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Noncrystalline Component in Dilute-Solution-Grown Crystals of *trans*-1,4-Polyisoprene

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ABSTRACT: Crystals of *trans*-1,4-polyisoprene usually in the α form were prepared from dilute amyl acetate solution at crystallization temperatures, T_c, of 10–36 °C using fractions of balata and gutta-percha with number-average molecular weights from 2×10^4 to 4×10^5. The total noncrystalline fraction, $1 - W_c$, was determined by density measurement and the surface fraction, F_s, for selected preparations by an epoxidation reaction. The number of monomer units per fold, calculated from the epoxidation results, was smallest for $\bar{M}_n = 2.4 \times 10^4$ and showed an increase with increasing crystallization temperature at constant $\bar{M}_n$.

Introduction

The amount and nature of the noncrystalline component at the surfaces of dilute-solution-grown crystals have been investigated for a number of polymers. However, many of the physical methods used measure the total noncrystalline content and therefore give little, if any, direct information concerning the location of this component. Chemically reactive polymers are of particular interest since the fraction of monomer units at the crystal surface, F_s, can be assessed if a quantitative reaction can be found. Determinations of F_s for dilute-solution-grown crystals of *trans*-1,4-polybutadiene (TPBD) have been carried out by epoxidation[1-4] and bromination reactions,[3-5] with the effects of molecular weight,[4] crystallization temperature,[4,5] concentration,[6] and solvent[1-4] being investigated. The surface fraction is a function of crystal thickness along the chain direction, L_c, the number of monomer units per fold, U, the average number of monomer units per chain end, $C/2$, and the number-average molecular weight, $\bar{M}_n$. The following equation relating these quantities was given earlier:[4]

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

where M_0 is the molecular weight of the repeat unit in the polymer and R is the repeat distance per monomer unit along the chain direction in the crystal. For TPBD crystals grown from samples with $\bar{M}_n$ ranging from 4700 to 1.2×10^5, U values of 2.5–6.5 were obtained, with C given by $0.79L/R$, where L is the lamellar thickness.

The purpose of the current study is to initiate investigation of the noncrystalline component in dilute-solution-grown crystals of *trans*-1,4-polyisoprene (TPI). Fractions of naturally occurring TPI (balata and gutta-percha) with $\bar{M}_n$ values of 2×10^4 to 4×10^5 and $\bar{M}_w/\bar{M}_n$ values of 1.2–1.5 were investigated. Crystallization conditions were mainly chosen[7] in order to yield material in the α form.[8] The total noncrystalline fraction was obtained for all samples using density measurements. The surface fraction was monitored for selected preparations by epoxidation at 0 °C and the number of monomer units per fold calculated. The results are presented and discussed below.

Experimental Section

Samples. A balata sample, obtained from Dunlop Sports Co., was purified by repeated precipitation from toluene solution into methanol. The trans-1,4 content of the purified balata crystallized from amyl acetate solution (0.05 g of polymer/100 cm^3 of solvent) was found to be 100% from ^{13}C NMR measurements, as carried out by F. A. Bovey and F. C. Schilling of Bell Laboratories using a Varian XL 200 instrument.

Fractions of balata TPI were prepared by fractional precipitation from toluene solution with methanol. A Waters GPC 200 instrument was employed to measure molecular weights[4,7] which were as follows: $\bar{M}_n = 3.8 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.5$), $\bar{M}_n = 2.9 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.4$), $\bar{M}_n = 2.8 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.4$), $\bar{M}_n = 2.3 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.3$), and $\bar{M}_n = 1.1 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.4$).

A gutta-percha sample obtained from Gabundan Produsen Karet Indonesia was fractionated on a diatomaceous earth column,[9] with amyl acetate as the solvent and 2-ethoxyethanol as the nonsolvent at 64 °C in the presence of 2,2′-methylenebis[4-methyl-6-*tert*-butyl] as antioxidant. The molecular weights of the gutta-percha fractions as found by GPC were as follows: $\bar{M}_n = 0.26 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.2$), $\bar{M}_n = 0.69 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.2$), and $\bar{M}_n = 2.1 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 1.3$).

