Crystallization of *trans*-1,4-Polybutadiene from Concentrated Solution

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ABSTRACT: Differential scanning calorimetry (DSC) measurements of the crystal–crystal transition endotherms, density determinations, and surface epoxidation have been carried out for *trans*-1,4-polybutadiene crystals prepared at weight fractions of 0.014–0.128 for samples having number-average molecular weights ($\bar{M}_n$) of 5900, 1.7×10^4, and 2.8×10^4 and polydispersities ($\bar{M}_w/\bar{M}_n$) between 1.6 and 1.9. For crystals prepared from one fraction ($\bar{M}_n = 2.8 \times 10^4$) secondary DSC endotherms in the crystal–crystal transition region are observed and these are attributed to nonisothermal crystallization in one case and to crystallization of an absorbed polymer layer in another. The effect of polymer concentration during crystallization on the average number of monomer units per fold is discussed.

Introduction

In a recent report[1] an investigation of the noncrystalline component as a function of molecular weight in dilute solution grown crystals of *trans*-1,4-polybutadiene (TPBD), using density, differential scanning calorimetry, and a chemical reaction at the crystal surfaces, was described. An analysis of the results obtained showed that the number of monomer units per chain fold varies, this value increasing with an increase in crystallization temperature. The morphology of polymer samples crystallized from concentrated solution is usually found to be of a complexity between that of crystals grown from dilute solution and those grown from the melt.[2,3] With the exception of the morphological investigations most studies on solution-grown polymer crystals to date have been confined to those prepared from relatively low concentrations (weight fraction of 0.001 or less).[2,3] However, in a recent report[4] the final degree of crystallinity of polyethylene was found to be dependent on both concentration and molecular weight, with a decrease and then an increase occurring in the crystallinity with increasing polymer weight fraction at relatively low molecular weights (2×10^4 to 2×10^5). It is, therefore, of interest to study the effect of polymer concentration on the amount and location of the noncrystalline component(s) and on the chain fold length in *trans*-1,4-polybutadiene crystals using the density, differential scanning calorimetry, and surface epoxidation techniques as employed earlier[1] for the investigation of dilute solution grown crystals. In this work the transition to be studied by DSC is one that involves a change from the monoclinic crystal structure[5] stable at room temperature to a high-temperature form;[6] the enthalpy and (apparent) transition temperature for this change have been investigated by various workers.[1,6–13] For solution-grown crystals the temperature location for this transition (50–78 °C) is lamellar thickness dependent; irreversible changes in thickness and therefore in the apparent transition temperature can occur when TPBD lamellas are first heated to 70–80 °C.[8] In the present study three fractions of TPBD with $\bar{M}_n$ = 5900 to 2.8×10^4 and $\bar{M}_w/\bar{M}_n$ = 1.6–1.9 at weight fractions of 0.014–0.128 in heptane were used. The results of this investigation are presented and discussed below.

Experimental Section

Samples. The three *trans*-1,4-polybutadiene (TPBD) fractions used in this work were prepared by fractional crystallization from a sample obtained from Uniroyal Inc. and are designated TPB-D-U. The fractionation procedure involved precipitation from 1% heptane solution at room temperature, redissolution, and sequential crystallization from 0.1% solution into five fractions at 56, 48, 45, 40, and 25 °C; the first, third, and fifth fractions were employed. The trans-1,4 content of one purified TPBD-U sample was shown by ^{13}C NMR to be 99.5%; that sample was similar to the highest fraction studied in this work but had a distribution broadened toward the low molecular weight end. All fractions employed in this study were shown by ^{1}H NMR to be free of 1,2 units.

Crystal Preparation. Crystals were prepared by precipitation from heptane solution at concentrations in the range 0.014–0.128 weight fraction using the following procedure: dissolution, precipitation at room temperature, redissolution at the minimum temperature (T_r), and crystallization in a constant temperature bath (T_c). The crystallization temperatures used included those employed previously at a weight fraction of 1.5×10^{-4}, i.e., 55 and 29 °C for F1, 36 °C for F2, and 29 °C for F3. In addition, crystallization temperatures chosen to keep $T_r - T_c$ = 12 °C, as done earlier,[1] were also used. For crystals formed from the highest molecular weight fraction at elevated temperatures (55, 60 °C), repeated washing with fresh heptane heated to the crystallization temperature was carried out until the filtrate, cooled to room temperature, showed no further precipitate. After washing with fresh heptane, a part of each crystal preparation was dried at room temperature prior to density and differential scanning calorimetry measurements.

