in that the characteristic ratio of poly(β-D-galactan) is greater than that of poly(β-D-xylan).

Two interesting points emerge from the results shown in Table II. The first is that, for a given bonding geometry (*e.g.*, e–e, a–e, etc.) the characteristic ratio is negatively correlated with the number of conformations of the dimer which are allowed according to the hard-sphere criteria of Rees and Scott.[8] This number of "allowed" conformations is clearly related (albeit somewhat crudely) to the degree of rotational freedom about the glycosidic bonds. The second point is that, for a given number of allowed conformations of the dimer, the characteristic ratio decreases as the bonding changes in the order a–a, e–e, e–a, a–e. It is important to notice that the characteristic ratio of a given polysaccharide depends both on the type of bonding and on the degree of rotational freedom about the glycosidic bonds.

Rees and Scott[8] have pointed out the correlation between the degree of rotational freedom and the number of substituents which are equatorial, and the above results indicate that, for a fixed bonding geometry, the characteristic ratio increases as the number and size of the equatorial groups increase.

It is unfortunate that numbers of "allowed" conformations are not available for α-D-galactose (1C) or α-L-gulose. In the former case, it is easy to rationalize the rather low characteristic ratio for an equatorial–equatorial-linked system in that both hydroxyls, as well as the $-CH_2OH$, are axial and we would therefore expect there to be many dimer conformations which are allowed.

Although the number of "allowed" conformations is not known for the α-L-gulose dimer, we would expect this number to be greater than for the α-L-galactose (C1) dimer, since the hydroxyl on C2 of gulose is axial while all other substituents are equatorial, as in the galactose case. However, the calculated values of the characteristic ratios are almost equal for these polymers.

In conclusion, it appears that the characterstic ratios of 1–4-linked polysaccharides are very dependent on the geometry of the bonding in the polysaccharide and are closely correlated with the degree of rotational freedom about the glycosidic bonds (or the fraction of conformations which are "allowed" according to the hard-sphere criteria of Rees and Scott).

Acknowledgments. The author wishes to acknowledge helpful correspondence with D. A. Rees and O. Smidsrød and the financial assistance of the National Research Council of Canada.

Infrared Spectra of Poly(*trans*-1,4-butadiene) Single-Crystal Mats

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ABSTRACT: High-resolution infrared spectra have been obtained in the 1000–1400-cm^{-1} region for crystal mats of poly(*trans*-1,4-butadiene) grown from six different solvents or solvent mixtures. It was found that the ratio of the ir band at 1350 cm^{-1}, an amorphous band, to that at 1335 cm^{-1}, a regularity band, varied with the solvent used and with thermal history. For selected preparations the fraction of monomer units at the crystal surfaces, α, was determined using an epoxidation reaction. A comparison of $\alpha/(1-\alpha)$ and I_{1350}/I_{1335} is used to provide information about the amorphous fraction in the various crystal preparations.

Infrared spectroscopy has been employed to study the nature of chain folding at the surfaces of crystals prepared from various polymers.[1–5] In particular, Koenig and coworkers have identified infrared bands due to unique fold conformations in poly(ethylene terephthalate)[1] and in poly(hexamethyleneadipamide).[3] However, all of the previous work was carried out on specimens for which no independent method was used to determine the amount of chain folding. One polymer for which such independent information is now available is poly(*trans*-1,4-butadiene), PTBD.[6,7] For this polymer the number of double bonds available for epoxidation has been determined for crystals grown from various solvents. The average number of monomer units per fold has been estimated from the epoxidation data, the crystal thickness, and the cell repeat distance. Although infrared spectra have been given for solvent cast samples of PTBD and a number of the infrared bands have been assigned,[8,9] spectra from single-crystal mats have not been reported to date.

In the present study the high-resolution infrared spectra in the 1000–1400-cm^{-1} region have been obtained for: (1) mats of poly(*trans*-1,4-butadiene) crystals prepared from dilute solutions of various solvents and solvent combinations, (2) mats annealed near to or above the crystal transition temperature,[10,11] (3) melt-cooled samples, and (4) a sample cast from solution. It is seen that by comparison of the relative intensities of certain ir bands with results for the epoxidation of the surface double bonds, the location of the amorphous fraction can be determined.

