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Quantitative Investigation of the Amorphous and Crystalline Components in *trans*-1,4-Polybutadiene from Solution. 1. Effects of Crystallization Temperature and Concentration

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ABSTRACT: *trans*-1,4-Polybutadiene (TPBD) fractions (M_v = 7000–36 000) with a 1% cis content were crystallized from solution as a function of crystallization solvent, temperature, and concentration. The resulting structures were characterized quantitatively by using epoxidation in suspension followed by carbon-13 NMR measurement in solution, which yields the fraction reacted and the unreacted and reacted block lengths, *A* and *B*, respectively. Agreement between the fraction epoxidized and the noncrystalline fraction from density measurement was obtained. Evidence for the rejection of cis units from the *trans*-polybutadiene crystal core was found from the carbon-13 NMR studies. Although the amorphous (surface) fraction remains constant, *A*, equated to the number of monomer units per crystal traverse, and *B*, equated to the average number of monomer units per fold, increase with crystallization temperature. *A* and *B* remain constant with a change in morphology from single lamellar to multilamellar and with crystallization concentration from 0.05% to 5% w/v. The average number of TPBD units rejected from the crystal core when cis unit rejection occurs is estimated and the average length of a fold containing no cis unit is found to be 3–5 units.

Introduction

The crystallization of flexible-chain polymers from solution yields relatively thin lamellar structures with an appreciable amorphous component residing at the large faces.[1] In these lamellas the chain direction is nearly perpendicular to the large faces and the long-chain nature of linear polymers necessitates chain folding at these faces. Considerable physical and chemical evidence has been gathered to support the chain-folding concept, but a method for the direct determination of the fold size in single lamellas has only recently been forthcoming.[2,3] The direct determination has been carried out on two polydienes, *trans*-1,4-polybutadiene[2] and *trans*-1,4-polyisoprene.[3] The method used involves a chemical reaction, such as epoxidation,[2–5] hydrochlorination,[6] or bromination,[7,8] at low temperatures with the available double bonds at the lamellar surfaces of the sample suspended in a solution of the low molecular weight reactant. The polymeric reaction products are then analyzed in solution by using carbon-13 nuclear magnetic resonance.

For this method to give a correct fold length for single lamellas, as well as the correct crystalline stem length, reaction must occur with all of the double bonds in the folds, the molecular weight must be high or a correction made for noncrystallizing chain ends, and appreciable penetration of the crystal core must not occur. One method of monitoring the reaction is by comparison of the fraction reacted with the amorphous fraction obtained by using an appropriate physical method, such as density[2–6] or solid-state carbon-13 NMR.[9] For a number of the preparations reported to date, discrepancies in the fraction reacted and in the noncrystalline fraction have been reported;[2,6,9] also in some cases excessive damage to lamellas has been observed by electron microscopy.[5,8] Further study of reaction conditions, particularly with respect to the reaction medium and reactant concentration, was necessary in order to correct these problems.

It is of interest to investigate the effects of molecular weight, crystallization conditions and the morphology on the average number of monomer units per fold and crystal stem length since few data are available. To date only three TPBD preparations, studied by using the chemical reaction/carbon-13 NMR method, have been reported on and since only one of these gave agreement between the fraction reacted and the amorphous fraction from density measurements,[2] a more detailed investigation of this polymer was in order. A study was initiated of the structures obtained by solution crystallization of relatively low molecular weight fractions (M_v = 7000 to 3.6×10^4) of high trans content 1,4-polybutadiene obtained by $RdCl_3$-initiated emulsion polymerization.[10,11] Crystallization was carried out at various temperatures using two solvents of different polarities and as a function of concentration *in one of these solvents*. Morphology was studied by using transmission and scanning electron microscopy and the crystalline/amorphous content obtained by density measurement. An epoxidation reaction of the double bonds at the lamellar surfaces was carried out in suspension at 0 °C using *m*-chloroperbenzoic acid and the resulting products were analyzed by 50 MHz carbon-13

