bands. The ratios of the 367- to the 412-nm band also agrees reasonably well with the calculated sequence ratios. However, since the bands become closer together as we go to higher wavelengths, overlapping becomes more severe and the intensity measurements, particularly of the 412-nm band, are less precise.

The agreement of the observed ratios with the calculated ratios supports the original assignments of the sets to diads, triads, tetrads, and pentads derived from conjugated diene sequences, and is consistent with a structure arising from 1,4 addition of 1-chloro-1,3-butadiene. These results confirm once again the validity of the theory underlying sequence distribution calculations from copolymerization data. There are few cases which permit such a direct analysis of sequence distribution in copolymerization.

Structural Studies of Isotactic Poly(*tert*-butylethylene oxide)

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ABSTRACT: The crystal structure (one of two crystal modifications) of the racemic sample of isotactic poly(*tert*-butylethylene oxide) was investigated by utilizing the X-ray diffraction method and conformational energy calculation. This polymer has a true asymmetric carbon atom in each monomeric unit, giving two types of optical isomers; rectus (*R*) and sinister (*S*). The unit cell is tetragonal, $P\bar{4}n2$-$D_{2d}{}^8$, with a = 15.42 Å and c (fiber axis) = 24.65 Å. The molecular chain has a helical structure and nine monomeric units turn four times along the helix in the fiber identity period. Four molecules of the (9/4) helix pass through the unit cell and two pairs of optical antipodes exist in definite positions in the unit cell. Consequently the unit cell is optically inactive. The result of the analysis also suggests the formation of two types of isotactic polymer chains from the mixture of *R* and *S* monomers in polymerization with diethylzinc–water as catalyst.

Poly(*tert*-butylethylene oxide) has a true asymmetric carbon atom in each chemical monomeric unit, O–CH_2–$C(-CMe_3)H$, and so there are two kinds of optical isomers in the case of the isotactic polymer chain. These planar zigzag models and the corresponding Fischer projections are illustrated in Figure 1. According to the nomenclature proposed by Cahn, Ingold, and Prelog,[1] the absolute configurations of these two optical isomrs can be indicated by rectus (*R*) and sinister (*S*). In the case of the racemic sample, both the optical isomers of the isotactic polymer chains must coexist. Therefore it is an interesting problem to determine the arrangement of two kinds of optical antipodes in the crystalline state. From this point of view, the structural studies of isotactic poly(*tert*-butylethylene oxide) are closely related to those of isotactic poly(propylene oxide)[2-5] and isotactic poly(propylene sulfide).[6]

Since crystalline poly(*tert*-butylethylene oxide) was synthesized,[7-11] the crystal structure has not yet been reported by any authors. In the present work, the crystal structure of the racemic sample was investigated by using mainly X-ray diffraction. It should be noted that the two most reasonable molecular models could be selected through the calculations of the intramolecular interaction energies according to the procedure as already described in the previous papers.[12-14] There are only a few examples[15-17] to which the conformational analysis has been applied for this purpose.

Experimental Section

Samples. The substance used in this study was polymerized from racemic *tert*-butylethylene oxide using diethylzinc–water (1:07) as catalyst, and the benzene-insoluble part of the raw polymer was used. The melting temperature measured by using a polarizing microscope was 136°. In this study, two kinds of crystal modifications were formed depending upon the conditions of crystallization. They were designated modifications I and II. A good crystalline and well-oriented sample of modification I was prepared by stretching a strip of an amorphous sample (prepared by quenching from melt) at about 120°, and annealing at about 110° under tension using a metal holder. On the other hand, a uniaxially oriented specimen of modification II was prepared by stretching a strip of a melt-quenched sample at a temperature a few degrees below the melting point, followed soon after by heat treatment at 130° under tension.

X-Ray Measurement. Throughout the present study, the X-ray photographs were taken by using nickel-filtered Cu Kα radiation. A cylindrical camera (diameter 10.0 cm) and a Weissenberg camera (diameter 9.0 cm) were used. The camera radii were corrected with the spacings of the reflections of aluminum powder. Reflection intensities obtained by the multiple film method were estimated visually by use of the standard intensity scale.