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Table I
Characteristics of PTBD Crystals

Sample	Solvent	Dissolution temp, °C	Precipitation temp, °C	% of polymer precipitating	Crystal thickness	No. of epoxidations	Final % of double bonds reacted
PTBD-K	Methyl isobutyl ketone	92	73				
	Heptane	78	64	75	150	4	14
	Toluene–ethanol	50	35				
	Toluene	50	23	40	95	1	19
	Benzene	52	8	35	60	2	27
PTBD-U	MIBK	88	55				
	Heptane	69	50	25	100	2	34
	Toluene–ethanol	50	35				
	Benzene–ethanol	42	33				

Experimental Section

Two PTBD samples were used as described previously;[7] the molecular weight of PTBD-U (from Uniroyal, Inc.) is about 10^4, while the PTBD-K (from Ube Kosan Co., Japan) which crystallized has a molecular weight about four times larger. The methods for crystal preparation from heptane, methyl isobutyl ketone (MIBK), and toluene were given previously.[7] For the PTBD-K crystals grown from benzene the dissolution temperature (52°) was well above the minimum value (*ca.* 30°). For the PTBD-K crystals grown from toluene–ethanol, a solution was made up in toluene at the minimum dissolution temperature, then ethanol was added until the solution showed the first signs of turbidity. For the PTBD-U crystals grown from the same solvent mixture, the polymer was mixed with ethanol at the minimum dissolution temperature for a pure toluene solution, then toluene added until solution took place. For the PTBD-U crystals from benzene–ethanol a solution in benzene was heated about 10° above the minimum dissolution temperature, then ethanol added until turbidity was first observed. The concentration of polymer in solution was 0.01–0.02 wt %.

The number of double bonds available for epoxidation was determined by the method used earlier.[7] For the runs using PTBD-U crystals from heptane and PTBD-K crystals from benzene, determinations were made at various times after the reaction was started.

For PTBD-K crystals from heptane and from toluene only one titration per reaction solution was carried out; this was done after 150 hr of reaction. In this way, much larger amounts of thiosulfate were used, with an improvement in the accuracy of the titration. Crystals thicknesses were estimated by electron microscopy using a Phillips EM 300 instrument.

For the ir determinations, crystal mats from heptane and MIBK were obtained by filtration using Millipore filters; the mats were then mounted between two KBr pellets. Crystals from toluene–ethanol, toluene, and benzene were resuspended in chloroform and a mat was formed by evaporation directly onto a KBr pellet. The mat of crystals from benzene–ethanol was formed by evaporation of the suspension onto a KBr pellet. A Perkin-Elmer 621 infrared grating double-beam spectrometer was used in high-resolution mode for the determinations. The crystal samples heated above the crystal transition temperature but below the melting point were studied in a Beckman variable-temperature cell. Melting and cooling of the crystal mat–KBr sandwich were carried out either in a vacuum oven or in a RIIC-VLT-2 variable-temperature unit. Since in the latter case the specimen was cooled by contact with a liquid nitrogen reservoir, a more rapid temperature change took place.

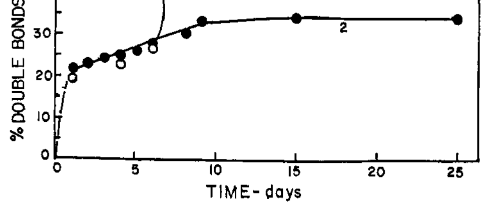

Figure 1. Epoxidation of PTBD-U crystals from heptane.

Peak intensities, given as ratios herein, were obtained from the area under the particular absorption after an appropriate choice of base line and the elimination of overlapping bands. Overlapping peaks were assumed to be guassian with the separation being carried out manually. Base lines drawn for peaks of interest in this study are shown in Figures 2 and 3.

Results

Characteristics of the crystal samples prepared for this study are given in Table I. The epoxidation results for PTBD-K crystals from heptane and from toluene after 150 hr of reaction agree well with the terminal values obtained by Stellman[6,7] (14 and 18%, respectively). The final epoxidation value given in Table I for PTBD-U crystals from heptane was found in only one of the two runs carried out; the results of these two epoxidations are given in Figure 1. The results show agreement up to about 6 days of reaction, at which time for run no. 1 a sharp increase in per cent of double bonds reacted is observed, with this quantity leveling off at 50%. This behavior is believed to be due to penetration of the crystals by the epoxidizing agent. Since the epoxidation reaction is being used to obtain the fraction of double bonds on the crystal surfaces (see below), the lower value (from run no. 2) of per cent of double bonds reacted is reported in Table I. That crystal penetration could occur, as assumed for run no. 1, was borne out by the fact that under the electron microscope, the reacted crystals exhibited numerous cracks and depressions.

Infrared spectra were obtained on crystal mats of all the specimens listed in Table I, in some cases as many as four different crystal mats of the same sample from the same solvent being run. Some representative spectra in the 1000–1400-cm^{-1} region are given in Figures 2 and 3. In Figure 2, ir spectra at room temperature for a PTBD-K–heptane crystal mat and for the same mat after heating above the melting point to about 160° and cooling by contact with liquid nitrogen are given. There are peaks at 1050, 1075, 1120, 1230, 1335, and 1350 cm^{-1} as reported earlier.[8] As noted previously[9] and as confirmed in this study, the 1050-, 1220-, and 1335-cm^{-1} bands disappear on heating above the crystal transition temperature (53–77°, depending on the preparation)[10] and therefore are "regularity" bands,[12] while the bands

(12) G. Zerbi, F. Ciampelli, and V. Zamboni, *J. Polym. Sci., Part C*, No. 7, 141 (1964).