Crystallization. Crystallization was carried out from amyl acetate solution at temperatures T_c in the range 10–36 °C, at 0.05% (0.05 g of polymer/100 cm^3 of solvent) concentration. The technique used involves dissolution (T_d), precipitation at 0 °C, heating to a temperature T_r that caused disappearance of the precipitate for high molecular weight polymer, and crystallization at T_c. The crystal suspensions were filtered and washed with amyl acetate at T_c. The mats were then either dried for density measurements or resuspended for epoxidation.

Crystal Morphology. Crystal morphology and lamellar thickness were determined by electron microscopy on Pt–Pd-shadowed samples at an angle of tan $-1 = {}^1/_3$ using a Phillips EM 300 instrument.

Density Measurement. Densities were determined with a water–ethanol density gradient column at 25 °C. All samples were pressed at 3.4×10^7 Pa to eliminate air. The weight fraction of the noncrystalline component, $1 - W_c$, was calculated under the assumption of a two-phase system using an amorphous density,[10] ρ_a, of 0.905 g cm^{-3} and a crystalline density,[8] ρ_c, of 1.05 g cm^{-3}.

Electron and X-ray Diffraction. Electron diffraction was done on unshadowed specimens using the Phillips EM 300 instrument. X-ray diagrams were obtained with a cylindrical film camera.

Epoxidations. Reaction of the double bonds at the crystal surfaces was carried out in amyl acetate suspension at 0 °C, with enough *m*-chloroperbenzoic acid (MCPBA) being added to the liquid phase to react with about 80% of the double bonds present in the polymer samples. Two procedures for adding the MCPBA were used: either all was added at the beginning of the reaction or half was added then and half after 7 days. For most of the epoxidations [MCPBA]$_0$ was 0.2 g/100 cm^3 of solvent, although concentrations as low as 0.1 and as high as 1.0 g/100 cm^3 were used. The progress of the reaction was followed with time. After recovery of the epoxidized crystals, they were dried, dissolved in deuterated chloroform, and subjected to ^{1}H NMR using a JEOL JNM MH100. The CH, CH$_2$, and CH$_3$ resonances for TPI are found[11] at 5.1, 2.0, and 1.6 ppm and for epoxidized units they are at 2.7, 1.6, and 1.3 ppm. The fraction epoxidized was generally determined by using the areas under both the CH resonance peaks

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Table I[a]
Density (g cm^{-3}) of TPI Crystals Grown from Dilute Amyl Acetate Solution

	$\bar{M}_n \times 10^{-5}$								
T_c, °C	3.8	2.9	2.8	2.3	2.1	1.1	0.69	0.26	av
10	0.970	0.970 (2)	0.968 (2)			0.963			0.969
20	0.974 (5)	0.975 (5)	0.970 (2)	0.972 (2)	0.973	0.974	0.973	0.978 (2)	0.974
25	0.975	0.976 (3)	0.975						0.976
30	0.982	0.978 (4)	0.972 (2)		0.970		0.976	0.981	0.977
32	0.980	0.978 (4)	0.973 (2)						0.977
34		0.980 (2)							0.980
36			0.978						0.978

[a] The number of separate samples studied is indicated in parentheses if more than one was used.

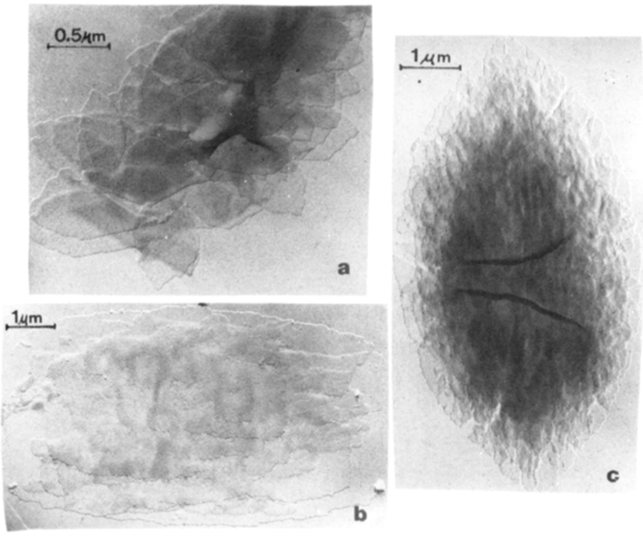

Figure 1. *trans*-1,4-Polyisoprene crystals ($\bar{M}_n = 2.9 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.4$) grown from amyl acetate: (a) T_r = 40 °C, T_c = 30 °C; (b) T_r = 50 °C, T_c = 20 °C; (c) T_r = 40 °C, T_c = 20 °C.