The fiber photographs of modifications I and II of poly(*tert*-butylethylene oxide) are given in Figures 2a,b, respectively. Figure 3 shows the Weissenberg photograph with its schematic representation which was taken by setting the uniaxially oriented specimen with the fiber axis perpendicular to the camera axis,

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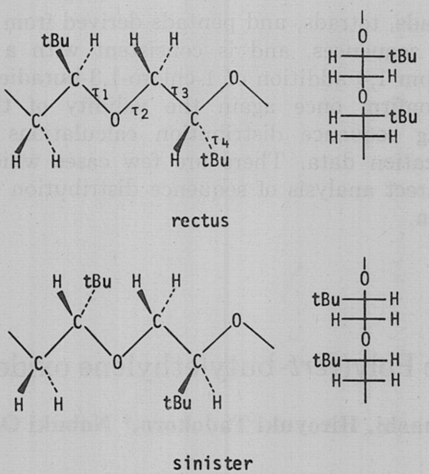
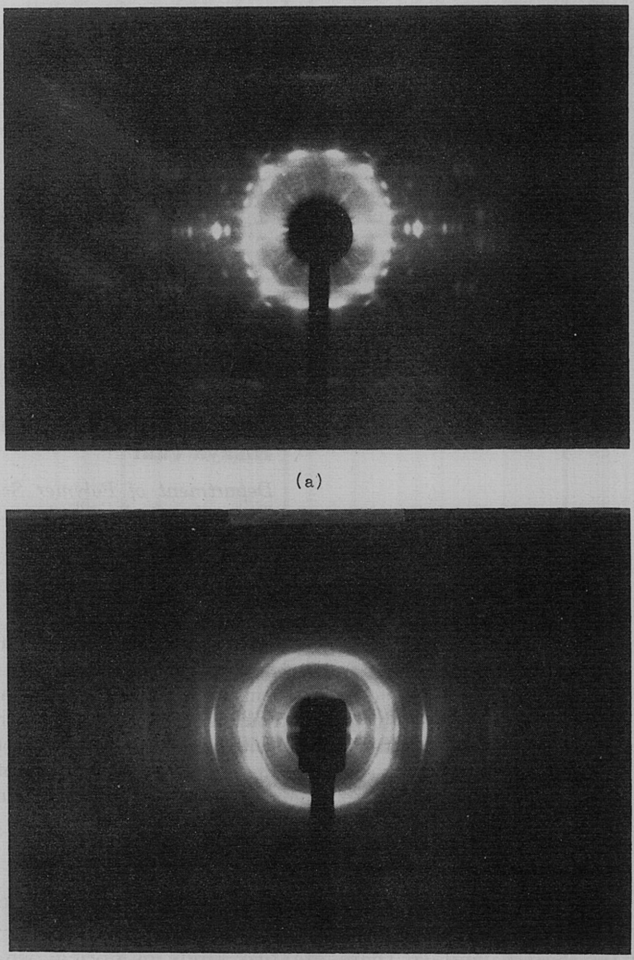


Figure 1. Absolute configurations of two kinds of optical isomers for isotactic poly(*tert*-butylethylene oxide).


(a)

(b)

Figure 2. X-Ray fiber photographs of isotactic poly(*tert*-butylethylene oxide): (a) modification I; (b) modification II.

and by oscillating the specimen around the camera axis by 200°. The photographs of modification I reveal the characteristic feature that the reflection intensities decrease rapidly with the increase of the Bragg angle and that the streaks are observed along some layer lines, *i.e.*, the 4th, 6th, and 9th layer lines.

In this report, the structural studies of modification I will be described. The structure analysis of modification II is now in progress.