Morphology. Morphological studies were carried out with a Zeiss photomicroscope with interference contrast optics and a Philips 300 electron microscope employing Pt–Pd-shadowed specimens.

Density Measurement. Determination of the density was carried out with a water–ethanol density gradient column at 25 °C. The weight fractions of the crystalline and the noncrystalline components, W_c and $1 - W_c$, were calculated assuming a two-phase system and an amorphous density,[14] ρ_a, of 0.874 g cm^{-3} and a crystalline density,[5] ρ_c, of 1.03 g cm^{-3}.

Differential Scanning Calorimetry. Measurements were made with a DuPont 990 thermal analyzer at a heating rate of 20 °C/min with sample weights of 2 mg or less.

Epoxidations. Reaction of the double bonds at the crystal surfaces was carried out in toluene at 6 °C with an excess amount of *m*-chloroperbenzoic acid present[15] using resuspended crystals; after 5–10 days the crystals were recovered, washed and freeze-dried, dissolved in deuterated chloroform, and subjected to ^{1}H NMR analysis using a JEOL JNM MH100 spectrometer. The percent epoxidation was determined from both the CH and CH_2 resonances, found, respectively, at 5.3 and 2.0 ppm in TPBD and 2.65 and 1.57 ppm in epoxidized units.

Results

The crystal preparation conditions, which include the weight fraction of polymer (w_2), the redissolution temperature (T_r), the crystallization temperature (T_c), and the amount of the original material recovered after the crystallization step on a percentage basis (% recovd), along with molecular weight information are given in Table I for TPBD samples F1b, F2b, and F3b. The number-average molecular weights ($\bar{M}_n$) for F1b, F2b, and F3b are higher and the molecular weight ratios $\bar{M}_w/\bar{M}_n$ are larger than for those found for the fractions F1, F2, and F3 used earlier[1]

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Table I
Preparation of TPBD Crystals

polymer desig	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	w_2	T_r, °C	T_c, °C	% recovd
F1b	2.8×10^4	1.9	0.014	70	55	61
			0.068	72	60	70 ± 10
			0.068	72	55	88
			0.068	72	29	(100)
F2b	1.7×10^4	1.8	0.068	54	42	(100)
			0.068	54	36	(100)
F3b	5900	1.6	0.068	52	40	(100)
			0.068	52	29	(100)
			0.128	54	42	(100)
			0.128	54	29	(100)

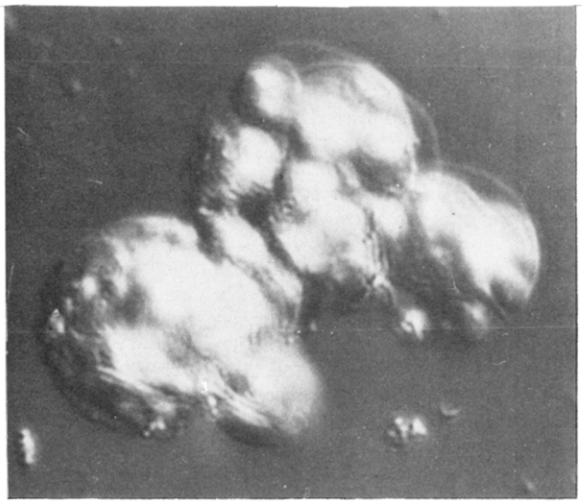

Figure 1. Optical micrograph of TPBD crystals grown from concentrated ($w_2 = 0.068$) heptane solution at 60 °C. Magnification 1120×.

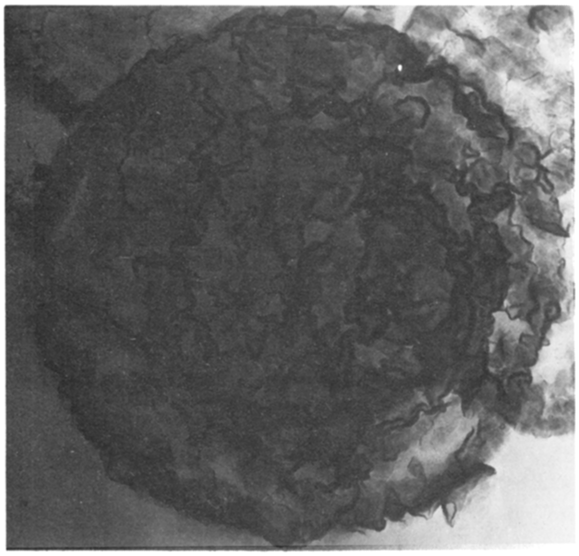

Figure 2. Electron micrograph of TPBD crystal grown from concentrated heptane solution ($w_2 = 0.068$) at 60 °C. Magnification 4080×.

