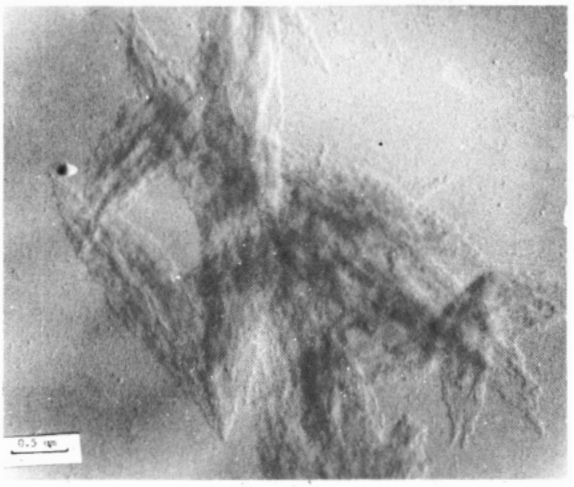


Figure 1. Transmission electron micrograph for 89% *trans*-polybutadiene crystallized from 0.05% amyl acetate solution at 10 °C.

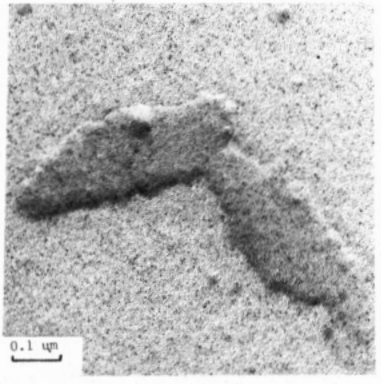


Figure 2. Transmission electron micrograph for 89% *trans*-polybutadiene crystallized from 0.05% diethyl ketone solution at 10 °C.

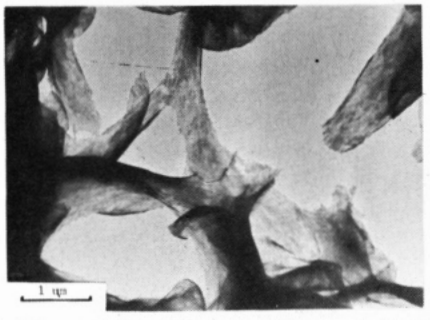


Figure 3. Transmission electron micrograph for 89% *trans*-polybutadiene crystallized from 1% amyl acetate solution at 10 °C.

timated by the shadowing length as 11 nm (an average from six edge measurements).

A three-dimensional gel structure is obtained when 89% *trans*-PBD is crystallized at concentrations of 0.7 and 1% in amyl acetate at 10 °C. Transmission electron micrographs were obtained for a piece of the gel, as shown in Figure 3; the lamellar nature is apparent.

Carbon-13 NMR Results. The carbon-13 NMR spectrum of unreacted 89% *trans*-PBD in solution is given in Figure 4 and shows the presence of trans-1,4, cis-1,4, and 1,2 units. On the basis of the earlier work[2] and the work of Clague et al.,[4] the spectrum can be assigned as given in Table I.

From the integration of the carbon-13 NMR spectrum the cis-1,4 and 1,2 contents are estimated as 10 and 1.5%, respectively.

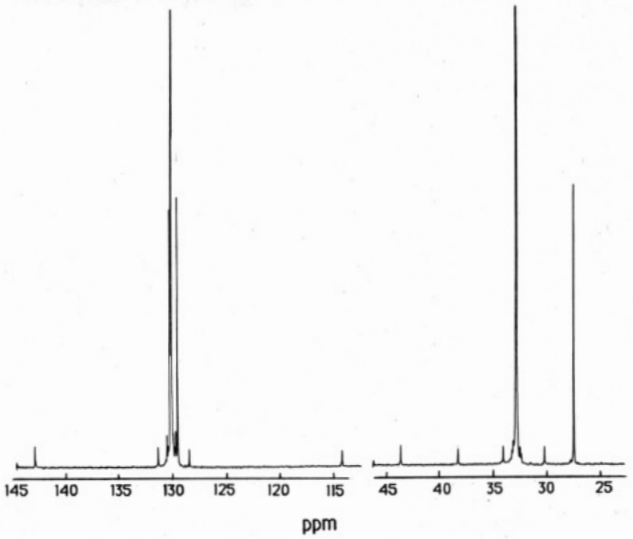


Figure 4. Carbon-13 NMR spectrum at 50.32 MHz for 89% *trans*-polybutadiene in $DCCl_3$ solution.

