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Molecular Weight Dependence of the Noncrystalline Component in Dilute-Solution-Grown *trans*-1,4-Polybutadiene Crystals

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ABSTRACT: Eight *trans*-1,4-polybutadiene preparations were obtained by crystallization from dilute heptane and, in one case, toluene solutions. The crystal preparations, as characterized by gel permeation chromatography, had $\bar{M}_n$ values of 4700 to 1.2×10^5 and $\bar{M}_w/\bar{M}_n$ values of 1.3 to 2.7. Mats of these crystals were investigated by differential scanning calorimetry, density measurements in a gradient column, low-angle X-ray diffraction and/or electron microscopy, and reaction at the crystal surfaces with *m*-chloroperbenzoic acid in toluene. The heat of transition from DSC was found to be proportional to the specific volume. The number of monomer units per fold, U, and the number per chain end, $C/2$, were obtained from an equation that relates these two parameters to the crystal thickness, L_c, the fraction of double bonds at the crystal surfaces, the repeat distance along the polymer chain, and $\bar{M}_n$. Assuming U to be constant and C to be a function of the lamellar thickness, L, values of 3.8 monomer units per fold and $0.79L/2R$ units per chain end were obtained. Assuming C to remain at $0.79L/R$ and allowing U to vary yield values that show a decrease occurring with decreasing crystallization temperature.

Introduction

In earlier reports[1-4] investigations of the noncrystalline component at the surfaces of solution-grown *trans*-1,4-polybutadiene, TPBD, lamellas using epoxidation, bromination, and broad-line NMR in the presence of a nonprotonated liquid were described. Some evidence was given to suggest that the surface component is composed of two parts, one due to the chain folds and the other to the chain ends or cilia, the latter component becoming of greater importance at lower molecular weights. Calculation of the average number of monomer units per fold from the values for the surface component and the lamellar thickness yielded values of 2.5–5.5 for the three preparations studied.[4,5] In this earlier work infrared spectroscopy[2] and differential scanning calorimetry[6] were used to estimate the total noncrystalline content in order to determine the presence of any material within the crystals that was not available to determination by surface techniques.

Table I
Characteristics of TPBD Samples

sample	polymer prep conditions	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
W	urea canal complex	7.9	3.5
V		2.2	2.5
U	$RhCl_3$-sodium alkylbenzenesulfonate	0.70	3.0

The purpose of the current study was to investigate the noncrystalline component in TPBD lamellas over a wider molecular weight range (4700 to 1.2×10^5) than that previously covered, using the epoxidation method to evaluate the surface fraction and density measurements to evaluate the total noncrystalline content. In this investigation molecular weight fractions with $\bar{M}_w/\bar{M}_n \approx$ 1.3–2.7 are used. Differential scanning calorimetry measurements in the regions of the crystal–crystal transition and the melting transition were also made for each sample to determine the usefulness of ΔH_{Tr} and/or ΔH_m in assessing the total noncrystalline fraction. A method of analysis of the epoxidation results was developed to enable determination of the number of monomer units per fold

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and a parameter related to the number of monomer units per chain end.

Experimental Section

Samples. Three *trans*-1,4-polybutadiene preparations were used in this study: TPBD-U, supplied by Uniroyal Inc., TPBD-V, supplied by Polysar Ltd., and TPBD-W, obtained from Dr. C. E. Wilkes of BFGoodrich. Some preparative characteristics and the number-average molecular weight, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$, both from GPC for purified material, are given in Table I. Four samples (designated F1, F2, F3, and UH45) were obtained from the TPBD-U polymer, and one sample each was obtained from the TPBD-V and TPBD-W polymers by fractional crystallization. The following procedure was used to obtain F1, F2, and F3. The U polymer was first precipitated from 1% heptane solution at room temperature and then fractionally crystallized at 56 °C, 50 °C, 48 °C, 45 °C, 38 °C, and room temperature, starting with a 0.1% heptane solution. The 56 °C, 45 °C, and room-temperature fractions were recrystallized at the same temperatures from 0.05% heptane solution, yielding F1, F2, and F3, respectively. The sample designated UH45 was prepared directly from the purified U polymer by precipitation from 0.01% heptane solution at 45 °C. For both TPBD-V and -W a sizeable gel portion was separated following dissolution in toluene; the soluble part was recovered by precipitation in methanol at room temperature.