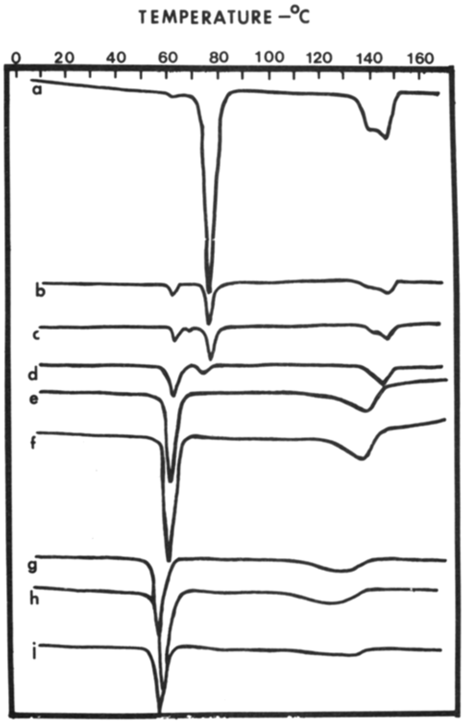

Figure 3. DSC scans for TPBD crystals grown from concentrated solution: (a) F1bH60, $w_2 = 0.068$; (b) F1bH55, $w_2 = 0.068$; (c) F1bH55, $w_2 = 0.014$; (d) F1bH29, $w_2 = 0.068$; (e) F2bH36, $w_2 = 0.068$; (f) F2bH42, $w_2 = 0.068$; (g) F3bH29, $w_2 = 0.068$; (h) F3bH40, $w_2 = 0.068$; (i) F3bH29, $w_2 = 0.128$.

($\bar{M}_n$ was 2.7×10^4, 1.2×10^4, and 4700 and $\bar{M}_w/\bar{M}_n$ was 1.5, 1.4, and 1.3, respectively, for F1, F2, and F3). It is to be noted that when F1b is crystallized at 55 and 60 °C at w_2 values of 0.014 and 0.068 a significant portion is not recovered, as determined by weighing; however, this is accompanied by little if any change in $\bar{M}_n$. A fractionation effect was found earlier[1] for crystallization of F1 at a w_2 of 1.5×10^{-4} and a T_c of 55 °C; a similar effect was observed for F1b at this w_2 in the current study. Since no polymer was recovered from the filtrates during washing of the crystals (and cooling of the filtrates to room temperature) for F1b crystallized at 29 °C and for F2b and F3b, the amount recovered is taken as 100%. Except for F1b crystallized at a w_2 of 0.014 and a T_c of 55 °C, all preparations were carried out in duplicate and DSC, density, and epoxidation studies were made on each of these.

From optical microscope investigation the F1b at 55 °C and F1b at 60 °C preparations were found to contain single lamellas with and without screw dislocation overgrowths, as well as multilamellar objects. A photomicrograph showing a group of lamellas (F1b at 60 °C) is given in Figure 1. Since the multilamellar objects for this preparation varied considerably in thickness, it was possible to obtain electron micrographs of some of the thinner ones, as shown in Figure 2. For the other preparations (F2b and F3b) the dimensions are too small to allow observation with an optical microscope. Under the electron microscope thick (multilamellar) objects were observed in these preparations.

DSC scans for all but one preparation (F3b at 42 °C) are given in Figure 3. In the crystal–crystal transition region (50–75 °C) the preparations from F2b and F3b show one endotherm at a temperature position similar to that for preparations at $w_2 = 1.5 \times 10^{-4}$ as given in ref 1. For F1b, on the other hand, an additional one or two endotherms are apparent. For F1b crystallized at 60 °C, F1bH60, the small low-temperature endotherm is only about 2% of the total. For F1b crystallized at 55 °C, F1bH55, with $w_2 = 0.068$, the additional endotherms vary in size relative to the principal one, the endotherm peak height ratio being 1:2.4 for one preparation and 1:6.4 for the other. In the case of F1b crystallized at 29 °C, F1bH29, the secondary endotherm is at a higher temperature than the primary one, and again this additional endotherm varied in relative size for the two preparations, i.e., 1:4.7