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Table I
***trans*-1,4-Polybutadiene Preparation Conditions**[a]

$[RdCl_3]/[1,3\text{-BD}]$	[DSS]/ [1,3-BD]	reactn temp, °C	reactn time, days
0.01	0.10	50	4
0.01	0.05	50	4
0.01	0.05	60	4
0.0025	0.05	22	21
0.0025	0.05	25	70
0.0050	0.05	50	4
0.0050	0.05	50	7
0.0020	0.05	50	20
0.0050	0.025	50	10
0.005	0.025	50	9
0.002	0.025	40	18
0.0025	0.05	50	20

[a] Polymerized in water emulsion with $RdCl_3$ as catalyst and dodecyl sodium sulfate, DDS, as emulsifying agent; $1,3\text{-BD}/H_2O$ = 50 g/100 g where 1,3-BD is 1,3-butadiene.

NMR to find the fraction reacted as well as the reacted and unreacted block lengths. In order to bring the reaction to completion the *m*-chloroperbenzoic acid/double bond ratios chosen were larger than those used previously; some preparations were epoxidized for various times and in liquid media that included amyl acetate, chloroform/ether, and toluene, in order to establish conditions for complete reaction. The results of this work and an accompanying study using a 10/90 *cis*/*trans*-polybutadiene, reported in a subsequent paper, show that the cis-1,4 units are excluded from the crystal core and any of them present, therefore, increase the average chain fold length and the noncrystalline fraction.

Experimental Section

Polymer Preparation. The TPBD samples were synthesized by emulsion polymerization of 1,3-butadiene in the presence of rhodium ions.[10,11] Various experimental conditions were used, as given in Table I; yields were about 60%. Intrinsic viscosities of 43–52 cm^3/g were obtained in toluene at 30 °C giving viscosity average molecular weights of $(1.6–2.0) \times 10^4$.[12]

Fractionation. Fractionation by successive solution[13,14] was used. A 2% (w/v) polymer solution was prepared in a 5/95 mixture by volume of toluene/heptane at 60–70 °C containing antioxidant, the solution cooled to room temperature, precipitation allowed to occur, and the mixture heated to 40 °C and kept at that temperature with stirring for 24 h. The precipitate was separated at 40 °C and the polymer remaining in solution recovered. A 10/90 mixture of toluene/heptane was then added to the precipitate separated at 40 °C and partial dissolution carried out a second time. This process was repeated with 15/85, 20/80, 25/75, 30/70, 35/65, and 40/60 toluene/heptane mixtures. Viscosity average molecular weights of all fractions were obtained and found to be from 2000 to 36 000. The fractions from one preparation were subjected to gel permeation chromatography using polystyrene standards and M_w/M_n was found to be 1.5–1.8.

Crystallization. Two crystallization procedures were employed, direct and precooled. In direct crystallization TPBD is dissolved at 80–90 °C in amyl acetate or at 60–70 °C in cyclohexane, held there for 20 min. and then placed in a bath held at the crystallization temperature, T_c. In the precooling procedure TPBD is dissolved, cooled to 0 °C and held there until precipitation occurs, and slowly heated to the temperature, T_r, at which redissolution occurs, and the solution placed in a constant temperature bath at T_c for 1 day. With amyl acetate T_r was 49–58 °C and with cyclohexane it was 24–34 °C. For both types of preparation the resulting precipitates are recovered and washed with fresh solvent at T_c, part of it is dried at T_c for density measurements, and the remainder is resuspended for epoxidation.

Epoxidation. The resuspension of the TPBD lamellar structures was carried out in a liquid containing *m*-chloroperbenzoic acid, MCPBA, at 0 °C and reaction allowed to occur for various periods of 2–31 days. The MCPBA/double-bond (DB) ratio was in the 0.8–1.9 range and the reaction liquids included amyl acetate, toluene, and chloroform/ether. The partially epoxidized TPBD structures were recovered and washed with fresh reaction liquid a number of times and then dried at 0 °C.