Sample Characterization. The molecular weight distribution for each sample was obtained with a Waters-200 analytical GPC with toluene at 85 °C as the solvent; calibration was carried out with five polyisoprene standards in the 1.0×10^4 to 8.0×10^4 range, two polybutadiene standards with weight-average molecular weights of 1.0×10^3 and 2.7×10^3, and squalene (molecular weight 411). For molecular weights above 8.0×10^4 an extrapolation of the results for the polybutadiene and polyisoprene standards was made, paralleling a curve obtained from a series of polystyrene standards. The GPC scan for squalene yielded $\bar{M}_w/\bar{M}_n = 1.06$; therefore 0.06 was subtracted from the $\bar{M}_w/\bar{M}_n$ values obtained from the GPC for each of the TPBD preparations as a boundary-spreading correction.

Trans-1,4 contents of 99.5% for UH45 and >99.7% for VH53 were found with ^{13}C NMR by F. A. Bovey and F. C. Schilling at Bell Laboratories using a Varian XL-200 instrument. Due to the method of polymer synthesis the trans-1,4 content of TPBD-W is expected to be 100%.

Crystal Preparation. Crystals were prepared from 0.01% (w/v) heptane (H) or 0.02% toluene (T) solution by the following procedure: dissolution, precipitation at room temperature, redissolution at the minimum temperature, and isothermal crystallization. In all but two cases, the difference between the final crystallization temperature, T_c, and the redissolution temperature, T_r, was kept constant.

Density Measurement. Determination of the density for all but one sample was carried out on a water–ethanol density gradient column at 25 °C. For sample F1H55 the flotation method using ethylene glycol and water was employed. All samples were pressed at 3.4×10^7 Pa to eliminate air. Samples pressed at 1.7×10^7 to 7.5×10^7 Pa were found to agree in density value within 0.003 g cm^{-3}. The weight fraction of the noncrystalline component, $1 - W_c$, was calculated assuming a two-phase system using an amorphous density,[7] ρ_a, of 0.874 g cm^{-3} and a crystalline density,[8] ρ_c, of 1.03 g cm^{-3}.

Differential Scanning Calorimetry. Measurements were made with a DuPont 990 thermal analyzer with sample weights of 2 mg or less; most of the runs were made at a heating rate of 20 °C/min. Rates as low as 1 °C/min did not cause any appreciable change in any of the four parameters measured—the apparent transition temperature, T_{Tr}, the apparent melting temperature, T_m, the enthalpy of transition, ΔH_{Tr}, and the enthalpy of melting, ΔH_m. The T_{Tr} and T_m values were taken as the point of intersection of the linear extrapolation of the base line and the low-temperature portion of the endotherm in question.

Lamellar Thickness. Lamellar thickness was determined either by low-angle X-ray scattering with a Rigaku-Denki small-angle goniometer or by electron microscopy on Pt–Pd-shadowed samples, using the LAXS results to calibrate.

Epoxidations. Reaction of the double bonds at the crystal surfaces using dried mats of TPBD was carried out in toluene at 6 °C with an excess amount of *m*-chloroperbenzoic acid present.[1,4] After 5–10 days, the crystals were recovered, washed and freeze-dried, dissolved in deuterated chloroform, and subjected to ^1H NMR using a JEOL JNM MH100. The fraction of double bonds epoxidized was determined from both the CH and CH_2 proton resonances. The CH and CH_2 resonances are found at 5.3 and 2.0 ppm in TPBD and at 2.65 and 1.57 ppm in epoxidized units.