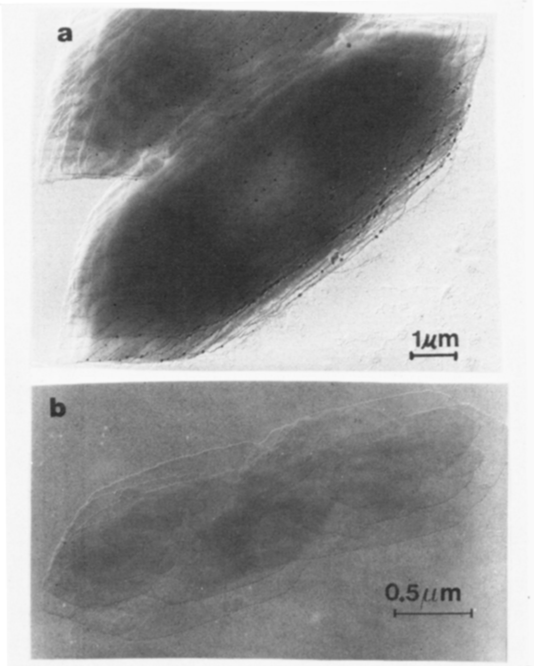

Figure 2. *trans*-1,4-Polyisoprene crystals ($\bar{M}_n = 2.6 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.2$) grown from amyl acetate: (a) T_r = 40 °C, T_c = 30 °C; (b) T_r = 40 °C, T_c = 20 °C.

and the CH_3 resonance peaks, although in a few cases only the first was used. For the latter calculation the following equation was employed:

$$F_s = 3A_5/(3A_4 - A_5) \tag{2}$$

where A_5 is the area under the resonance at 1.3 ppm and A_4 the area under the resonance at 1.6 ppm.

Results

Crystals of balata with $\bar{M}_n = 10^5$–4×10^5 were prepared from 0.05% amyl acetate solution at T_c's of 10, 20, 25, 30, 32, 34, and 36 °C with a T_r of 40 °C; crystals were also prepared at a T_c of 20 °C with a T_r of 50 °C, which is well above the minimum temperature necessary to bring about redissolution. Some changes in crystal morphology were observed, as can be seen in Figure 1. Crystallization at 25–36 °C from a T_r of 40 °C gave small elongated hexagonal-shaped crystals, a representative sample of this being given in Figure 1a. Crystallization at 20 °C as well as at 10 °C with cooling from 40 °C gave overgrown ellipsoidal-shaped crystals (Figure 1c) while crystallization at 20 °C with cooling from 50 °C led to rectangular-shaped lamellas (see Figure 1b). When selected-area electron diffraction was carried out on individual crystals from the 50/20 °C preparation, the β-TPI patern was the only one observed. However, filtering and then drying at room temperature for 2 days yielded a dry mat showing principally the α-crystalline form. Crystals with a T_r = 40 °C and grown at T_c = 20 °C had the α pattern from both electron and X-ray diffraction. Crystals with T_r = 50 °C and T_c = 0 °C showed the β pattern in X-ray diffraction.

When a low molecular weight fraction of gutta-percha ($\bar{M}_n = 2.6 \times 10^4$) was crystallized at 20 and at 30 °C (T_r = 40 °C), overgrown hexagonal-shaped crystals were formed, as shown in Figure 2.

