

Conformation of the Fold of *Trans*-1,4-Polybutadiene

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ABSTRACT The conformation and the sudden tightening which Takayanagi has suggested, for the fold loop of *trans*-1,4-polybutadiene single crystals and cast films have been discussed from the studies on the assignment and the resolution of the IR spectrum near 1450 cm^{-1} . Four conformation sensitive methylene scissoring bands were assigned by the rotational state of the $\text{CH}_2\text{—CH}_2$ rotational axis and by crystallinity or noncrystallinity. From two parameters determined experimentally and the assumption of a Lorentzian representation for each band, the spectrum was resolved into four bands, and the ratios between band intensities were obtained as a function of annealing temperature. The average conformation in the noncrystalline part of the as-grown samples was considered nearly the same to that of the random coil. By annealing above 60°C , the ratios were suddenly changed. It was concluded that the average conformation in the noncrystalline part became *gauche*-rich. Under reasonable assumptions, the numbers of *trans* mers $N(\text{T})$ and *gauche* mers $N(\text{G})$ per fold of the single crystal were estimated; $N(\text{T})=2\text{—}3$, $N(\text{G})=3\text{—}2$ for the as-grown sample and $N(\text{T})=0\text{—}1$, $N(\text{G})=3\text{—}2$ for the 80°C annealed sample.

KEY WORDS Polybutadiene / Single Crystal / Fold / Tightening of Fold / Annealing Effect / Conformation / Conformation Sensitive Band / Resolution of Bands / Crystal-Field Splitting /

Takayanagi, *et al.*,¹ have suggested that *trans*-1,4-polybutadiene (TPBD) single crystals annealed below 55°C have loose fold loops, but the loop is suddenly tightened by annealing above 55°C , accompanied by a sudden thickening of the lamellae and disappearance of the α_a peak of dynamic viscoelastic loss. The infrared and epoxidation studies of Woodward, *et al.*,²⁻⁴ have not supported this suggestion. On the other hand, White, *et al.*,⁵ have supported this suggestion with their studies on infrared band parameters.

In this paper, we give the assignment and the method of resolving the IR spectrum of TPBD in the region of 1450 cm^{-1} and analyze the conformation of the fold.

EXPERIMENTAL

The sample of TPBD, which was kindly provided by Prof. Takayanagi, was prepared by

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Ube Kosan Co. Ltd. The *trans*-content of this sample was $>95\%$ according to infrared analysis.

The single crystals were grown from an 0.05% benzene solution at 15°C during 24 hr. The cast films were prepared from CCl_4 solutions at room temperature. Annealings were carried out at the designated temperatures for a period of 90 min.

In order to prevent any orientation of the crystals and to obtain suitable intensities, the infrared specimens of the single crystal were prepared as follows. After crystallization, the crystals were separated from the growth liquid, washed several times with 15°C benzene and finally mixed with 15°C benzene and KBr powder. Then, the benzene was removed from the well stirred mixture by freeze-drying. The specimens were prepared, as KBr pellets, from either the as-prepared or the annealed freeze-dried mixture. The amounts of benzene and KBr powder were 20 cc and 6 g, respectively, per 100 cc of the original growth liquid.

Infrared measurements were carried out at

room temperature, with the exception of liquid nitrogen temperature for solid 1,5-hexadiene. The spectra were recorded using a JASCO (Japan Spectroscopic Co. Ltd.) model IR-G double-beam infrared grating spectrometer. The base line of the wave number (ν) vs. absorbance ($D = \ln(I_0/I)$ in this paper) plot was drawn between the point ($\nu = 1500 \text{ cm}^{-1}$, $D = D(\text{obsd}) - 0.025$) and the point ($\nu = 1410 \text{ cm}^{-1}$, $D = D(\text{obsd}) - 0.035$). Each band was assumed to be Lorentzian.

Density measurements for the single crystal mats and the cast films were carried out at 25°C by the flotation method using the ethanol-water, ethanol-ethyleneglycol or water-glycerine system.