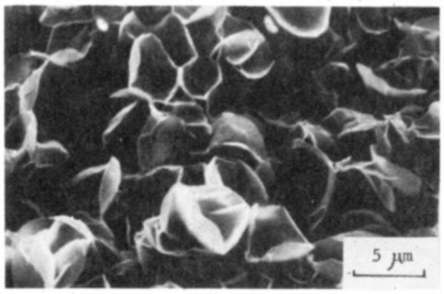


Figure 1. Scanning electron micrograph of TPBD structures crystallized from 0.05% amyl acetate solution at 30 °C (M_v = 1.2 × 10^4) and reacted with OsO_4 in suspension.

Carbon-13 NMR. Quantitative carbon-13 NMR spectra were obtained at 50.32 MHz using gated proton decoupling, a 90° pulse, an 8333-kHz spectral width, 32K memory, and a 10-s relaxation delay.[2] Me_4Si was used as internal reference. Intensities were measured by computer integration in all block copolymer analyses. For some of the TPBD fractions number-average molecular weights were approximated from the machine-derived intensity of a peak at 17.6 ppm relative to that for the CH_2 carbon resonance at 32.7 ppm.

Electron Microscopy. A Phillips EM300 transmission electron microscope was used to view precooled samples after gold/palladium (80/20) shadowing and a Cambridge Stereoscan S4 scanning electron microscope was used to investigate directly crystallized preparations following reaction with OsO_4 in suspension, deposition on aluminum, and coating with gold.

Density. Density was determined with a water/ethanol gradient column at 25 °C. All samples were pressed at 1.7×10^7 Pa to eliminate air. The weight fraction of the noncrystalline fraction was calculated by assuming a two-phase model using a crystalline density (ρ_c) of 1.03 g cm^{-3}[15] and an amorphous density (ρ_a) of 0.874 g cm^{-3}.[16]

Results

Carbon-13 NMR spectra, obtained on selected TPBD fractions used in this work, showed large resonances at 130.0 and 32.7 ppm (relative to Me_4Si) due to CH and CH_2 carbons in *trans*-1,4-polybutadiene units, smaller resonances at 129.4 and 27.4 ppm due to CH and CH_2 carbon atoms in *cis*-1,4-polybutadiene units, and in most, but not all, cases a very small resonance at 17.9 ppm, attributed to methyl groups, in agreement with results for low molecular weight compounds.[17] The number average degree of polymerizations obtained from the machine-calculated absorption intensities for the 17.9 and 32.7 ppm resonances were found to be in approximate agreement (±10% to ±20%) with viscosity-derived values divided by 1.5.

Crystallization from 0.05% amyl acetate or cyclohexane solution of TPBD fractions with M_v = 7000–(3.6 × 10^4) using the precooling (self-seeding) method yields mainly hexagonal single lamellas.[4] For lamellas grown from amyl acetate at 30 °C, shadow-casting measurements gave a lamellar thickness of 13 ± 2 nm (nine determinations). Direct crystallization (without self-seeding) of TPBD fractions from 0.5%, 1%, 2% and 5% (w/v) solution yields curved multilamellar sheaflike structures, some of which are roughly hexagonal in shape. Representative scanning electron micrographs for preparations obtained at concentrations of 0.05%, 1%, and 2% are shown in Figures 1–4. It is seen that the size, shape, and complexity of the multilamellar structures varies considerable for the same preparation.

Epoxidation of the various TPBD fractions in suspension leads to the disappearance of the 50-MHz carbon-13

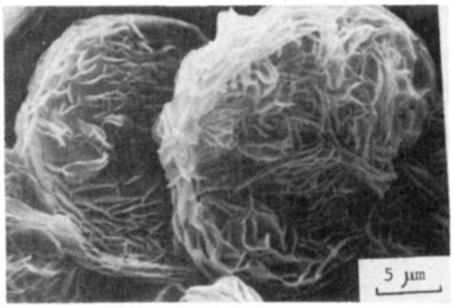


Figure 2. Scanning electron micrograph of TPBD structures crystallized from 1% amyl acetate solution at 30 °C ($M_v = 2.2 \times 10^4$) and reacted with OsO_4 in suspension.