The densities obtained for mats of TPI crystals grown at various crystallization temperatures, T_c, from 0.05% amyl acetate solution are given in Table I as a function of the number-average molecular weight ($\bar{M}_n$). The number of separate samples studied is indicated in parentheses if more than one was used; these numbers include samples prepared by cooling from different temperatures since no systematic change in the density with this temperature, T_r, was noted. The largest number of measurements were made on the samples crystallized at a T_c of 20 °C. At T_c = 20 °C no systematic change in the density occurs with molecular weight from 3.8×10^5 to 0.69×10^5. A small increase in density is observed for T_c = 20 °C when the molecular weight is decreased to 0.26×10^5. If all determinations at a particular T_c are averaged, the values found are those given in the last column of Table I; the average deviation for each of these was within ±0.003. The average density value is found to increase with increasing T_c in the range 10–34 °C. the effect on the density of keeping *trans*-1,4-polyisoprene crystals in contact with amyl acetate at the crystallization temperature, 20 °C, for 1 and 2 months with frequent changes of the liquid was monitored for a sample with $\bar{M}_n = 2.9 \times 10^5$. Density values of 0.971, 0.976, and 0.977 g cm^{-3} were obtained for freshly prepared crystals and for crystals in contact with amyl acetate for 1 and 2 months, respectively.

Table II
Noncrystalline Fraction and Number of Monomer Units per Fold for Dilute-Solution-Grown *trans*-1,4-Polyisoprene Crystals

$\bar{M}_n \times 10^{-5}$	T_c, °C	$1 - W_c$[a]	L,[b] nm	F_s[c]	U[d]
2.1	10			0.54 ± 0.04	
2.9	10	0.50	7.8		8
2.9	20	0.46	9.0	0.41 ± 0.02	8
0.69	20	0.48		0.43 ± 0.02	8
0.26	20	0.44		0.33	6
2.9	25	0.46	11.5		
2.9	30	0.44	12.5	⩾0.38	⩾10
2.9	32	0.44			
2.9	34	0.43			

[a] Noncrystalline fraction calculated with density values given in Table I. [b] Lamellar thickness from electron microscopy. [c] Fraction of monomer units in epoxidized crystals by ^{1}H NMR. [d] Number of monomer unit per chain fold.

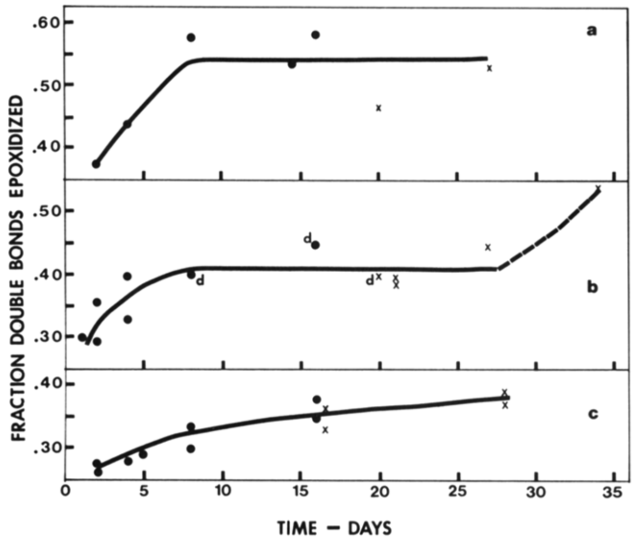

Figure 3. Reaction of *m*-chloroperbenzoic acid in amyl acetate at 0 °C with *trans*-1,4-polyisoprene lamellas grown at different crystallization temperatures: (●) ([MCPBA]$_0$/[DB]$_0$) ca. 0.8; (×) ([MCPBA]$_0$/[DB]$_0$) ca. 0.4 with additional MCPBA added after 7 days to give a ratio of ca. 0.8. (a) $\bar{M}_n = 2.1 \times 10^5$, $T_c = 10$ °C; (b) $\bar{M}_n = 2.9 \times 10^5$, $T_c = 20$ °C (d denotes that duplicate determinations gave the same value to two significant figures); (c) $\bar{M}_n = 2.9 \times 10^5$, $T_c = 30$ °C.

A total noncrystalline content, $1 - W_c$, at each T_c used was obtained from the density values in Table I and is given in Table II. The average deviation for this quantity is ±0.02. A decrease in $1 - W_c$ with increasing T_c is seen to occur.