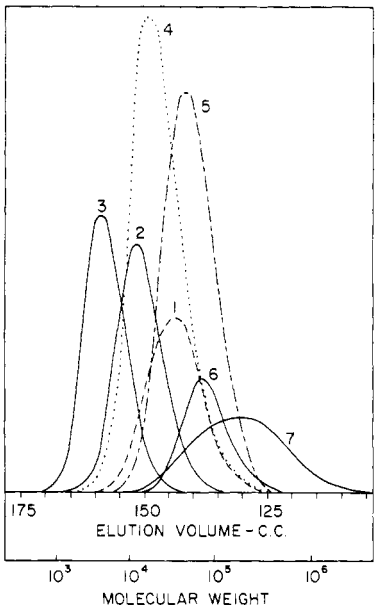

Figure 1. Gel permeation chromatograms for TPBD fractions: (1) F1; (2) F2; (3) F3; (4) UH45; (5) F1H55; (6) VH53; (7) WH62.

Results

Eight dilute-solution-grown TPBD crystal preparations with number-average molecular weights ranging from 4700 to 1.2×10^5 were studied. Molecular weight distribution curves from GPC are given in Figure 1 for four of these crystal samples and for the precursors of the other four. F1 is the precursor for two crystal preparations, F1H29 and F1T15, F2 for F2H36, and F3 for F3H29. The sample designation indicates the parent polymer or fraction (W, V, U, F1, F2, and F3), the solvent (H = heptane and T = toluene), and the crystallization temperature, T_c. Except for UH45 and F1H29, T_c was 12 °C below the redissolution temperature, T_r; for F1H29, $T_r - T_c$ was 38 °C and for UH45 it was 10 °C. Holding $T_r - T_c$ constant generally necessitates the use of T_c's which decrease with decreasing $\bar{M}_n$; the one exception involves VH53 with $\bar{M}_n$ of 6.9×10^4 and F1H55 with $\bar{M}_n$ of 4.4×10^4. It can be seen in Figure 1 that the sample with the highest molecular weight, WH62, has the broadest distribution, covering 2 decades. It is also observed that crystallization of F1 from dilute heptane solution at 55 °C brings about further fractionation.

Differential scanning calorimetry results for three of the eight TPBD crystal samples prepared are given in Figure 2. All eight samples showed only one endotherm in the crystal–crystal transition region (54–74 °C). However, the presence of small amounts of water in the DSC pan along with TPBD did cause the appearance of a second smaller endotherm on the low-temperature side. A smaller endotherm was reported earlier and was attributed to the polymer.[9] The melting endotherm, as can be seen in Figure 2, broadens and displays more than one component as the molecular weight is decreased. The results of the calorimetric measurements are given in Table II in terms of the apparent transition temperature, T_{Tr}, the enthalpy of

Table II
Calorimetric, Density, Epoxidation, and Lamellar Thickness Results for Solution-Grown TPBD Crystals

sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_{Tr}, °C	ΔH_{Tr}, kJ mol^{-1}	T_m, °C	ΔH_m, kJ mol^{-1}	ρ, g cm^{-3}	$1 - W_c$[a]	F_s[b]	L,[c] nm	L_c,[d] nm	U[e]
WH62	12	2.7	74	6.8	142	4.5	0.998	0.20	0.14	27	23	6.5
VH53	6.9	1.4	72	5.4	129	3.2	0.996	0.21	0.19	11.8	9.2	4
F1H55	4.4	1.5	72	5.9	133	3.4	1.005	0.16	0.15	24	19.5	5
F1H29	2.7	1.6	54	4.2	136	3.6	0.986	0.27	0.24	8.3	6.0	3.5
F1T15	2.7	1.6	54	4.3	135	3.6	0.988	0.26	0.22	9.0	6.8	3.5
UH45	1.7	1.7	60	4.4	132	3.3	0.987	0.26	0.23	11.0	8.0	4
F2H36	1.2	1.4	56	4.2		3.1	0.984	0.28	0.26	10.3 (25.8)	7.3	4
F3H29	0.47	1.3	54	4.0		2.5	0.984	0.28	0.27	9.1	6.3	2.5

[a] Total noncrystalline fraction, determined by density. [b] Surface fraction, determined by epoxidation. [c] Lamellar thickness. [d] Crystal thickness. [e] Fold length, expressed as butadiene units.