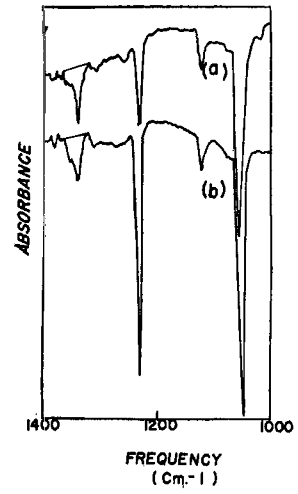

Figure 2. High-resolution ir spectra of a poly(*trans*-1,4-butadiene)–PTBD-K crystal mat at 25°: (a) as prepared from heptane (78°/64°), (b) after melting and fast cooling.

at 1075 and 1350 cm^{-1} increase in magnitude (see Figure 3) and are associated with "amorphous" conformations. Melting and fast cooling of the PTBD-K–heptane specimen leads to an increase in the 1350- and 1220-cm^{-1} peaks and a decrease in the 1335-cm^{-1} peak. The change in the 1220-cm^{-1} peak is believed to be due to a randomization of the *c* crystallographic axis, since this adsorption has a strong parallel component.[8] In the single-crystal mat a large number of chains are nearly parallel to the radiation direction, leading to only a small amount of interaction, whereas upon melt crystallization the chain direction would be randomized and a larger interaction would then occur. The increase in ratio of the intensity of the 1350-cm^{-1} peak to that of the 1335-cm^{-1} peak is believed to reflect a decrease in conformations associated with crystalline parts and an increase in the conformations taken up by the chains in the "amorphous" or disordered areas. Comparison of a spectrum from a mat with that from a KBr–polymer crystal pellet indicates little if any effect of chain orientation on I_{1350} and I_{1335}.

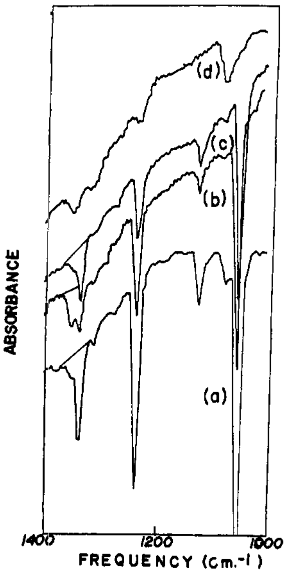

Figure 3. High-resolution spectra of PTBD-U crystal mats: (a) as prepared from heptane (69°/50°), spectra at 25°; (b) as prepared from toluene–ethanol (50°/35°), spectra at 25°; (c) crystal mat from toluene–ethanol, spectra after heating at 80° and recooling to 25°; (d) crystal mat from toluene–ethanol, spectra at 80°.

TABLE II
I_{1350}/I_{1335} FOR PTBD CRYSTAL MATS AT 25°

Sample	Solvent	I_{1350}/I_{1335} As prepared	After 80° annealing
PTBD-K	MIBK	0.2	0.2
	Heptane	0.2	0.1
	Toluene–ethanol	1	0.4
	Toluene	1.2	0.6
	Benzene	0.9	0.3
	Benzene cast film	0.3	
	Melt formed	0.5	
PTBD-U	MIBK	0.2	0.3
	Heptane	0.3	0.2
	Toluene–ethanol	1.3	0.2
	Benzene–ethanol	1.2	0.3
	Melt formed	1	

TABLE III
COMPARISON OF EPOXIDATION AND IR RESULTS FOR PTBD CRYSTALS

Sample	Solvent	$\alpha/(1-\alpha)$	I_{1350}/I_{1335}
PTBD-K	MIBK	0.28[a]	0.2
	Heptane	0.16	0.2
	Toluene	0.23	1
	Benzene	0.37	1
PTBD-U	Heptane	0.52	0.3

[a] Calculated from data in ref 7.

As is observed in Figure 3, a change in solvent of crystallization leads to changes in I_{1350}/I_{1335}. This ratio was calculated for all specimens as shown in Table II. Owing to the weakness of these bands and to considerable overlap (see Figure 3), the accuracy of these numbers, especially for samples where the two peaks are of almost equal height, is not very high. However, these numbers do reflect the changes which are noticeable in the spectra themselves. In addition to the effect of solvent of crystallization on this ratio, it is found that for those crystal preparations with values of $I_{1350}/I_{1335} \geq 1$ heating above the transition temperature leads to a reduction of this ratio by a factor of 2 or more.