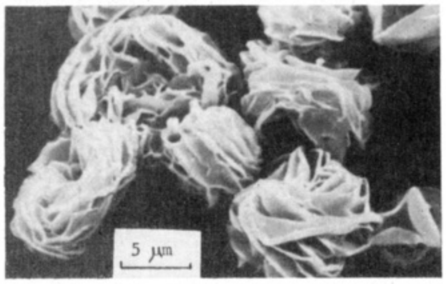


Figure 3. Scanning electron micrograph of TPBD structures crystallized from 2% amyl acetate solution at 30 °C ($M_v = 2 \times 10^4$) and reacted with OsO_4 in suspension.

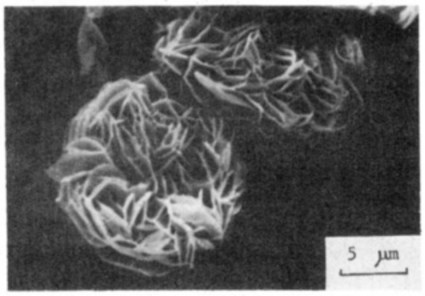
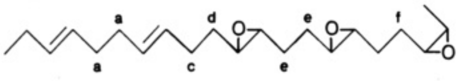


Figure 4. Same as Figure 3 but different field.

NMR resonances at 27.4 and 17.9 ppm, suggesting that all double bonds in *cis*-polybutadiene units and in units next to the chain end react. In addition, small resonances appear in the 56.4–56.9 ppm range and at 29.8 ppm, indicative of oxirane and methylene carbon atoms, respectively, in isolated epoxidized *cis*-polybutadiene units.[2] The remainder of the carbon-13 NMR spectrum for suspension epoxidized TPBD is similar to that reported earlier,[2] but with some partial splittings of DDDOO olefin resonances at 129.3 and 130.7 ppm, the OOO and DOO oxirane resonances at 57.9 and 58.2 ppm, and the DDOO methylene resonance at 32.2 ppm. The average number of monomer units in an unreacted sequence, A, was obtained from the intensities of the methylene resonances for carbon atoms a (32.7 ppm) and d (32.1, 32.2 ppm) by using[2]

$$A = ([a] + [d])/[d] \tag{1}$$

where a and d designate the carbon atoms, as shown, and



[] denotes the intensity. To obtain the average number of monomer units in a reacted sequence, B, the intensities for carbon atoms d, e (28.5, 28.8 ppm), and, for the epoxidized oxirane cis-polybutadiene resonances, f were used:

$$B = ([d] + [e] + [f])/[d] \tag{2}$$

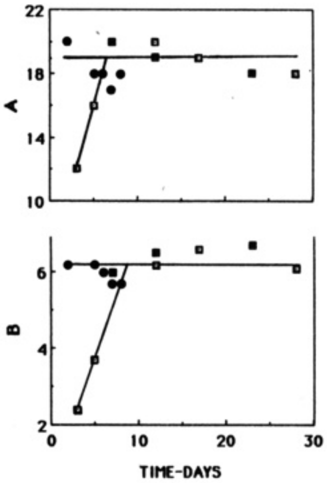


Figure 5. Average block lengths vs. time for TPBD lamellas crystallized from 0.05% cyclohexane solution at 20 °C and epoxidized in suspension at 0 °C with (□) [MCPBA]/[DB] = 1.2 in amyl acetate, (■) [MCPBA]/[DB] = 1.9 in amyl acetate, and (●) [MCPBA]/[DB] = 0.8 in toluene; X_n = 250–270.