The lamellar thickness was determined by electron microscopy for crystals prepared at T_c's of 10, 20, 25, and 30 °C for the TPI preparation with a $\bar{M}_n = 2.9 \times 10^5$; the number of different fields studied were 6, 19, 10, and 10, respectively. The mean values obtained are given in Table II; the average deviation for these measurements is ±1 nm.

Epoxidation of crystals in suspension was carried out on samples from five preparations; the fraction of double bonds epoxidized at various reaction times in amyl acetate at 0 °C is plotted in Figures 3 and 4 for these. Duplicate determinations agreed within ±0.02. It can be seen from these data that from 25 to 40% of the total number of double bonds present are epoxidized after 2 days under the conditions used. The reaction rate then diminishes and, at least for three of the five preparations studied, the amount epoxidized becomes constant after about an additional 6 days. Taking this as representative of the fraction of monomer units at the lamellar surfaces, F_s, yields the number given in Table II. With respect to the $T_c = 30$ °C preparation (Figure 3c), a constant value was not reached; therefore the fraction found after 28 days of reaction was used, thereby representing a lower limit. The limits of precision in Table II for F_s are the average deviations in the available data points; this is seen to be largest for the samples prepared at the lowest crystallization temperature (10 °C). Comparison of F_s with $1 - W_c$ in Table II shows agreement within experimental error at $T_c = 10$ °C where the two preparations used differ by about 30% in molecular weight, near agreement for the samples with $\bar{M}_n = 2.9 \times 10^5$ and 0.69×10^5 ($T_c = 20$ °C), and a difference of about 30% for the preparation with $\bar{M}_n = 2.6 \times 10^4$, with F_s having the smallest value. A few epoxidation experiments were performed with [MCPBA]$_0$ other than 0.2 g/100 cm^3 with [MCPBA]$_0$/[DB]$_0$ constant. Using the preparation with $\bar{M}_n = 2.1 \times 10^5$, we obtained the following results:

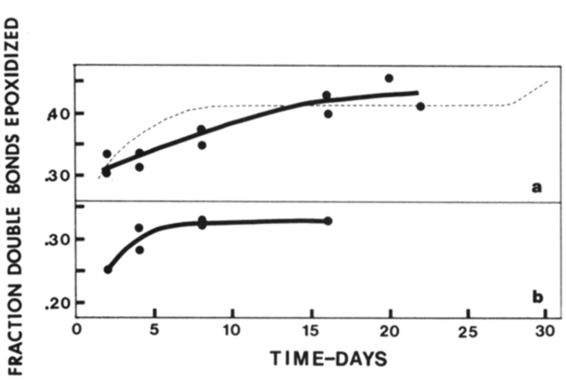

Figure 4. Effect of molecular weight on the reaction of *m*-chloroperbenzoic acid in amyl acetate at 0 °C with *trans*-1,4-polyisoprene lamellas grown at $T_c = 20$ °C: (a) (●) $\bar{M}_n = 6.9 \times 10^4$, (- - -) $\bar{M}_n = 2.9 \times 10^5$; (b) $\bar{M}_n = 2.6 \times 10^4$.

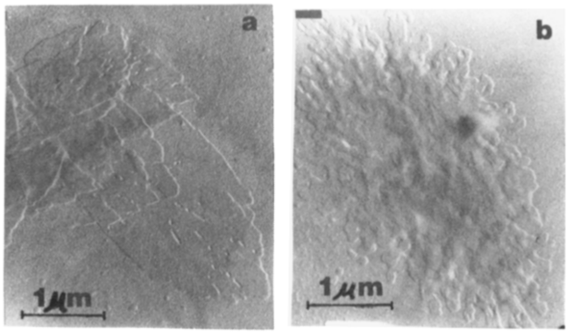

Figure 5. (a) *trans*-1,4-Polyisoprene crystal ($\bar{M}_n = 2.9 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.4$, $T_r = 40$ °C, $T_c = 30$ °C) epoxidized in amyl acetate at 0 °C for 27 days. (b) Crystal ($\bar{M}_n = 2.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.2$, $T_r = 40$ °C, $T_c = 10$ °C) epoxidized for 16 days.