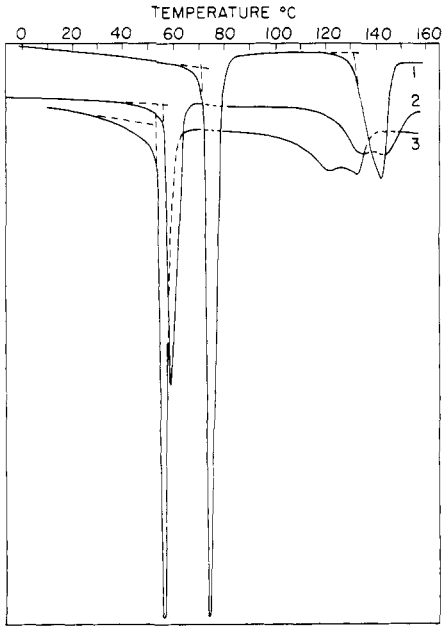

Figure 2. Differential scanning calorimetry scans for dilute solution (0.01%) crystals from three TPBD fractions: (1) F1H55; (2) F2H36; (3) F3H29.

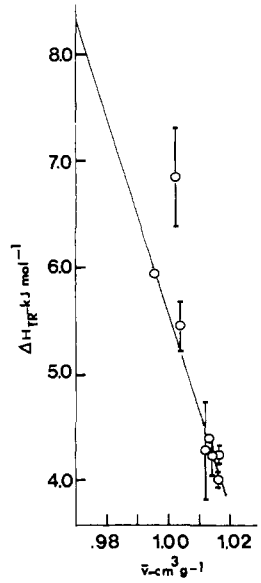

Figure 3. Enthalpy of crystal–crystal transition vs. specific volume for dilute-solution-grown TPBD crystals.

transition, ΔH_{Tr}, the apparent melting temperature, T_m, and the enthalpy of melting, ΔH_m. Melting temperatures are not listed for F2H36 and F3H29 due to the presence of broadened multiple endotherms. The number of duplicate determinations of enthalpy varied from three to six. The T_{Tr} and ΔH_{Tr} values bear a more regular relationship to T_c than to molecular weight, showing first a decrease and then leveling off with decreasing T_c. The enthalpy of transition, ΔH_{Tr}, is found to be proportional to the specific volume, as shown in Figure 3, with only one sample having a substantial deviation (WH62). The error bars in Figure 3 give the average deviation for the multiple measurements made. Extrapolation of the straight line in Figure 3 to a $\bar{v}$ value corresponding to 100% crystallinity yields a ΔH_{Tr} of 8.2 kJ mol^{-1}; a literature value[10] for this quantity is 7.8 kJ mol^{-1}.

The values of the density, ρ, and the total noncrystalline fraction, $1 - W_c$, of each sample derived therefrom are also given in Table II. The precision of the $1 - W_c$ values is ±0.01.

In the next column of Table II, F_s, the fraction of monomer units at the crystal surfaces, as determined by epoxidation of crystal mats in toluene suspension at 6 °C is given. Use of a higher epoxidation temperature, 12 °C, for sample WH62 led to no significant change in the double bonds epoxidized. The fraction of double bonds reacted, as assessed from the CH and CH_2 ^1H NMR shifts, agreed to within ±0.03; the majority of determinations made were within ±0.01, while duplicate determinations using either the CH or CH_2 ^1H NMR bands agreed within ±0.02. The number of determinations for a particular preparation varied from one to five. The effect of using dried mats instead of suspended crystals[1,4] was studied by making multiple determinations on both types of samples employing the UH45 preparation. Mean values of 0.23 ± 0.02 (five determinations) and 0.25 ± 0.02 (six determinations) were found for the fraction of double bonds epoxidized, respectively. These results can be compared with those gathered earlier[4] on similarly prepared and epoxidized crystals for which 0.27 ± 0.02 was obtained from two runs. The earlier value is larger but this could be due to the different detection methods used or to the smaller lamellar thickness (8.2 nm) measured. Previously, the amount of unreacted epoxidizing agent was monitored by infrared spectroscopy whereas in the present work the polymer is analyzed; the method currently in use is more direct and presumably more accurate.