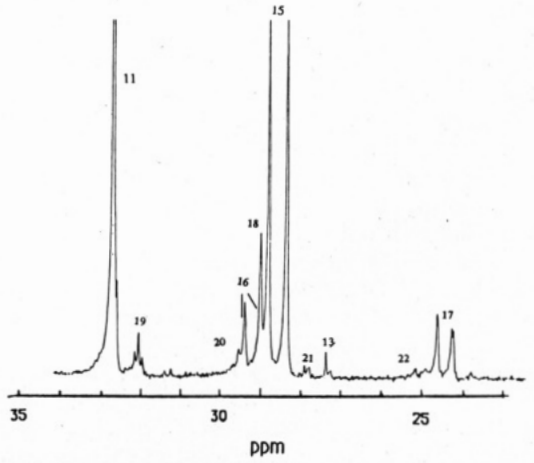
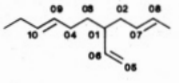
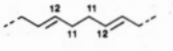
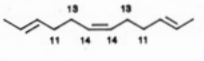


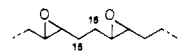
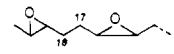
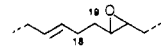
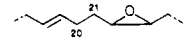
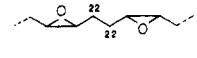
Figure 5. Carbon-13 NMR spectrum at 50.32 MHz of the CH_2 region for 89% *trans*-polybutadiene epoxidized in suspension at 0 °C. Spectrum taken in $DCCl_3$ solution.

Table I
Carbon-13 NMR Assignments for Polybutadiene

no. of carbon	position, ppm	
01	43.6	
02	38.3	
03	34.3	
04	30.3	
05	114.6	
06	142.9	
07	128.7	
08	131.5	
09	130.8	
10	130.0	
11	32.7	
12	130.0	
13	27.4	
14	129.4	

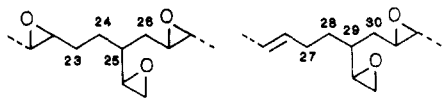
The carbon-13 NMR solution spectrum was obtained for 89% *trans*-PBD lamellas epoxidized in suspension by using *m*-chloroperbenzoic acid. The peaks at 114 and 143 ppm attributed to the olefinic carbon in a 1,2 unit in the unepoxidized polymer disappear in this spectrum, suggesting that all detectable 1,2 units are at the lamellar surfaces and can be epoxidized completely. The oxirane and methylene parts of this spectrum are given in Figure 5. It is observed that a small resonance at 27.4 ppm is

Table II
Assignments of Methylene Carbons of Suspension Epoxidized Polybutadiene

no. of carbon	position, ppm		
15	28.3	28.8	
16	29.0	29.4	
17	24.3	24.7	
18		29.0	
19		32.2	
20		29.8	
21		28.0	
22		25.3	

still present. As assigned in Table I, this resonance represents methylene carbon atoms between a trans and a cis unit. It suggests that a small amount (about 5%) of the cis units are present in the crystalline core and unavailable for a suspension reaction. The principal resonances that appear in the spectrum of the suspension-epoxidized product of 89% *trans*-PBD are associated with the trans-1,4 and cis-1,4 units; all of these assignments have been given previously,[2] and those for methylene carbon atoms as found in the present work are shown in Table II. The only difference between the shifts given in Table II from those given earlier[2] is that for carbon 20 as taken from the spectrum for a model compound. These assignments are given in terms of diads. An indication that the spectrum is sensitive to tetrads is the triplet at 32.2 ppm, believed to be due to two overlapping doublets; these doublets are tentatively attributed to DDO(trans)O(trans) and DDO(trans)O(cis), where D represents a diene unit and O an oxirane unit.

Small resonances at 23.9, 25.0, 25.8, 27.3, 27.8, 31.3, and 31.8 ppm are associated with epoxidized 1,2 units (carbon atoms 23–30, as shown below). These resonances have not been assigned and will not be used in the quantitative analysis given below. Since the contribution of 1,2 units is only 1.5%, the error involved in ignoring them is small (<3% for *A* and *B*).