T_c, °C	[MCPBA]$_0$, g/100 cm^3	time, days	fraction epoxidized
20	0.1	10	0.43
20	0.4	8	0.47
20	1.0	8	0.61
30	1.0	8	0.49

Comparison of these results with those in Figure 3 shows that at least at [MCPBA]$_0$ = 1.0 g/100 cm^3, the epoxidation amount is about 50% higher than those obtained at 0.1 and 0.2 g/100 cm^3. Electron microscopy was carried out on epoxidized *trans*-1,4-polyisoprene lamellas recovered after 2–35 days of reaction. The amount of damage to the crystals was assessed in a qualitative way as light (L), moderate (M), heavy (H), and very heavy (VH), as given in Table III. Examples of light and heavy damage

Table III
Electron Microscope Observations of Epoxidized TPI Crystals

$\bar{M}_n$	T_c, °C	epoxidation time, days	$[\mathrm{MCPBA}]_0$, g/100 cm^3	damage[a]
2.6×10^4	20	4	0.2	L
		8	0.2	L
		16	0.2	L
6.9×10^4	20	8	0.2	L
		16	0.2	M
2.1×10^5	10	16	0.2	H
	20	8	1.0	VH
	30	8	1.0	H
2.9×10^5	20	2	0.2	M-H
		4	0.2	M
		16	0.2	M
		21	0.2	M
		35	0.1[b]	VH
	30	8	0.2	L
		16	0.2	L
		27	0.2	L-M

[a] L = light, M = moderate, H = heavy, and VH = very heavy. [b] An equal amount of MCPBA was added after 7 days.

are shown in the electron micrographs given in Figure 5. It was found that crystal damage increases with increasing $\bar{M}_n$, $[\mathrm{MCPBA}]_0$, and reaction time and with decreasing T_c.

The effect of keeping epoxidized crystals in contact with amyl acetate at 0 °C to bring about desorption of any adsorbed noncrystalline material was studied by using crystals from a preparation with $\bar{M}_n = 2.9 \times 10^5$ and $T_c = 20$ °C that had been epoxidized for 21 days. The epoxidized crystals were washed and left suspended in amyl acetate while over the next 45 days the wash liquid was changed four times. Electron microscope examination of epoxidized crystals after suspension in amyl acetate for 30 days showed considerable loss of material from the edges when compared with epoxidized crystals receiving the usual washing procedure, as can be seen in Figure 6. Not all of the crystals scanned were changed to the extent evident in Figure 6b, but all those viewed showed damage. The fraction epoxidized after the usual washing procedure was found by ^{1}H NMR analysis to be 0.39 while for two samples washed for 45 days it was 0.37.

Calculations of the average number of monomer units per fold, U, was carried out by using eq 1, employing the F_s values given in Table II for all but the $T_c = 10$ °C preparation since in this case F_s exceeded $1 - W_c$. Therefore for $T_c = 10$ °C, F_s was taken as 0.50. L_c, the crystal thickness along the chain direction, was expressed in terms of the lamellar thickness, L, by the equation given earlier:[4]

$$L_c = \frac{(1 - F_s)\rho_a L}{(1 - F_s)\rho_a + F_s \rho_c} \tag{3}$$

where ρ_a is the amorphous density[10] and ρ_c the crystalline density.[8] L was assumed to be independent of $\bar{M}_n$ and only to depend on T_c. The R value employed (0.439 nm) is that given by Takahashi, Sato, Tadokoro, and Tanaka;[8] use of the value given by Fisher[12] (0.46 nm) would yield U values 5% lower. The value of C, the number of monomer units per two chain ends or cilia, was taken as $0.79(L/R)$, as found in an analysis[4] of results for *trans*-1,4-polybutadiene. This parameter can be omitted from eq 1 if $\bar{M}_n$ is large and L_c small, as is the case for the preparation with $\bar{M}_n = 2.9 \times 10^5$. For the preparation with $\bar{M}_n = 0.26 \times 10^5$, omitting C yields a U value that is larger by one monomer unit. From the values given in Table II a 30% increase in U occurs with about a threefold change in $\bar{M}_n$ (0.26×10^4 to 0.69×10^4) but no further change is apparent when $\bar{M}_n$ is increased another fourfold. At the highest $\bar{M}_n$ used, an increase in U of at least 25% takes place when T_c is changed from 10 to 30 °C.