Following the completion of the work described above, a sample of epoxidized UH45 crystals was analyzed by both ^1H NMR and ^{13}C NMR in deuteriochloroform solution using a Varian XL-200 instrument; in this work, carried out by F. A. Bovey and F. C. Schilling at Bell Laboratories, values of 0.19 and 0.16 were obtained for the fraction epoxidized from the ^1H and ^{13}C NMR results, respectively. These are to be compared with F_s values of 0.22 obtained in these laboratories on the same UH45 preparation and

of 0.25 ± 0.02 from six separate preparations using the JEOL 100-MHz instrument. There is some discrepancy between the values obtained at 200 and 100 MHz by ^{1}H NMR. Due to the better resolution achieved at 200 MHz this value is considered to be more accurate than that obtained at 100 MHz. Thus the values given for F_s in Table II may be somewhat high, although the general trends are believed to be correct.

Comparison of each F_s value with the corresponding value of $1 - W_c$ from density shows the latter to be consistently larger. For UH45, using the 200-MHz value, an increase of 40% occurs.

Experimental values for the lamellar thickness, L, are also included in Table II. Two L values are listed for F2H36, the larger one having a much lower X-ray intensity. This sample showed two orders of reflection for the more prominent line. The LAXS patterns for UH45, VH53, F1H55, and WH62 exhibited one, one, two, and four orders of reflection, respectively. The L values for F1H29, F3H29, and F1T15 were obtained by electron microscopy using the LAXS spacing for F2H36 to correct for shrinkage effects or inaccuracies in the shadowing procedure. As shown below, in order to calculate a value of the average number of monomer units per fold, it is necessary to know L_c, the crystal thickness along the chain direction. This was obtained from L by assuming that the crystalline part with thickness L_c is sandwiched between two noncrystalline portions with total thickness $L - L_c$. It is further assumed that L_c was directly proportional to the fraction of crystalline material present ($F_c = 1 - F_s$) and inversely proportional to ρ_c and $L - L_c$ is directly proportional to F_s and inversely proportional to ρ_a. The equation derived is

$$L_c = \frac{\rho_a(1 - F_s)L}{\rho_a(1 - F_s) + \rho_c F_s}$$

The values of L_c, given in the first column of Table II, were calculated from L and F_s with this equation.

Discussion

It was found in this investigation that fractional crystallization from heptane of TPBD in the 5×10^3 to 10^5 molecular weight range leads to considerable narrowing of the molecular weight distribution, depending on the degree of undercooling used. In fact, fractionation was found to occur in dilute solution for a sample with $\bar{M}_w/\bar{M}_n = 1.6$. Therefore, unless the degree of undercooling and molecular weight are large in the preparation of dilute-solution-grown crystals of TPBD, a considerable fraction of the lower molecular weight components remains in the soluble portion.