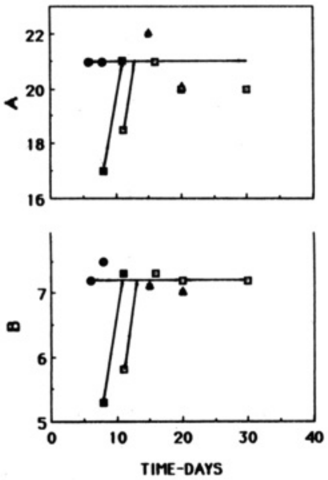


Figure 6. Average block lengths vs. time for TPBD lamellas crystallized from 0.05% and 1% amyl acetate solutions at 30 °C and epoxidized in suspension at 0 °C with (□) [MCPBA]/[DB] = 0.9 in amyl acetate, (■) [MCPBA]/[DB] = 1.2 in amyl acetate, (●) [MCPBA]/[DB] = 0.8 in toluene 1% solution crystallization, and (▲) [MCPBA]/[DB] = 1.3 in chloroform/ether; X_n = 250–300.

The correction in B for the epoxidized cis units was made by using the oxirane carbon atom resonances rather than those for the cis methylene carbon atoms due to the clearer resolution of the former. The fraction reacted, F_e, is obtained from

$$F_e = B/(A + B) \tag{3}$$

A and B can also be obtained from the olefin and oxirane resonances.[2] When this was done, close agreement was found with the values from eq 1 and 2. The fraction of *cis*-polybutadiene units (q) present in a preparation was obtained from the epoxidation results, as follows:

$$q = [f]F_e/([e] + [f]) \tag{4}$$

The dependence of A, B, and F_e on epoxidation time was investigated under various conditions which included different epoxidation media and/or different *m*-chloroperbenzoic acid/double-bond ratios for various TPBD preparations. The results obtained for crystallization in cyclohexane at 20 °C are given in Figure 5 and those for crystallization in amyl acetate at 30 °C in Figure 6. It is observed that, after a period of time depending on the

Table II
Crystalline/Amorphous Parameters for TPBD from Solution: Effect of Molecular Weight[a]

X_n	cryst solvent	cryst temp, °C	epox liq	M/D[b]	no.	A[c]	B[d]	F_e[e]	$1 - W_c$[f]
100	cyclohexane	10	AA	1.3	1	17	5.7	0.25	
120					1	17	5.6	0.25	
380					1	16	5.1	0.24	
440					1	15	4.9	0.25	
160	amyl acetate	30	Tol	0.45	1	20	7.0	0.26	
280			Tol	0.8	1	20	7.3	0.27	
300			AA	0.9	3	20	7.2	0.26	0.27
300			AA	1.2	1	20	7.7	0.27	
320			Tol	0.8	1	20	7.3	0.26	
440			AA	1.2	1	21	7.5	0.27	

[a] Fraction of *cis* units, 0.01; crystallization concentration, 0.05% (w/v); reaction time, 6–30 days. [b] [*m*-Chloroperbenzoic acid]/[double bonds]. [c] Average number of monomer units in an unreacted sequence in the original lamellas. [d] Average number of monomer units in a reacted sequence. [e] Fraction of double bonds reacted. [f] Amorphous content from density measurements.

Table III
Crystalline/Amorphous Parameters for TPBD from Solution: Effect of Crystallization Temperature[a]

cryst condns						
solvent	temp, °C	X_n	A	B	F_e	$1 - W_c$
cyclohexane	10	440	15	4.9	0.25	
	15	440	17	5.6	0.25	0.27
	20	440	18	6.0	0.25	0.27
	25	440	19	6.5	0.26	0.26
	27	440	21	6.9	0.25	0.27
amyl acetate	20	300	19	7.2	0.28	
	20	440	19	6.3	0.25	0.26
	30	300	20	7.3	0.26	
	30	440	21	7.5	0.27	
	40	300	22	8.2	0.27	
	45	300	24	9.2	0.28	

[a] Crystallized from 0.05% (w/v) solution; *cis* content 0.01; epoxidized in amyl acetate; [MCPBA]/[DB] = 1.2–1.9; reaction time 13–17 days.

reaction medium and the reactant concentration ratio, A and B level off. The F_e values obtained are in agreement with the amorphous fraction from density ($1 - W_c$), as shown below. In subsequent experiments reaction times and concentration ratios to give complete reaction were used.