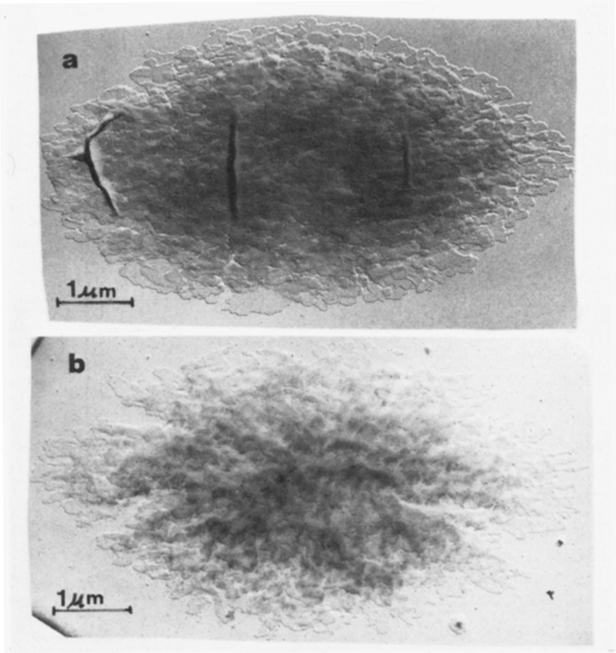

Figure 6. Effect of washing epoxidized *trans*-1,4-polyisoprene crystals with amyl acetate ($\bar{M}_n = 2.9 \times 10^5$, $T_c = 20$ °C): (a) crystal washed and immediately recovered; (b) crystal washed for 30 days with three changes of amyl acetate.

Discussion

The crystallization conditions used for most of the preparations in this work, involving precipitation at 0 °C, redissolution at the minimum temperature necessary, T_r, and crystallization at a T_c from 10 to 36 °C were found earlier[7] to yield the α crystalline form, as determined by differential scanning calorimetry in all cases and confirmed for some by X-ray analysis. Use of a T_r of 50 °C, which is well above the minimum temperature necessary to cause redissolution, yielded a dried sample with the same endotherm temperature as when T_r was 40 °C. This was found in the present work by X-ray diffraction to give the α form. However, 50/20 °C lamellas have different shapes than the 40/20 °C ones ($\bar{M}_n = 2.9 \times 10^5$) and they show only a β electron diffraction pattern, whereas the 40/20 °C lamellas show only the α pattern. Therefore, there is a β-to-α transformation taking place in the 50/20 °C crystals when in contact with amyl acetate and/or during the drying process. A $\beta \rightarrow \alpha$ transformation was shown[7] to occur when as-received synthetic TPI was swollen at 35 °C for 17 h in amyl acetate. Apparently, there is a temperature above which α-form nuclei are unstable and therefore cooling from above this temperature leads to crystallization of the β form. The effect of thermal history on the crystal form of the final dried product for TPI is under further investigation and will be reported on in greater detail at a later date.

In using a chemical reaction to obtain the fraction of monomer units present at the fold surfaces in polymer lamellas, one assumes that reaction at the lateral surfaces and in the crystal core is negligibly small. In the present work the lateral surface area is calculated to be approximately 2% or less of the total, depending on the preparation, and therefore the reaction taking place there can be neglected. There was evidence obtained from electron microscopy that during the reaction with MCPBA, penetration of the crystal core of TPI lamellas does take place, the severity of this depending on T_c and $\bar{M}_n$ as well as other factors. The observed constancy within experimental error for the double bonds epoxidized at least over part of the reaction time period for four of the five preparations studied suggests that this penetration has only a small effect up to about 20 days of reaction time.

Although the general trends in F_s and $1 - W_c$ are the same with $\bar{M}_n$ and T_c, there are marked differences in the values at low $\bar{M}_n$. The surface fraction of TPI crystals ($\bar{M}_n = 2.9 \times 10^5$) has received some study by a bromination reaction and again the general trends found with T_c are the same.[13] However, marked deviations in the values at T_c = 30 °C occur (F_s is 0.45 from bromination vs. 0.37 from epoxidation).