It was also found in this work that the total noncrystalline fraction, as calculated from density measurements, for TPBD crystals grown from dilute heptane or toluene solution is larger than the fraction available for epoxidation at the crystal surfaces. Similar results were obtained recently[11] for *trans*-1,4-polyisoprene crystals. One possible explanation is that the actual density at the crystal surfaces is not the same as that extrapolated from values for the melt. In order to give smaller values for $1 - W_c$ (larger values for W_c), ρ_a would have to be smaller than that used. This is in agreement with experimental results[12] and calculations[13] for polyethylene, the latter using space-filling models and assuming a tight fold. If the crystallinity, W_c, is given by $1 - F_s$, values as low as 0.81 g cm^{-3} (UH45, $F_s = 0.16$) can be obtained for ρ_a in TPBD crystals. If, on the other hand, the density of the surface fraction is that gotten by extrapolation from the melt, then the larger values for $1 - W_c$ as compared with F_s show that a noncrystalline component in addition to that available for reaction must exist. This additional component could possibly be due to one or more of the following: entirely or partially hidden folds,[14] other crystal defects,[15] or polymer molecules absorbed at the surfaces.[16]

The one sample (WH62) that shows a significant positive deviation from the straight-line plot of the enthalpy of transition vs. specific volume is that with the highest molecular weight, broadest molecular weight distribution, and highest transition temperature. These crystals also had the largest lateral dimensions and thickness and showed few screw dislocation growths. It is expected that crystal perfection would lead to a high value for the enthalpy of transition, and, apparently, for this preparation this is the dominating factor.

For a dilute-solution-grown crystal the surface fraction, F_s, will consist of three components, one due to the folds, another due to noncrystallizing chain ends, and the third due to the lateral crystal surfaces. For the crystals investigated the lateral surface area did not exceed 4% of the total surface area and therefore only the first two components are considered. Each chain of degree of polymerization N will have F_sN chain units at the two surfaces, and this can be written in terms of the number of monomer units per fold, U, the number of folds per chain, F, and the number of monomer units in the two noncrystallizing chain ends, C. For a polydisperse system it can be shown that the number-average DP, $\bar{N}_n$, should be used, giving the following equation:

$$\bar{N}_n F_s = \bar{M}_n F_s / M_0 = UF + C \qquad (1)$$

where $\bar{M}_n$ is the number-average molecular weight of the polymer and M_0 is the molecular weight of a monomer unit. If it is assumed that the remaining monomer units in the chain, $\bar{N}_n(1 - F_s)$, are in a crystalline core, the following equation is obtained:

$$\bar{N}_n(1 - F_s) = L_c(F + 1)/R \qquad (2)$$

where L_c is the crystal thickness along the chain direction, R is the repeat distance in the chain direction, and $F + 1$ is the number of chain traverses. Combination of eq 1 and 2 with elimination of F yields

$$U = \frac{L_c}{R}\left\{\frac{F_s\bar{M}_n}{M_0} - C\right\} \Big/ \left\{\frac{\bar{M}_n(1 - F_s)}{M_0} - \frac{L_c}{R}\right\} \qquad (3)$$

which for large $\bar{M}_n$ gives

$$U \approx \frac{L_c F_s}{R(1 - F_s)} \qquad (4)$$

Equation 3 is more exact than the equation given earlier[4] but leads to similar results. It was assumed in previous work on TPBD that the average length of a chain end is half the lamellar thickness, L, and therefore C is given by L/R. It is reasonable to assume that C is a function of L/R without specifying the proportionality constant and therefore C can be given by $a(L/R)$. Substitution of this in eq 3 and rearranging yield

$$\frac{F_s\bar{M}_n R}{LM_0} = \frac{UR}{L}\left\{\frac{R\bar{M}_n(1 - F_s)}{L_c M_0} - 1\right\} + a \qquad (5)$$

Therefore a plot of $F_s\bar{M}_n R/LM_0$ vs. $(R/L)\{R\bar{M}_n(1 - F_s)/L_cM_0 - 1\}$ should yield a straight line with a slope equal to U and an intercept equal to a, if U and a are independent of molecular weight and other parameters such as the crystallization temperature, T_c, the undercooling, $T_r - T_c$, and the crystallization solvent. A plot of the results using F_s and L_c values given in Table II and an R value[8] of 0.483 nm is given in Figure 4. With the exception