When polybutadiene lamellas are subjected to complete surface epoxidation, a copolymer containing alternating blocks of unepoxidized polybutadiene and epoxidized polybutadiene units results. A method to obtain *A* and *B* for epoxidized *trans*-1,4-polybutadiene lamellas using carbon-13 NMR intensities has been given previously in terms of the CH_2 carbons in the unreacted sections, the CH_2 carbons in the reacted sections, and the junction carbons between reacted and unreacted sections.[2] In the present work this analysis is similar to the earlier one but has been modified to include the presence of cis–1,4 units. As stated above, the presence of 1,2 units is ignored in this analysis. The relationships used for calculation of *A*, *B*, and fe are given in eq 2–4. The numbers in the equations

$$A = 1 + ([11] + [13])/([19] + [21]) \quad (2)$$

$$B = 1 + ([15] + [16] + [17] + [22])/([19] + [20]) \quad (3)$$

$$\text{fe} = B/(A + B) \quad (4)$$

refer to resonances assigned as given above, and the bracket signifies the integrated intensity. There are two carbon atoms (18 and 19) that represent a junction between a *trans*-butadiene section and an epoxidized *trans*-butadiene and two others (20 and 21) representing that involving an epoxidized *cis*-butadiene. It is only necessary to use one of each or a mean of each pair in calculations of *A* and *B*; resonances 19 and 21 are chosen because there is no overlap between these resonances and any others while that is not the case for resonances 18 and 20, the other choices. The overlap of 18 with one part of 16 causes an apparent difference in intensity between 18 and 19.

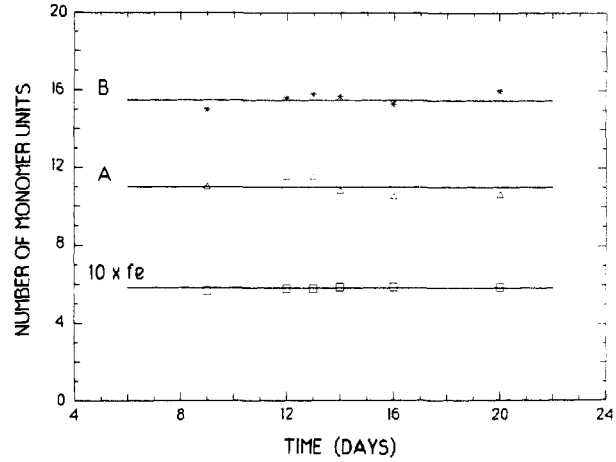


Figure 6. *A*, *B*, and fe versus epoxidation time for 89% *trans*-polybutadiene.

Table III
Expoxidation Results for 89% *trans*-PBD

crystallizatn conditns[a]	*A*[b]	*B*[c]	fe[d]
0.05% AA at 10 °C	11	15.5	0.59
0.7% AA at 10 °C	12	16	0.58
1% AA at 10 °C	11.5	17	0.59
0.05% DEK at 10 °C	11	16	0.59
0.05% DEK at 20 °C	10.5	15	0.59

[a] AA ≡ amyl acetate; DEK ≡ diethyl ketone. [b] Average number of monomer units per crystal stem. [c] Average number of monomer units per fold. [d] Fraction epoxidized.

The carbon-13 NMR spectrum was obtained for 89% *trans*-PBD epoxidized in solution to 95% completion; this showed no resonance (carbon 23–30) in the region near 32.2 ppm. Since the resonances at 32.2 ppm are used as junction contributions and their relative intensity is small, any overlap with other peaks would cause a large error.

The effect of reaction time on the epoxidation of 89% *trans*-PBD lamellas was studied for material crystallized from 0.05% amyl acetate solution at 10 °C. A MCPBA concentration of 0.01 g/cm^3, a mole ratio of MCPBA to double bonds of three, and various times from 9 to 20 days were used. *A* and *B* fluctuate by one monomer unit over this reaction time (Figure 6).

The effects of crystallization concentration, solvent, and temperature on the epoxidation results for 89% *trans*-PBD were investigated. Results for samples crystallized from amyl acetate solution at concentrations of 0.05, 0.7, and 1% at 10 °C and from 0.05% diethyl ketone at 10 and 20 °C are given in Table III in terms of *A*, *B*, and fe obtained at reaction times of 10–14 days. For the five preparations considered, the *A* values are constant at 11 ± 1 monomer units and the *B* values are constant at 16 ± 1 monomer units.