RESULTS AND DISCUSSION

Assignment of Conformation Sensitive Bands

The spectra in the region of 1450 cm^{-1} for TPBD and its model compound 1,5-hexadiene are shown in Figure 1. The bands in this region have been assigned to methylene scissoring, $\delta(\text{CH}_2)$, or vibrations of the $-\text{CH}_2-\text{CH}_2-$ group, except for the band at 1420 cm^{-1} for

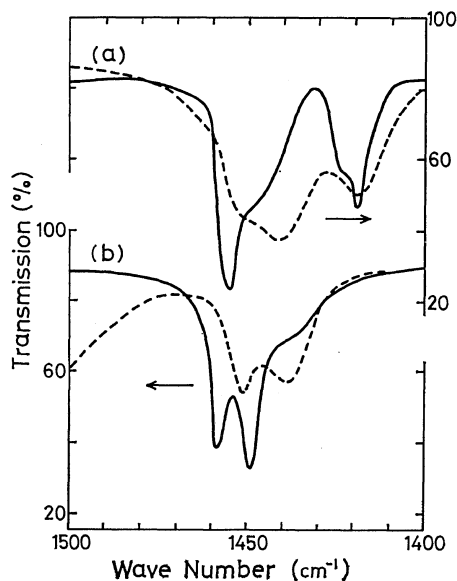


Fig. 1. IR spectra: (a) 1,5-hexadiene, the solid (or broken) curve represents the spectrum of the crystal (or the liquid); (b) TPBD, the solid (or broken) curve represents the spectrum of the single crystal (or the CCl_4 solution).

1,5-hexadiene due to the methylene deformation vibration of the $-\text{CH}=\text{CH}_2$ group.

These molecules have three C—C axes of internal rotation, which are inserted between two C=C bonds. The possible conformations of these axes are *trans* (T) and two *gauches* (G and G') for the central C—C axis, and *cis* (C) and two *skews* (S and S') for the two C—C axes adjacent to the double bond. According to Shimanouchi, *et al.*,⁶ the possible conformations of 1,5-hexadiene are CTC, CGC, CTS, CGS', STS, SGS, SG'S, STS', and SGS'. The conformation of TPBD (in its low temperature crystal) and 1,5-hexadiene molecules in their crystalline states are established to be STS' by X-ray^{7,8} and infrared⁶ studies. But in the non-crystalline state, many conformations are possible. The frequency of the $\delta(\text{CH}_2)$ vibration will be affected by the conformation.

The calculation of normal vibrations for a TPBD chain having an STS' conformation was carried out by Neto, *et al.*⁹ and recently by Tadokoro, *et al.*¹⁰ From these calculations, the bands at 1449 cm^{-1} for crystalline TPBD and at 1453 cm^{-1} for crystalline 1,5-hexadiene can be assigned to the $\delta(\text{CH}_2)$ vibrations of the STS' chain, which belongs to an A_u -species and is highly localized, 97%,¹⁰ upon the $\delta(\text{CH}_2)$ coordinate.

The relative intensity of the 1458-cm^{-1} band for the TPBD crystal increases with increasing crystallinity, as shown in Figure 2. Therefore, this band is a crystalline band. The space

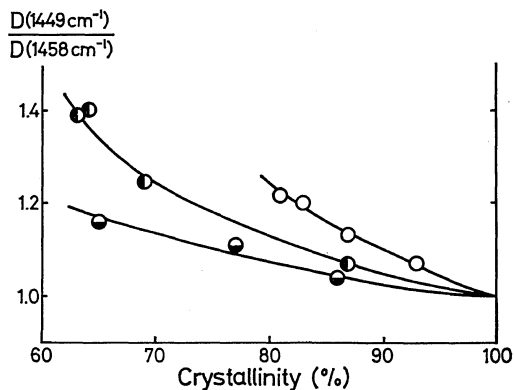


Fig. 2. $D(1449 \text{ cm}^{-1})/D(1458 \text{ cm}^{-1})$ vs. crystallinity for the single crystal (○), for the fast cast film (●), and for the slow cast film (◐).