The A, B, and F_e obtained using fractions with different molecular weights for cyclohexane (T_c = 10 °C) and amyl acetate grown (T_c = 30 °C) lamellas are given in Table II. It is observed that A remains constant within ±1 for a 4-fold change in molecular weight for preparations from a particular solvent and crystallization temperature, T_c, combination; B decreases with molecular weight for cyclohexane grown lamellas. For amyl acetate grown lamellas there is no consistent change in B with X_n. The large variation in the reactant concentration ratio ([MCPBA]/[DB]) may account for some of the changes observed.

The effect of crystallization temperature was studied for two samples with a number-average degree of polymerization of 300 and 440; the results are given in Table III, where it is observed that both A and B increase but F_e fluctuates with increasing T_c. It is also seen that the fraction reacted agrees with the amorphous content from density measurements ($1 - W_c$).

Table IV
Crystalline/Amorphous Parameters for TPBD from Solution: Effect of Crystallization Concentration[a]

X_n	C, %[c]	A	B	F_e	$1 - W_c$
320	0.05	20	7.3	0.27	0.27
280	1.0	20	7.3	0.27	0.27
320	1.0	21	7.1	0.25	0.25
280[b]	2.0	20 ± 1	7.5 ± 0.4	0.28	0.27
280	5.0	20	7.1	0.26	0.26

[a] Crystallized from amyl acetate at 30 °C; *cis* content 0.01; epoxidized in toluene; [MCPBA]/[DB] = 0.8 for 6–8 days. [b] Mean of two determinations. [c] Crystallization concentration.

The effect of polymer concentration in the 0.05–5% range was investigated for two polymers with M_n = 280 and 320. A, B, and $1 - W_c$ remain constant within the experimental uncertainty, as seen from Table IV.

Discussion

The attainment of constant unreacted, A, and reacted, B, block lengths when the surface epoxidation of TPBD is carried out as a function of time and the agreement of the fraction reacted, F_e, with the amorphous fraction from density, $1 - W_c$, suggest that reaction occurs with all of the double bonds in the fold surfaces without significant penetration of the crystal core. This allows the A values to be equated to the crystalline stem length in a lamella. The A values obtained in this study do not change with molecular weight (M_v) in the 8000–36000 range or with concentration in the 0.05–5% (w/v) range, but they do increase with temperature, as is expected from lamellar thickness studies.[18] Assuming that the thicknesses of the crystalline core and the amorphous surface regions are inversely proportional to the crystalline and amorphous densities and directly proportional to the fraction in each portion, the lamellar thickness, L, can be obtained from A by using[18]

$$L\ (\text{nm}) = 0.483A \cos 114°[1 + [F_e/(1 - F_e)](\rho_c/\rho_a)] \quad (5)$$

where 0.483 is the crystal repeat distance in nanometers.[15] The A values of 15–23 and the corresponding F_e values found in this study yield L values of 10–15 nm, placing these lamellas in regime 1, as defined by Finter and Wegner.[19] For the samples grown from 0.05% amyl acetate solution at 30 °C, a value of 13 nm is calculated, in agreement with L from electron microscopy (13 ± 2 nm). In an earlier study[2] of TPBD using epoxidation and carbon-13 NMR, three samples crystallized from heptane were investigated; the [MCPBA]/[DB] used was 0.4 and the reaction time 5 days. For one of these samples the fraction reacted was in agreement with the noncrystalline content from density[2] and from solid-state carbon-13 NMR;[9] a B value of 5.6 was found for this sample. For the other two samples F_e was significantly lower than $1 - W_c$ and B was 3.0 and 5.0. It is concluded from the present study that under the conditions used previously the reaction may not have been carried to completion in every case, resulting in errors in F_e and B.