Density, DSC, and X-ray Scattering Measurements. Density measurements on the samples of 89% *trans*-PBD crystallized from 0.05% diethyl ketone at 10 and 20 °C and from 0.05, 0.1, 0.3, 0.7, and 1% amyl acetate at 10 °C gave a value of 0.948 ± 0.002 g/cm^3. Crystallinities were not calculated due to the lack of a density value for the mixed

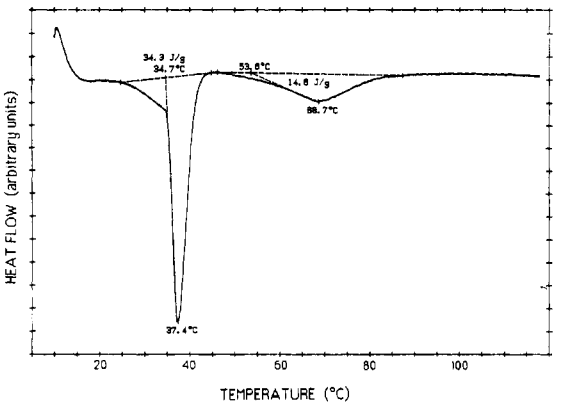


Figure 7. Differential scanning calorimetry plot for dried gel of 89% *trans*-polybutadiene.

Table IV
Results of DSC Measurements on Polybutadienes

sample	cryst conds[a]	T_{tr}, °C	ΔH_{tr}, J/g	T_m, °C	ΔH_m, J/g
99% *trans*-	0.05%, 30 °C	54	57	130	48
PBD	1%, 30 °C	53	57	130	49
89% *trans*-	0.05%, 10 °C	38	35	69	15
PBD	1%, 10 °C	37	35	69	15

[a] From amyl acetate solution.

trans-1,4 and cis-1,4 amorphous component.

Wide-angle X-ray scattering measurements were carried out on 89% *trans*-PBD crystallized from amyl acetate solution at 10 °C for concentrations of 0.05% (dried lamellar mats) and 1% (dried gel) and on the 99% *trans*-PBD crystallized from amyl acetate solution at 30 °C at concentrations of 0.05 and 1%. The X-ray scattering patterns of these four samples were found to be the same.

DSC measurements were carried out on the 89% *trans*-PBD samples crystallized from amyl acetate solution at 10 °C at 0.05 and 1% concentrations and on the 99% *trans*-PBD crystallized from 0.05 and 1% amyl acetate at 30 °C. Figure 7 is a representative DSC plot. It can be seen that there are two clear endotherms: the lower one corresponds to the crystal–crystal transition and the higher one to the melting process. The results of these measurements are given in Table IV in terms of the transition temperature T_{tr}, the melting temperature T_m, the enthalpy of transition ΔH_{tr}, and the enthalpy of melting ΔH_m. No difference in DSC parameters are observed for 89% *trans*-PBD lamellas (from 0.05% solution) or as dried gel (from 1% solution). However, the DSC parameters for these samples are significantly lower than the corresponding ones for the 99% *trans*-PBD. ΔH_{tr} is lower by about 40%, ΔH_m is lower by 70%, and T_{tr} and T_m shift by 16 and 61 deg, respectively.

Discussion

From the surface epoxidation/carbon-13 NMR results, both A and B values remain constant at 11 ± 1 and 16 ± 1, respectively, for partially crystalline 89% *trans*-PBD independent of the crystallization temperature, solvent, and concentration. For the 99% *trans*-PBD when crystallized from 0.05% amyl acetate, A decreases with decreasing crystallization temperature above 20 °C but remains constant at lower temperatures at 19 monomer units. One possible cause of this constancy of A for the two polymers is that the supercooling of these solutions is large, and, as has been observed for other polymers,[5] the crystalline thickness reaches a limiting value.

Another more likely explanation of the constancy of A and B for 89% *trans*-PBD is that at high cis content the crystalline stem length is determined by this parameter and is approximately equal to the most probable segment length. (The segment length is defined as the number of monomer units between two successive noncrystallizable units, i.e., cis units, 1,2 units, and chain ends.) In paper 2 of this series,[3] the probability of a segment with x trans monomer units was given as $p^x(1 - p)$, where p is the fraction of trans units; therefore, the length weighted probability of segments with x trans monomer units is $xp^x(1 - p)$. The maximum of that probability gives $x_m = -1/\ln(p)$. For 89% *trans*-PBD, x_m is calculated as 9, a value that is in reasonable agreement with the A value of 11 ± 1 monomer units. The average segment length, $1/q$, where $q = (1 - p)$, the fraction of cis and 1,2 units, is 9. The crystal thickness would be controlled by the cis content only when the most probable segment length is less than the size of the critical nucleus.