Table II
Heat of Transition and the Noncrystalline Fraction for TPBD Grown from Solution at Various Concentrations[a]

sample	$\overline{M}_n \times 10^{-4}$	w_2	ΔH_{Tr}, kJ mol^{-1}	ρ, g cm^{-3}	$1 - W_c$	F_s
F1H55	4.4	1.5×10^{-4}	5.9	1.005	0.16	0.15 0.12[b]
F1bH55	2.8	0.014	5.2	0.995	0.22	0.21
		0.068	5.4	0.994	0.22	0.19
F1bH60	2.8	0.068	5.8	0.995	0.22	0.19
F1H29	2.7	1.5×10^{-4}	4.2	0.986	0.27	0.24
F1bH29	2.8	0.068	3.8	0.989	0.25	0.25
F2H36	1.2	1.5×10^{-4}	4.2	0.984	0.28	0.26
F2bH36	1.7	0.068	3.6	0.985	0.27	0.29
F2bH42	1.7	0.068	3.6	0.986	0.27	0.29
F3H29	0.47	1.5×10^{-4}	4.0	0.984	0.28	0.27
F3bH29	0.59	0.068	3.7	0.980	0.30	0.29
F3bH40	0.59	0.068	3.5	0.982	0.29	0.30
F3bH29	0.59	0.128	3.6	0.983	0.29	0.29
F3bH42	0.59	0.128	3.7	0.984	0.28	0.26

[a] The data for $w_2 = 1.5 \times 10^{-4}$ were taken from ref 1, with one exception as noted. [b] From ^{13}C NMR.[16]

and 1:2.3. From DSC time base scans the enthalpy of the crystal–crystal transition, ΔH_{Tr}, taking all the pertinent endotherms into account, was obtained as given in Table II. For duplicate preparations ΔH_{Tr} showed a maximum average deviation of ±0.3. Comparison of the current data with that obtained earlier at $w_2 = 1.5 \times 10^{-4}$ (see Table II) shows a decrease in ΔH_{Tr} with an increase in the concentration to a w_2 of 0.068.

In the next two columns of Table II the density, ρ, and the noncrystalline fraction, $1 - W_c$, calculated from the density are given. For duplicate preparations the maximum average deviations were ±0.004 and ±0.02 for ρ and W_c, respectively; the average of the deviations observed for W_c was ±0.01. The total noncrystalline content, $1 - W_c$, shows a significant change with concentration only for F1 (and F1b) crystallized at 55 °C, for which an increase in this quantity occurs with increasing concentration.

In the last column of Table II the surface fraction, F_s, determined by epoxidation with *m*-chloroperbenzoic acid of the double bonds present, is given. These values are averages of areas under CH and CH_2 ^{1}H NMR resonances. It was found in this study that the values obtained from the CH resonance yielded larger values than those from the CH_2 resonance with one exception. For duplicate preparations the maximum average deviation was ±0.03. The average value for the deviation observed for F_s was ±0.02. It was pointed out earlier that the epoxidation values given in ref 1 for dilute solution grown TPBD crystals might be somewhat high; as is seen in Table II F_s from ^{13}C NMR for one preparation of F1H55 is smaller than the mean value found by ^{1}H NMR.[16] Irregardless of this the general trends in the results are believed correct. From Table II it can be seen that F_s increases with concentration for all preparations.

Discussion

DSC endotherms indicative of the crystal–crystal transition were obtained earlier[1] for dilute solution grown TPBD lamellas, using fractions (F1, F2, and F3) similar to those employed in this work; for all the dilute solution preparations single endotherms were observed, the temperature position of which shifted to lower temperature with decreasing crystallization temperature, T_c. For crystals grown from concentrated solution using fractions with $\overline{M}_n$'s of 1.7×10^4 and 5900, one transition endotherm is observed in about the same position as for dilute solution grown crystals. However, when a fraction with an $\overline{M}_n$ of 2.8×10^4 is used for crystallization at high concentrations, two or more transition endotherms are observed, the major ones being in the same temperature region as found for lamellas grown from dilute solution at similar temperatures. Therefore, the crystal–crystal endotherm behavior for TPBD crystallized from solution is dependent on molecular weight and polymer concentration as well as on T_c. The presence of significant secondary endotherms in this transition region shows that the final dried product contains crystalline components with more than one lamellar thickness. Either all of these components appear during the crystallization process or some appear then and the remainder crystallize during recovery of the principal crystal component. In the case of sample F1b crystallized at 29 °C it is reasonable to attribute the secondary endotherm to the occurrence of some nonisothermal crystallization at a temperature or temperatures higher than T_c, due to the high concentration and the relatively low T_c, in agreement with the recent assignment by Finter and Wegner.[13] When crystallization is carried out at relatively small degrees of supercooling one DSC endotherm at a higher temperature, due to the large lamellar thickness (20–30 nm), is expected.[1,13] The secondary endotherm at about 65 °C found for F1b crystallized at 55 °C cannot be due to the presence of material crystallized at that temperature or above but corresponds to lamellas crystallizing at a lower temperature with a thickness of about 8–10 nm. As noted in the preceding section, this preparation had a considerable fraction of soluble material remaining in solution after crystallization at 55 and 60 °C, respectively, was complete. Therefore, a possible explanation for the presence of the secondary endotherm for F1bH55 is that part of this noncrystallizing material is adsorbed on the crystal surfaces[17] and is not entirely desorbed upon washing; however, upon cooling from T_c to room temperature this adsorbed layer crystallizes to form lamellas with a lower transition temperature. The almost negligible secondary component in F1bH60 would then be explained by more rapid desorption at the higher temperature during the washing process.