group of the low-temperature crystal of TPBD is P_{21}/a^8 and its factor group is C_{2h} . Four chains are included in the unit cell. Hence, the $\delta(\text{CH}_2)-A_u$ mode of a chain splits into four modes belonging to A_g , B_g , A_u , and B_u species in the crystal-field. Only the later two bands are infrared active. Therefore, this band can be assigned to a crystal-field splitting band of the $\delta(\text{CH}_2)$ vibration of a STS' chain.

In the CCl_4 solution of TPBD and in liquid 1,5-hexadiene, two bands are observed at 1451 cm^{-1} and 1438 cm^{-1} . These bands arise from many $\delta(\text{CH}_2)$ vibrations owing to the many conformations in the noncrystalline state. As will be shown later, their half widths are larger than those of either the 1458-cm^{-1} or the 1449-cm^{-1} band. Nevertheless, the observation of many $\delta(\text{CH}_2)$ vibrations closely concentrated around 1451 cm^{-1} and 1438 cm^{-1} , may be due to the fact that the frequencies of these vibrations strongly depend on the rotational states of the CH_2-CH_2 rotational axis. The 97-% localization of the 1449-cm^{-1} band upon the $\delta(\text{CH}_2)$ coordinate, supports this consideration. Therefore, the 1451-cm^{-1} band lying near the 1449-cm^{-1} band can be assigned to XTY conformations, and the 1438-cm^{-1} band, to XGY conformations, where X and Y represent C, S or S' conformations.

In the following, the bands at 1458 cm^{-1} , 1449 cm^{-1} , 1451 cm^{-1} , and 1438 cm^{-1} are abbreviated as the T_c' , T_c , T_A and G_A bands, respectively.

Separation of the Bands

In order to determine the relative intensity between the bands T_c and T_c' , the relationship between the crystallinity and the ratio $D(1449\text{ cm}^{-1})/D(1458\text{ cm}^{-1})$ was determined. See Figure 2, where the crystallinity was estimated from the density, d , using the values of $d_c=1.03\text{ g/cm}^3$ ⁸ and $d_a=0.874\text{ g/cm}^3$.¹¹ By extrapolation of the curves to 100-% crystallinity, it can be concluded that the peak heights of bands T_c and T_c' are the same. The half widths of both bands, extrapolated to 100-% crystallinity, were also the same, 4.5 cm^{-1} .

From the spectral resolution for a CCl_4 solution of TPBD, as shown in Figure 3, the half widths of the bands T_A and G_A were 9.0 cm^{-1}

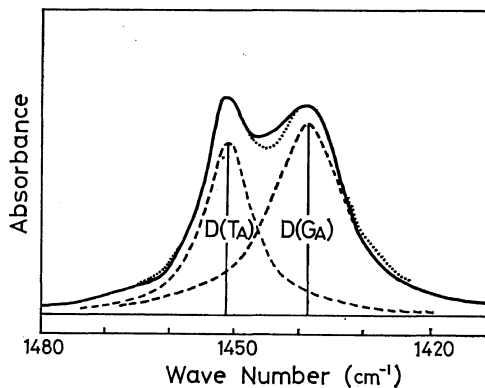


Fig. 3. Resolution of the CCl_4 solution spectrum. The dotted curve represents the synthetic spectrum from the resolved curves.

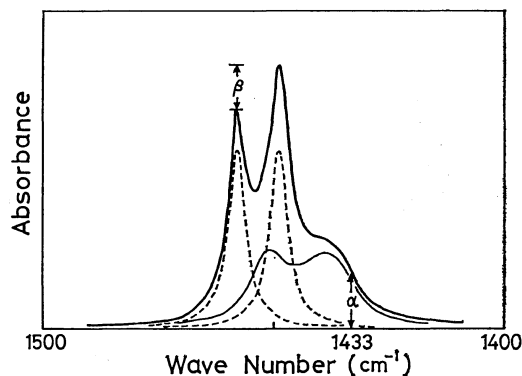


Fig. 4. An example of the resolution of the single crystal spectrum. The outside curve represents the observed spectrum, and the inside curves represent resolved bands.

and 14.0 cm^{-1} , respectively. In the following analysis, it is assumed that these values are not changed in the single crystal and the cast film.