The value of B of 16 is significantly higher than those found for 99% *trans*-PBD which ranged from 5 to 9 and depended on the crystallization temperature and solvent.[1] This increase in B is due to the increase in the cis (and 1,2) content. The rejection of most cis units and all 1,2 units from the crystalline core during the crystallization process leads to rejection of some trans units adjacent to the cis or 1,2 units rejected. This in turn leads to a mixture of folds containing trans units only or trans units plus cis (or 1,2) units.

In a previous paper a statistical treatment of crystallinity was formulated for a random polydiene copolymer containing cis units as the minor component mixed with trans units.[3] The assumptions made in that treatment are (1) the cis units are randomly placed in the chain, (2) the cis units are completely rejected from the crystal core, (3) folding is by adjacent reentry, and (4) the fold length, B', is constant if the fold does not contain a cis unit rejected from the crystal core. The three types of folds considered possible are those containing trans units only, those containing an interior cis unit preceded and/or followed by trans units and having the same length as that containing trans units only and those containing one or more rejected cis units, rejected trans units, and the trans units associated with an all trans fold. In that work a segment was defined as a piece of the polymer chain between two successive noncrystallizable units, i.e. cis units and chain ends. The average number of monomer units appearing in crystal traverses per segment is calculated in terms of A, B', and an integer, n, running from 1 to a value dictated by the degree of polymerization for the chain. To obtain the crystalline fraction the average number of monomer units in a crystal traverse is divided by the average number of monomer units per segment.

For the lamellas of *trans*-1,4-polybutadiene containing 1% cis units the application of this treatment suggested that B' was 3 or 4 monomer units. For the lamellas from 89% *trans*-PBD, X_n = 3700. Since 95% of the total cis units and all of the 1,2 units are found at the lamellar surface, the equivalent q is 0.11. The results of the crystallinity calculation as a function of A and B' were obtained and are given in Figure 8. The fe value for 89% *trans*-PBD lamellas is 0.59, and A is 11 (Table III). Taking 1 − fe as the crystallinity, one experimental point is obtained, as given also in Figure 9. The best agreement with the theoretical curves is for B' of 3. This result for a relatively high cis/high molecular weight polybutadiene agrees well with those values for samples with a cis content and molecular weight about 10 times lower. It is of interest to apply this statistical treatment to the crystallization of other systems in which randomly placed chain units are

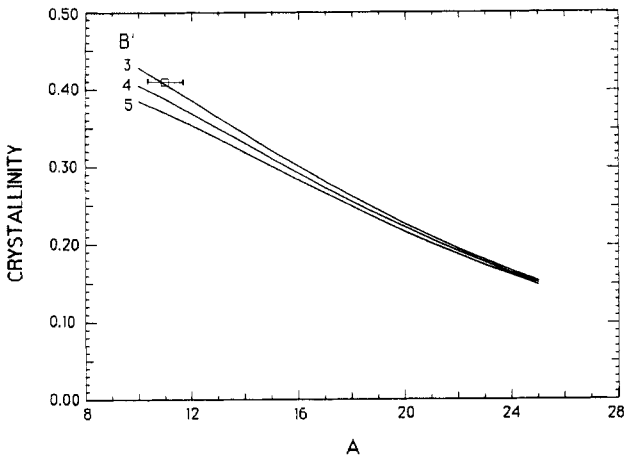


Figure 8. Calculated and experimental crystallinity for 89% *trans*-polybutadiene.