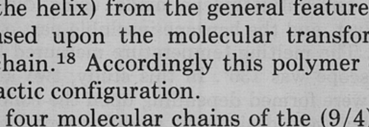
Analysis

Unit Cell and the Molecular Structure. From the fiber photograph shown in Figure 2a, 57 independent Bragg reflections were observed on the layer lines from the equatorial to the 10th. All the reflections could be satisfactorily indexed by a tetragonal cell with the cell dimensions, a = 15.42 Å and c = 24.65 Å (fiber period).

The most probable molecular structure was considered to be a (9/4) helix (refer to the Appendix concerning the notation of the helix) from the general features of the fiber diagram, based upon the molecular transform theory of the helical chain.[18] Accordingly this polymer chain should have an isotactic configuration.

Assuming four molecular chains of the (9/4) helix in the unit cell, the calculated density is 1.02 g/cm^3, and this value is acceptable in comparison with the observed density, 0.96 g/cm^3, measured by flotation method in water–1-propanol mixture at 24°.

Conformational Analysis. Conformational analysis was applied in order to select the most reasonable molecular models. The numbering of the internal rotation angles of the main chain, τ_1, τ_2, and τ_3, and that of the side chain, τ_4, is denoted as follows



$$\begin{array}{l} \phantom{C_{II}H_I(-1)-(-}\tau_1\ \tau_2\qquad\ \tau_3 \\ C_{II}H_I(-1)\text{-}(\text{-}O\text{-}C_IH_2\text{-}C_{II}H_I\text{-})\text{-}O(+1) \\ | \qquad\qquad\qquad\qquad\quad |\,\tau_4 \\ C_{III}Me_3(-1) \qquad\quad\ \ C_{III}Me_3 \end{array}$$

$\tau_1[C_I(-1)C_{II}(-1)OC_I]$, $\tau_2[C_{II}(-1)OC_IC_{II}]$,

$\tau_3[OC_IC_{II}O(+1)]$, and $\tau_4[H_IC_{II}C_{III}Me]$

The conformations of the main chain can be restricted by using the helical parameter equations proposed by Miyazawa,[19] under the assumption of a (9/4) helix with a fiber period of 24.65 Å. The possible sets of the internal rotation angles are on two closed curves in a cube defined by the three-dimensional cartesian coordinates, τ_1, τ_2, and τ_3, each covering from 0 to 360°.[14] In Figure 4, the projection on the $\tau_2\tau_3$ plane is shown and the τ_1 values of several points are given. The two curves correspond to the right-handed and left-handed helices.

The intramolecular potential energies were calculated for R and S configurations on the closed curve of the right-handed helical conformation. In these calculations, internal rotation barriers, van der Waals interactions, and electrostatic interactions were taken into account. The calculations were carried out by the same method as in the previous investigations.[12-14] The sinusoidal function, $V_0(1 + \cos 3\tau)$, was used as the internal rotation barriers. The height of the barrier V_0 was assumed to be 2.0 kcal/mol of bond for the C–C bond and 1.0 kcal/mol of bond for the C–O bond.[20,21] The potential functions for the van der Waals interactions were approximated by Lennard–Jones "6–12" type functions according to the procedures developed by Scott and Scheraga[22-24] with some modifications of parameters. The methyl group was considered as a united atom in this study and additivity in the atomic polarizability and the effective number of outer shell electrons was assumed. The van der Waals radius of the