In the single crystal spectra, all four bands, T_c , T_c' , T_A , and G_A , are included. To resolve the spectra into these bands, two parameters determined experimentally, α and β , are introduced: $\alpha=D(1433\text{ cm}^{-1})$ and $\beta=D(1449\text{ cm}^{-1})-D(1458\text{ cm}^{-1})$. Because the absorbances of the bands T_c and T_c' can be neglected at 1433 cm^{-1} and the peak heights of the T_c and T_c' bands are the same, the parameters α and β can be represented as follows:

$$\begin{aligned}\alpha &= L_{T_A}(1433\text{ cm}^{-1}) + L_{G_A}(1433\text{ cm}^{-1}), \\ \beta &= L_{T_A}(1449\text{ cm}^{-1}) + L_{G_A}(1449\text{ cm}^{-1}) \\ &\quad - L_{T_A}(1458\text{ cm}^{-1}) + L_{G_A}(1458\text{ cm}^{-1}),\end{aligned}$$

where L_{T_A} and L_{G_A} are the values of the Lorentzians of the bands T_A and G_A at the designated wave numbers. These Lorentzians are represented by the peak heights, $D(T_A)$ and $D(G_A)$, and the half widths given above. By solving the equations, the following relationships are obtained,

$$D(T_A) = -0.60\alpha + 0.191\beta,$$

$$D(G_A) = 1.68\alpha - 0.182\beta.$$

The peak height of the band T_c , $D(T_c) \equiv D(T_c')$, also can be easily calculated. An example of the resolution of the observed spectrum is shown in Figure 4.

Conformation of the Fold

The ratios $D(G_A)/D(T_A)$ and the densities of the single crystals and the fast cast films are shown in Figure 5 and Table I, as a function of annealing temperature.

The $D(G_A)/D(T_A)$ ratios of the as-grown and the annealed up to 60°C samples, 1.5 for the single crystal and 0.7 for the fast cast film, are not so different from that in the CCl_4 solution, 1.1. The small difference between the single crystal and the fast cast film may be due to tie chains which have more *trans*-rich conformations than those of fold chains. In any case, the average conformation in the noncrystalline part of the as-grown samples is considered to be nearly the same as that of the random coil.

By annealing above 60°C, the ratio is suddenly increased, as shown in Figure 5. At the same

time, it has been reported by Takayanagi, *et al.*,¹ that the long period is also suddenly increased from 100 Å for the as-grown and the annealed up to 60°C samples to 160 Å for samples annealed at higher temperatures. This increasing ratio means that the average conformation in the noncrystalline part becomes *gauche*-rich.

If we assume that the noncrystalline part of

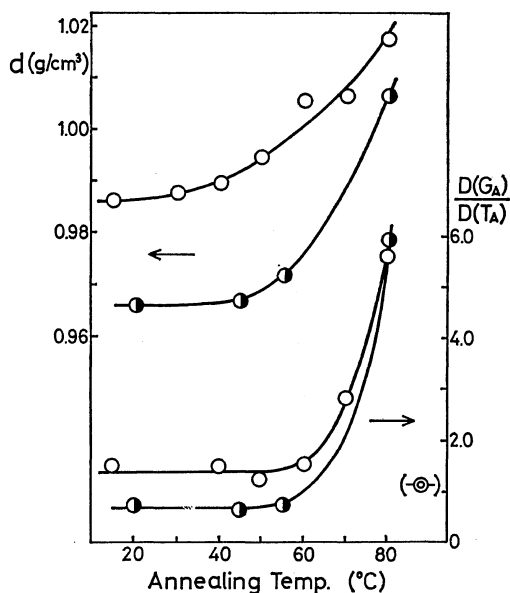


Fig. 5. $D(G_A)/D(T_A)$ and the density vs. the annealing temperature for the single crystal (○), and for the fast cast film (●). (⊖) represents $D(G_A)/D(T_A)$ of the CCl_4 solution.