It was found earlier for TPBD lamellas grown from solution that F_s was generally smaller than $1 - W_c$.[4] The possible causes given for that behavior were (1) the existence of a lower density for the surface fraction as compared to the value extrapolated from the melt, (2) the presence of partially or totally hidden folds or other defects within the crystal,[14,15] and (3) shielding of the fold surface by absorbed polymer chains.[16] It was found in the present work that a small decrease in total noncrystalline content does take place when TPI crystals are washed repeatedly over a 1–2-month period, which suggests that either some desorption or further crystallization occurs. However, it was also found in this investigation that prolonged washing of epoxidized crystals at 0 °C had only a small effect on F_s, although loss of material from the crystal edges was clearly evident. Any polymer chains adsorbed on the crystals are expected to be epoxidized to a high extent. Loss of these chains by desorption and removal during washing should therefore cause a decrease in F_s. Loss of material from the crystal edges should be a slower process and after the first layer is removed should not cause a change in F_s. Since for epoxidized TPI lamellas F_s shows only a small decrease with extended washing, it is concluded that shielding of the surface by an adsorbed layer does not occur to any appreciable extent.

The largest discrepancies between F_s and $1 - W_c$ for TPI appear at lower $\bar{M}_n$. However, the number of hidden folds or defects, if they exist in these lamellas, is expected to decrease with decreasing $\bar{M}_n$. From the limited amount of data available for TPI it is unlikely that the presence of hidden folds or other defects is the principal cause of the differences between F_s and $1 - W_c$. Therefore, of the three possible reasons for F_s being less than $1 - W_c$, the first one given above is the most likely.

The surface fraction, F_s, at a particular temperature for single-crystal lamellas should depend mainly upon two factors: the crystalline thickness and the number of monomer units per fold. The lamellar thickness for various polymers, i.e., polyethylene,[15] TPBD,[17] and isotactic polystyrene,[18] increases with decreasing T_c at high temperatures and then becomes invariant. When the lamellar thickness is increased, F_s should decrease, if the fold length remains constant. For TPI the number of monomer units per fold, U, increases with T_c and is smaller at low molecular weight ($\bar{M}_n = 2.6 \times 10^4$). U values for surface-epoxidized TPBD lamellas with $\bar{M}_n = 1.7 \times 10^4$ and 4.4×10^4 have been found[19] by ^{13}C NMR to be 2.4 and 3.0. Therefore at comparable molecular weights the number of monomer units per fold for TPI lamellas is about twofold larger than that for TPBD lamellas. U values for TPBD fractions were reported[4] to increase with crystallization temperature and to a lesser extent with $\bar{M}$, both effects in the same direction as for TPI.

When models of the fold surfaces for α-TPI are constructed with the crystal structures given by Takahashi, Sato, Tadokoro, and Tanaka[8] and by Fisher,[12] a tight adjacent reentrant fold is found[20] to contain three and four monomer units, respectively, assuming 110 folding.[21] These values are two-to-threefold smaller than those found by epoxidation measurement. This therefore suggests that if reentry folding takes place exclusively, then some fold looseness must also occur, particularly at higher molecular weights. Another possibility, in agreement with these results, is the presence of some nonadjacent reentry[22] mixed with tight adjacent reentry folding. As discussed above, the results of this study suggest that the presence of adjacent reentry folding with an adsorbed noncrystalline overlayer is not a viable model.

The method used in this investigation to obtain the number of monomer units per fold depends on the evaluation of a number of parameters, including the surface fraction, F_s, the lamellar thickness, L, the monomer repeat distance in the crystal, R, and the amorphous and crystalline densities, ρ_a and ρ_c, respectively. A more direct method of evaluation is preferable. As pointed out above, the average fold lengths for some *trans*-1,4-polybutadiene crystal samples have recently been determined by ^{13}C NMR analysis.[19] This method is currently being used to investigate *trans*-1,4-polyisoprene crystals.

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