A comparison of the ir results with the available epoxidation data is given in Table III. In the third column the ratios of the fraction of monomer units on the crystal surfaces available for reaction (α) to the fraction of units remaining in the body of the crystals $(1-\alpha)$ are given and in the fourth column, I_{1350}/I_{1335}, the ratios of the fraction of all "amorphous" conformations to all crystalline conformations (from Table II) are listed. For three of the five preparations, reasonably good agreement between the two values is found, considering the inaccuracies in the ir ratios. For two preparations, PTBD-K–toluene and PTBD-K–benzene, I_{1350}/I_{1335} substantially exceeds $\alpha/(1-\alpha)$.

Discussion

A number of previous investigations[10,11,13–16] have shown that polymer crystals grown from dilute solution can contain

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amorphous regions; it has usually been concluded that these are on the crystal surfaces, either associated with chain fold looseness[17,18] or with the presence of cilia.[15] The relatively good agreement between the epoxidation and ir results for PTBD crystals grown from two different solvents (Table III) supports the viewpoint that for certain preparations the amorphous regions can be predominantly on the crystal surfaces. On the other hand, the data for other preparations—PTBD-K crystals from toluene and from benzene—suggest that the amorphous content can exceed the amount on the surface; therefore, it has to be concluded that there are a considerable number of amorphous conformations residing within crystals grown in these solvents. This is also believed to be the case, from ir data alone, for PTBD-K crystals from toluene–ethanol and for PTBD-U crystals from toluene–ethanol and benzene–ethanol, assuming that the number of double bonds on the crystal surfaces is a function only of the crystal thickness and the molecular weight of the polymer.

From the results given herein there appears to be a correlation between the presence of internal amorphous conformations in PTBD crystals and the temperature of crystal growth. Those preparations with few internal amorphous conformations (MIBK and heptane) were grown at higher temperatures than those with a significant number of such conformations (from toluene or benzene). For the latter two solvents, dissolution of the polymer as received and crystal growth from them were carried out at temperatures below the crystal transformation temperature reported for benzene-grown crystals (53°).[11] Above this transition temperature, torsional motion of the chains can take place in the crystal lattice.[19] Upon cooling crystals grown above the transition temperature, considerable internal ordering may be possible before the transformation is complete. However, for crystals grown below this temperature, it appears that amorphous conformations are included in the crystal interior and they remain until the crystal is heated above the transition temperature. Subsequent cooling would then lead to a more ordered internal structure. In agreement with this is the decrease observed in I_{1350}/I_{1335} following the 80° heat treatment for crystals from toluene or benzene; these changes are believed to be too large to be accounted for by a change in the order of the surface fraction alone. As an example, the surface fraction would be expected to change for benzene-grown K crystals from 28 to about 14% (the value for heptane crystals), a total change of 14%. The actual change in the amorphous fraction is about 24%. A similar discrepancy is observed for toluene-prepared K crystals. Therefore, the ir results for annealed crystals are consistent with the hypothesis that internal disorder can be present in the crystals grown below the transition temperature. In addition, crystallization by solvent evaporation, a relatively slow process, leads to small amounts of disorder. Quenching from the melt, as expected, results in considerable internal disorder (see Table II).

Tatsumi, *et al.*,[11] have reported changes in dynamic mechanical and broad-line nmr results for mats of PTBD crystals grown from benzene solution at 18° and for the same mats subsequently annealed above 56°. These changes were attributed to chain fold tightening. However, the present results for benzene- and toluene-grown crystals do not support this type of explanation. First of all, from the epoxidation studies no appreciable differences in the number of monomer units per fold for crystals grown from various solvents are found. Although the total number of monomer units on the surfaces changes from preparation to preparation, the change in crystal thickness compensates for these differences, leaving the number of monomer units per fold essentially constant. This number was shown earlier[7] to be approximately 3.5; the present results for benzene-grown crystals yield the same value. Secondly, a change in internal order upon annealing is suggested by the magnitude of the changes in the I_{1350}/I_{1335} ratio for benzene- and toluene-grown crystals. The changes in dynamic mechanical and nmr results for PTBD crystals on annealing[11] can also be consistently explained as due to changes in internal order. The observed increase in crystal thickness accompanying the annealing treatment would lead to a decrease in the number of folds but would not necessarily lead to fold tightening as proposed earlier.[11]

Finally, there is no evidence from this investigation that for PTBD an ir band exists which is characteristic only of chain units in the folds, as was found for polyethylene terephthalate[1] and 66 nylon.[3] For PTBD all or most of the units comprising the folds contribute to the amorphous band at 1350 cm^{-1}.

Acknowledgment. We wish to thank Mrs. J. M. Stellman for her help in this study. This work was partially supported by a National Science Foundation Undergraduate Research Program at The City College.

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