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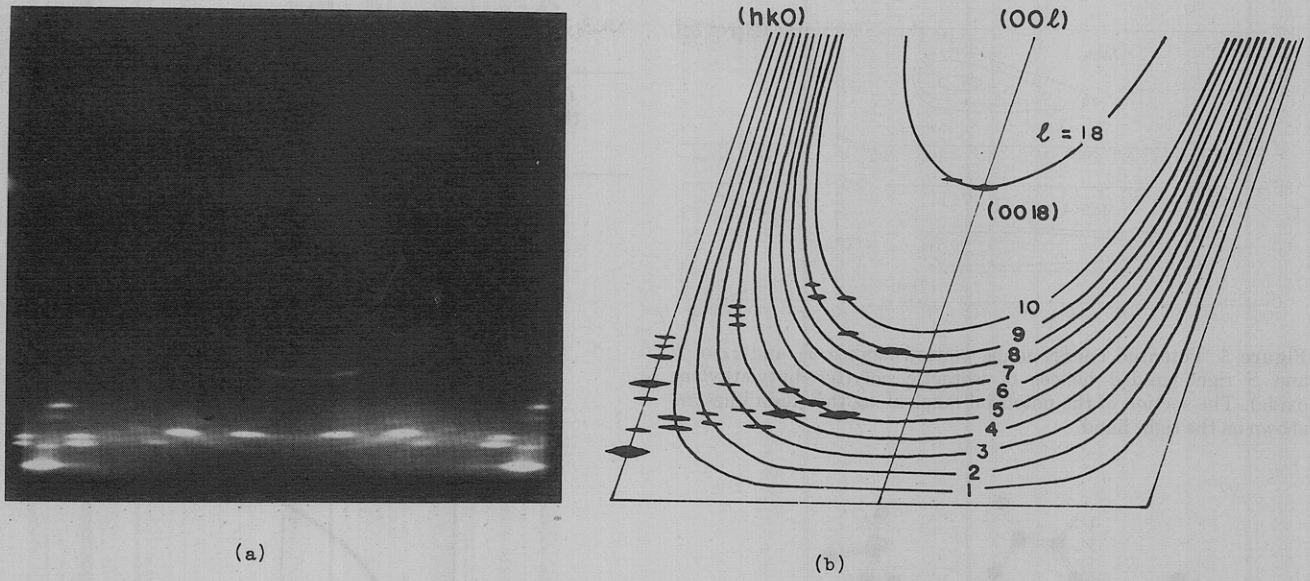

(a) (b)

Figure 3. Weissenberg photograph of isotactic poly(*tert*-butylethylene oxide) modification I: (a) Weissenberg photograph; (b) schematic representation of the photograph.

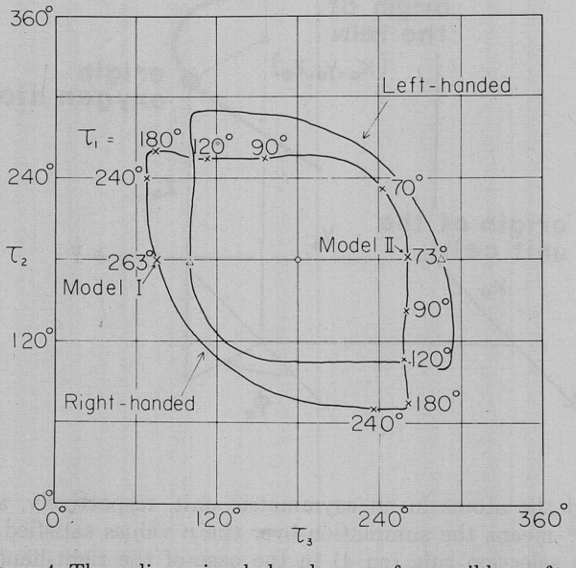

Figure 4. Three-dimensional closed curves for possible conformations of the main chain of isotactic poly(*tert*-butylethylene oxide).

methyl group was taken as 2.0 Å. Electrostatic interactions were calculated by using the well-known expression for interactions between two point dipoles. The point dipole was assumed to be at the midpoint of the C–O bond,[25] and the value of the C–O bond moment was taken as 0.74 D.[26] The dielectric constant was assumed to be 4.0.[22,23] The molecular parameters used in this study are C–C = 1.54 Å, C–O = 1.43 Å, C–H = 1.00 Å, and all bond angles = 109.5°.