Table I. Annealing temperature dependences of the ratios $D(G_A)/D(T_A)$, $D(T_A)/D(T_c)$, and $D(G_A)/D(T_c)$ and the density of TPBD.

Sample	Annealing temp, °C	Density, g/cm ³	$D(G_A)/D(T_A)$	$D(T_A)/D(T_c)$	$D(G_A)/D(T_c)$
Single crystal	As-grown	0.986	1.5	0.25	0.39
	40	0.990	1.5	0.27	0.42
	50	0.995	1.2	0.31	0.37
	60	1.006	1.5	0.17	0.25
	70	1.007	2.8	0.09	0.25
	80	1.018	5.6	0.04	0.23
Fast cast film	As-prepared	0.966	0.7	0.74	0.49
	45	0.967	0.6	0.80	0.48
	55	0.977	0.7	0.43	0.27
	80	1.007	5.9	0.04	0.23
CCl_4 solution	—	—	1.1	—	—

single crystals is composed only of folds, that is, lateral disorders or defects in crystals can be neglected, the average conformation of the fold can be estimated by the next two basic equations. (The suffix A of G_A and T_A are dropped for abbreviation.)

$$\frac{N(G)}{N(T)} = 2 \frac{f(G)}{f(T)} \exp \left\{ -\frac{E(G) - E(T)}{RT} \right\}$$

and

$$\frac{D(G)}{D(T)} = \frac{N(G) \cdot \kappa(G)}{N(T) \cdot \kappa(T)},$$

where $N(i)$, $f(i)$, $E(i)$, and $\kappa(i)$ are the number of mers, the rotational and vibrational partition function, the conformation energy, and the extinction coefficient respectively, and i is the conformational state. We assume that $f(G) = f(T)$. Using the value of 600 cal/mol for $E(G) - E(T)$ obtained from the temperature dependence of the spectrum in CCl_4 solution, the ratio $N(G)/N(T)$ in the solution is calculated from the upper equation. From this calculated ratio and the ratio $D(G)/D(T)$ observed in the solution at the same temperature, the ratio $\kappa(G)/\kappa(T)$ is calculated to be 1.5 from the lower equation. If we assume that this value does not change in the single crystal, the ratio $N(G)/N(T)$ in the fold can be calculated from the observed ratio $D(G)/D(T)$ by the inverse of the above process.

On the basis of these calculations, the value of the ratio $N(G)/N(T)$ was 1.0 for the as-grown single crystal and 2.5 for the 80°C annealed sample. If we assume that the density of the fold is equal to that of the bulk amorphous phase, the number of total mers per fold is roughly estimated to be five for the as-grown single crystal and to be three for the 80°C annealed sample, using the Takayanagi, *et al.*,¹ values for the long period, and the observed densities. Hence, the average conformation of the fold is considered to be about $N(T) = 2-3$, $N(G) = 3-2$ for the as-grown single crystal and about $N(T) = 0-1$, $N(G) = 3-2$ for the 80°C annealed sample.

We showed that eight bonds were necessary for the shortest regular (110) fold of polyethylene single crystals.¹² The distance between adjacent chains of a fold is 4.33 Å for polyethylene and 4.60 Å for TPBD. Because three rotational axes are included in a mer of TPBD, three mer folds of TPBD single crystals may be the shortest fold. It will be tight and rigid, and will not show the α_a dispersion of dynamic viscoelastic behavior. This consideration is in accord with the suggestion by Takayanagi, *et al.*,¹ mentioned at the beginning of this paper.

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