The surface fraction (F_s) and the total noncrystalline content from density measurement ($1 - W_c$) for each particular concentrated solution grown TPBD sample are found to be the same within experimental error with the possible exception of F1b55 and F1b60 at a w_2 of 0.068 (see Table II), which suggests that the two-phase model assumed in the calculation of $1 - W_c$ is approximately correct. However, for some dilute solution grown TPBD crystal preparations, F_s was found to be 30% lower than $1 - W_c$.[1,16] Possible reasons for this discrepancy include the use of a ρ_a value for the fold surface region which is too large and/or the presence of a noncrystalline component not available for epoxidation.

A considerable portion, if not all, of the noncrystalline material in TPBD lamellas is believed to be at the surfaces.[1] In structures crystallized from dilute solution the surface component is made up principally of two parts, chain folds and noncrystallizing chain ends. Multilamellar structures crystallized from concentrated solution would be expected to contain an interzonal component linking the lamellas, in addition to chain folds and chain ends.[3] An equation was given previously[1] for the number of monomer units per fold, U, in terms of $\overline{M}_n$, the surface fraction, F_s, the crystal thickness, L_c, the monomer repeat distance in the crystal, R, the molecular weight of a monomer repeat distance in the crystal, R, the molecular

Table III
Calculation of Number of Monomer Units per Fold for TPBD

sample	w_2	L,[a] nm	C	L_c, nm	U
F1H55	1.5×10^{-4}	24	39	20	5
F1bH60	0.068	26	43	20	6
F2H36	1.5×10^{-4}	10	17	7.3	4
F2bH36	0.068	10	17	7.0	5
F2bH42	0.068	11	18	7.3	5.5
F3H29	1.5×10^{-4}	9.1	15	6.3	2.5
F3bH29	0.068	9.1	15	6.1	3.5
F3bH40	0.068	11	18	7.0	3.5
F3bH29	0.128	9.1	15	6.1	3.5
F3bH42	0.128	11	18	7.6	2.5

[a] From data given in ref 1.

weight of a monomer unit, M_0, and the number of monomer units in the two chain ends per chain, C, as follows:

$$U = (L_c/R)\{(\bar{M}_n/M_0)F_s - C\}/\{(\bar{M}_n/M_0)(1 - F_s) - L_c/R\} \tag{1}$$

This equation can be used to calculate an average of the various fold lengths if only a small number of traverses from one lamella to others are present. With this assumption, application of this equation in the present work has been made for the preparations which show one lamellar component. In these calculations C was taken[1] as $0.79L/R$ and L_c was obtained from the equation

$$L_c = \frac{\rho_a(1 - F_s)L}{\rho_a(1 - F_s) + \rho_c(F_s)} \tag{2}$$

L, the lamellar thickness, is assumed to be the same as that found for dilute solution grown crystals of F1, F2, and F3 if T_c is the same. In the cases where T_c is different from those used previously, i.e., 40, 42, and 60 °C, interpolated dilute solution values were employed. The L, C, and L_c values used in these calculations and the U values found are given in Table III. An increase in U with a change in concentration from w_2 of 1.5×10^{-4} to w_2 of 0.068 is seen; however, this effect is not a large one, being about one monomer unit per fold. The increase in U with an increase in T_c and $\bar{M}_n$ as reported[1] for dilute solution grown crystals also occurs for crystals from concentrated solution. Although F_s and $1 - W_c$ first increase and then apparently level off as $\bar{M}_n$ and T_c decrease, U shows a decrease since the lamellar thickness, L, and therefore the crystal thickness, L_c, is also changing.

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