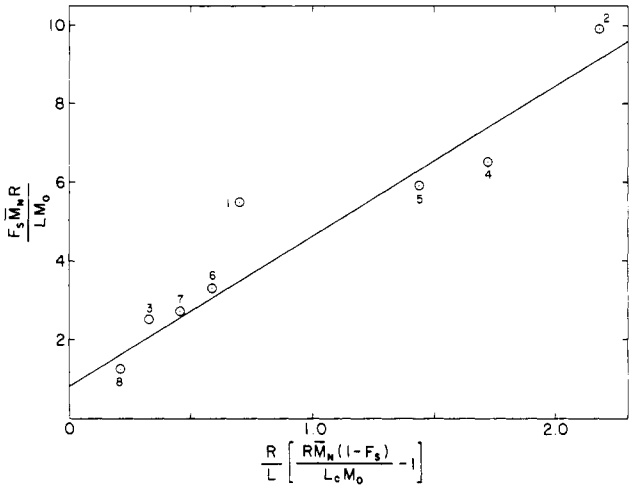

Figure 4. Determination of the average number of monomer units per fold and the average number of monomer units per chain end for dilute-solution-grown TPBD crystals: (1) WH62; (2) VH53; (3) F1H55; (4) F1H29; (5) F1T15; (6) UH45; (7) F2H36; (8) F3H29.

of WH62 the points define a straight line within ±10% error limits with an intercept of 0.79 and a slope of 3.8. However, taking C equal to $0.79L/R$ and calculating individual values of U using eq 3 yield the values given in the last column of Table II. In the above calculations the L_c values used were not corrected for chain tilt in the crystal. For TPBD this would lead to about a 10% increase in U, since the β angle is given[8] as 114°. Use of $1 - W_c$ in place of F_s in the above analysis yields approximately the same results with the exception of WH62. Using the ^{1}H NMR results at 200 MHz and the ^{13}C NMR results for UH45 gives U values of 3 and 2.5, respectively.

In analyzing the changes taking place in U for the series of samples F1, F2, and F3, one needs to consider two effects: that caused by changing molecular weight and that caused by changing crystallization temperature. Comparison of the results for F1H29 and F3H29 shows a decrease in U with decreasing molecular weight at the same T_c. However, the amount of this change is small when compared to that for the preparations F1H55, F2H36, and both F1H29 and F3H29, for which both molecular weight and T_c are decreasing. Most of the decrease in U for this series is apparently due to decreasing T_c, a result in agreement with an earlier study by Marchetti and Martuscelli.[17] The number of monomer units in a tight reentrant fold has been given as 3 for TPBD;[7] the lowest value found in this and previous work[1,4,5] is 2.5. The value of 6.5 for a sample with $\bar{M}_n = 1.2 \times 10^5$ is the largest found by the epoxidation method to date.

The values of U and C from this study depend upon the determination of a number of parameters: F_s, $\bar{M}_n$, L, ρ_a, the amorphous density, and ρ_c, the crystalline density. A more direct method of obtaining U and C is to carry out an evaluation by ^{13}C NMR of the amounts of the various sequences of epoxidized and nonepoxidized units in chemically reacted polydiene crystals. Such investigations are currently under way on TPBD and *trans*-1,4-polyisoprene crystals; the results will be reported on in subsequent publications.

Conclusions

For TPBD crystals grown from dilute heptane solution the noncrystalline fraction, as obtained from density measurements, is found to be larger than the fraction at the crystal surfaces available for a chemical reaction.

Assuming that the average number of monomer units per fold, U, and the average number of monomer units in the two chain ends, C, are not functions of molecular weight in the range 4700 to 6.6×10^4 gives a U of 3.8 and C of $0.79L/R$, where L is the lamellar thickness and R is the crystal repeat distance. Holding C constant at $0.79L/R$ and allowing U to vary lead to U values of 2.5–6.5 monomer units per fold in the $\bar{M}_n$ range 4700 to 1.2×10^5. The U value decreases with crystallization temperature and to a lesser extent with molecular weight.

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