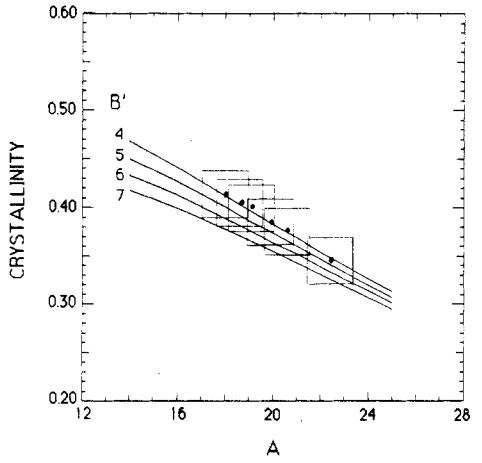


Figure 9. Calculated crystallinity for melt-crystallized polyethylene containing 7% short chair branches (●). Experimental results of Pakula (ref 6).

rejected from the crystal core, such as for polyethylene containing short-chain branches. The crystallinity as a function of crystalline stem length was experimentally determined by Pakula[6] for melt crystallized polyethylene containing 7% short-chain branches (35 CH_3 per 1000 carbon atoms). Comparison of crystallinity curves for B' of 4, 5, and 6 with the experimental values of q and X_n is given in Figure 9. Although the experimental uncertainty is large, assumption of adjacent reentry folding with $B' = 4$ fits the experimental results.

It was shown above that gelation takes place in 89% *trans*-PBD solution in amyl acetate at 10 °C when the concentration is greater than 0.7%. Transmission electron microscopy (Figure 3) shows that the gel is composed of connected multilayers. X-ray scattering, surface epoxidation, density, and DSC measurement results established that the gel has the same crystalline structure, the same crystalline stem length, and the same crystallinity as the single lamellar samples prepared at lower concentrations. The 99% *trans*-PBD does not form a gel structure on precipitation from amyl acetate solution at 10 °C up to a concentration of 5%. The difference in gelation behavior for these two polybutadienes cannot be explained in terms of their 10-fold difference of molecular weights. The dependence of the critical concentration on molecular weight is small.[7] At a concentration of 0.3%, only overgrown lamellas crystallized at 10 °C from amyl acetate for 89% *trans*-PBD; neither sheaf-like or spherulitic structures are observed, suggesting that few interlamellar linkages exist. However, the lamellas of this material have a fold

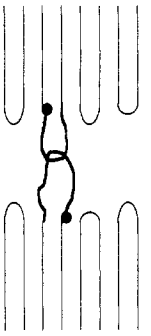


Figure 10. A schematic representation of fold entanglement.

length that is two or three times larger than that for 99% *trans*-PBD. This suggests that fold entanglement, as depicted in Figure 10, may be responsible for gelation in 89% *trans*-PBD.

Carbon-13 NMR results for 89% *trans*-PBD before and after epoxidation showed that about 1/20 of the cis units enter the crystalline core and the remainder are rejected. This is not in conflict with the earlier conclusion that all cis units are rejected from the crystalline core due to the limits of the detection. This small amount of cis units present in the crystalline part could have a significant effect on the thermal properties and act to lower T_{tr} and T_m, as observed (Table IV). The decrease in ΔH_{tr} is accounted for almost entirely by the change in crystallinity. The decrease in ΔH_m is apparently affected not only by the decrease in crystallinity but also by the change in the lamellar surface and/or the submerged cis units.

The effect on T_m of cis units entering the crystal core can be estimated from the equation given by Sanchez and Eby;[8] this equation is as follows:

$$1/T_m^0 - 1/T_m = -(R/\Delta H^0)\{\epsilon(X_c/RT_m) + (1 - X_c)\ln[(1 - X_c)/(1 - X)] + X_c \ln(X_c/X)\} \quad (5)$$

where T_m^0 is the melting point for the homopolymer crystal, T_m is the melting point for the copolymer crystal, ΔH^0 is the heat of fusion of the perfect crystal, ϵ is the mixture energy, X_c is the fraction of the second component in the crystalline part, X is the general fraction of the second component, and R is the gas constant. With $\epsilon = 0$, a cis content in the crystalline core X_c of 0.013, and $\Delta H^0 = 3.72$ kJ/mol,[9] this equation predicts a 20 °C decrease in the melting point. The observed decrease in T_m with an increase in cis content is considerably larger than that calculated. Part of this discrepancy could be caused by the approximate X_c value used and by setting ϵ equal to zero. T_m is also a function of crystal thickness. The observed twofold decrease in this parameter would also contribute to the decrease in T_m.

Conclusions

1. The technique of surface epoxidation followed by carbon-13 NMR analysis showed that the lamellas prepared by using a 10% cis-, 88.5% *trans*-, and 1.5% 1,2-polybutadiene and grown from solution under different crystalline conditions have the same crystalline stem length of 11 monomer units and the same crystallinity of 41%.