Changes in B with molecular weight are observed in this work but they appear to be dependent on the crystallization conditions with either no change or an increase of one unit in B, with a 4-fold decrease in molecular weight being observed. The amorphous regions at the crystal surfaces are expected to contain both chain folds and noncrystallizing chain ends. The disappearance of the methyl resonance at 17.9 ppm upon surface epoxidation suggests that all the chain ends (cilia) are rejected from the crystal core. If the average chain end length exceeds half of the fold length, an increase in reacted block size, B, with decreasing molecular weights at low values of the latter should occur; if half of the average fold length exceeds the average chain end length, B is expected to decrease with decreasing molecular weight.[20] It is possible to calculate a fold length and a chain end length from the molecular weight dependence of B; when this is done, an average chain end length about half the average fold length is obtained for the amyl acetate grown lamellas, while for cyclohexane grown lamellas the average chain end length exceeds half the average fold length. It, therefore, appears reasonable to assume that the average chain end length is approximately equal to $B/2$ and the average fold length is approximately equal to B.

Increases in B with temperature are observed with values ranging from 5 to 9. In a study to be reported on separately, the crystallization of a 10% *cis*-90% *trans*-butadiene copolymer leads to still larger values of B (20–22 with A of 11–13). The carbon-13 NMR results show that all or most of the cis units in the polybutadiene samples used are to be found in the epoxidized part of the block copolymer; therefore during the crystallization process the cis units are rejected from the crystalline core. During crystallization at constant temperature, the crystalline stem length will show only small variations and therefore the rejection of each cis unit at low cis contents should lead to the exclusion of from 0 to A trans units, preceding each cis unit in this chain, from the crystalline core. This will cause the average number of monomer units per fold to increase with the cis content. In order to estimate the average value for a fold not containing a cis unit, it is assumed that the cis units are randomly placed and each cis unit causes the rejection of $A/2$ trans units which leads to $qX_nA/2$ trans units rejected per chain. The number of these excess trans units per each of the $X_n/(A + B)$ folds per chain present will be $qA(A + B)/2$. Therefore, the fold containing no cis units will have $B - qA(A + B)/2$ trans units.

For the samples investigated in this work with a cis content of 1% this correction yields values of 3–5 monomer units per an all-trans fold, assuming, as discussed above, that no chain end correction is needed. This corrected B value increases with an increasing crystallization temperature of 25 deg by about 0.5 of a monomer unit for a particular crystallization solvent, whereas the change in the uncorrected B value with temperature is 2–3 units. Therefore a large amount of the increase in B with temperature is probably due to the presence of cis units. The tightest all-trans fold found in this work is for the cyclohexane grown lamellas at 10 °C with an average number of monomer units of 3.

No change in fold size occurs in the concentration range used for crystallization in this study. Therefore, either there are few single chains common to more than one lamella in the multilamellar structures found at 1–5% w/v concentrations or the interlamellar traverse length has an average value equal to that for a chain fold. Calculations of the mole percentage of tie chain entries in a fold surface have been made by using parameters for melt crystallized polyethylene;[21] at crystallinities of 75% or less the mole percentage of tie chain entries was calculated to be 2% or less depending on the lamellar thickness and the molecular weight. Interlamellar traverses of that number would not be detected by the methods used in the present study.

Conclusions

Epoxidation in suspension accompanied by carbon-13 NMR can be used to investigate quantitatively the fold surfaces of solution-crystallized *trans*-1,4-polybutadiene with the proper choice of reaction conditions.

Evidence was found by using carbon-13 NMR for rejection of cis-polybutadiene units and chain ends from the *trans*-polybutadiene crystal core during the crystallization process.

The number of monomer units per fold in *trans*-1,4-polybutadiene increases with crystallization temperature with values of 5–9 being found in this study; this parameter remains constant when the morphology is changed from single lamellas to multilamellar structures.

The number of monomer units per crystal traverse increases with temperature and was found to be 15–24 in this investigation; the increases in this parameter and in the number of monomer units per fold with temperature cause the fraction reacted and the density-derived crystallinity to remain constant.

Acknowledgment. This work was supported by a PSC/CUNY faculty research award.

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

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