2. Calculation of the crystallinity using the statistical treatment proposed previously yields a value of three monomer units for the minimum fold length, B', in agreement with the values obtained for 1% *cis*-/99% *trans*-polybutadiene. This result strongly favors adjacent reentry folding.

3. Polybutadiene containing 10% cis, 88.5% trans, and 1.5% 1,2 units forms a gel structure in amyl acetate solution at 10 °C with the critical concentration of 0.7%

(w/v). X-ray scattering, density, DSC, and surface epoxidation show that the gel and single lamellas have the same crystalline structure, crystalline stem length, and crystallinity. Transmission electron microscopy established that the gel is a connected lamellar structure. On the basis of the average fold length of 16 monomer units for 89% *trans*-PBD, a "fold entanglement" mechanism of gelation is proposed.

4. About 5% of the cis units in the 10% cis-containing polybutadiene enter the crystalline core of the lamellas. This leads to a much lower transition temperature, melting point, and enthalpy of fusion than that measured for the 1:99 *cis*-/*trans*-polybutadiene.

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Registry No. Polybutadiene, 9003-17-2.

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Structural Change Accompanying Volume Change in Amorphous Polystyrene As Studied by Small and Intermediate Angle X-ray Scattering

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ABSTRACT: X-ray intensities scattered at small and intermediate angles from amorphous polystyrene were measured to study the change in the structure of the material as its volume was altered by five different methods. The volume changes were effected by (i) temperature change above T_g, (ii) temperature change below T_g, (iii) densification by application of pressure above T_g and subsequent release of the pressure at room temperature, (iv) spontaneous volume expansion of the pressure-densified material, and (v) spontaneous volume contraction on isothermal annealing below T_g (physical aging). The intensity data were examined either directly or after transformation into the density fluctuation function, the latter evaluated as a function of the size of the region of interest. The results show that the large scale density fluctuation correlates fairly well with the change of specific volume, irrespective of the different methods used to induce it. On the other hand, the small scale density fluctuation, indicating the degrees of local ordering, depends very sensitively on the method of volume change employed. In particular, (a) the volume contraction by temperature change above T_g and by physical aging gives rise to enhanced short-range ordering, (b) the volume contraction by temperature change below T_g and the spontaneous volume expansion of pressure-densified sample are accompanied with little change in local structural ordering, and (c) the pressure-densified samples, despite their much higher density, exhibit greatly reduced local ordering. The results suggest that the properties of glassy materials, such as the mechanical relaxation rate, are determined not only by the free volume content but also by the state of local packing of segments. The results also show that an approximate measure of the local structural order can be obtained in practice by measuring the height of the amorphous peak intensity.

I. Introduction

The concept of free volume has been one of the most widely utilized in interpreting phenomena associated with the glass transition and glassy state of polymers. The early work by Fox and Flory[1] and by Simha and Boyer[2] led to the suggestion that the glass transition point could be regarded as an iso-free volume state. The Doolittle equation,[3] giving the relationship between the viscosity and free volume of liquids, has provided a theoretical basis for the WLF equation. The physical aging of glassy polymers, which is manifested as slow increase[4] with time in mechanical moduli accompanied by slow contraction[5] of volume, can be rationalized in terms of the decreasing free volume leading to increased mechanical relaxation time.

The free volume is envisaged as the excess space, unoccupied by molecules, which is dynamically shared by the molecules in their thermal motion. It is usually defined as the difference between the total volume and the "occupied" or "core" volume of the molecules. The latter is often defined differently by different workers. The simplicity and plausibility of the concept underlie its wide acceptance for the interpretation of a variety of physical phenomena. The lack of a precise definition of the occupied volume, however, renders its *quantitative* application difficult. The incorporation of more explicit definition of free volume in recent theories[6,7] remedies this deficiency to some extent, without, however, clarifying its molecular meaning entirely.

Even on a qualitative level, inadequacy of the simple free volume concept has been noted over the years in many instances. For example, specimens of the same glassy polymer, brought to the state of the same density, may exhibit very different properties depending on their prior thermal histories. Such a "memory effect" was described by Kovacs[5] in the volume expansion and contraction following a two-step temperature jump. Similarly, the rate of expansion of volume of pressure-densified glasses after pressure release[8,9] depends on the pressure to which they

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