The potential maps around the minima are partially shown in Figure 5, in which the contours are drawn against τ_1 and τ_4. For any τ_1 value, the other two τ values are uniquely fixed. It is sufficient to calculate in the range covering from 0 to 120° for τ_4, since the *tert*-butyl group has three equivalent methyl groups. Each optical isomer has a potential minimum, corresponding to a stable conformation of the right-handed helix; model I [$\tau_1 = 263°$, $\tau_2 = 180°$, $\tau_3 = 73°$, and $\tau_4 = 64°$] for *S* polymer, and model II [$\tau_1 = 73°$, $\tau_2 = 183°$, $\tau_3 = 263°$, and $\tau_4 = 55°$] for *R* polymer. These two minima give just the same potential energy value, 8.5 kcal/mol of monomeric unit. Molecular models I and II of right-handed upward helices are illustrated in Figure 6. When the atoms of the main chain in the monomeric unit, O–C_IH_2–C_{II}(–CMe_3)H, go upward in the order, O, C_I, C_{II}, we designate it the upward chain. The most characteristic difference between the models is that the oxygen atoms are at the innermost positions in model I, while the methylene groups are innermost in model II.

Molecular Structure Factor. Since plural helical chains pass through a unit cell in the present case, the phase relation between the X-rays diffracted by the chains in the unit cell should be taken into account for the calculations of the structure factors. But, at this stage of the analysis, the molecular structure factor was examined as a first approximation. In the fiber photograph, the relevant intensity should be cylindrically averaged,[27] which can be expressed as

$$\langle F_{\mathrm{M}}^2(R,l/c)\rangle_\Psi = \sum_n^* (A_n^2 + B_n^2) \tag{1}$$

$$A_n = \sum_{j=1}^{7} f_j J_n(2\pi R r_j) \cos\,[n(\pi/2 - \phi_j) + 2\pi l z_j/c] \tag{2}$$

$$B_n = \sum_{j=1}^{7} f_j J_n(2\pi R r_j) \sin\,[n(\pi/2 - \phi_j) + 2\pi l z_j/c] \tag{3}$$

where R, Ψ, and l/c are the cylindrical coordinates of a point in the reciprocal space, f_j is the atomic scattering factor, and r_j, ϕ_j, and z_j are the cylindrical coordinates of the jth atom in the asymmetric unit. J_n is the nth-order Bessel function and $\Sigma_n{}^*$ means the summation over the n values satisfied by the selection rule

$$l = 4n + 9m \tag{4}$$

where m is any integer. In the numgrical calculation, the

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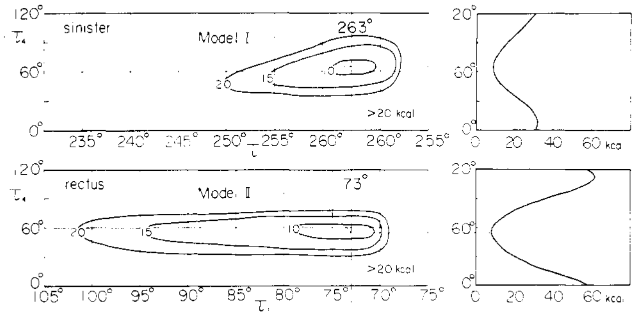


Figure 5. Potential energy maps plotted against τ_1 and τ_4 of R and S right-handed helices of isotactic poly(*tert*-butylethylene oxide). The section of the potential maps along the chain lines are shown on the right hand.

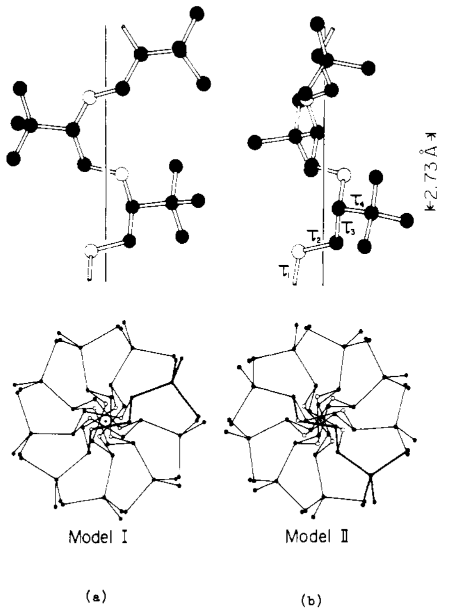
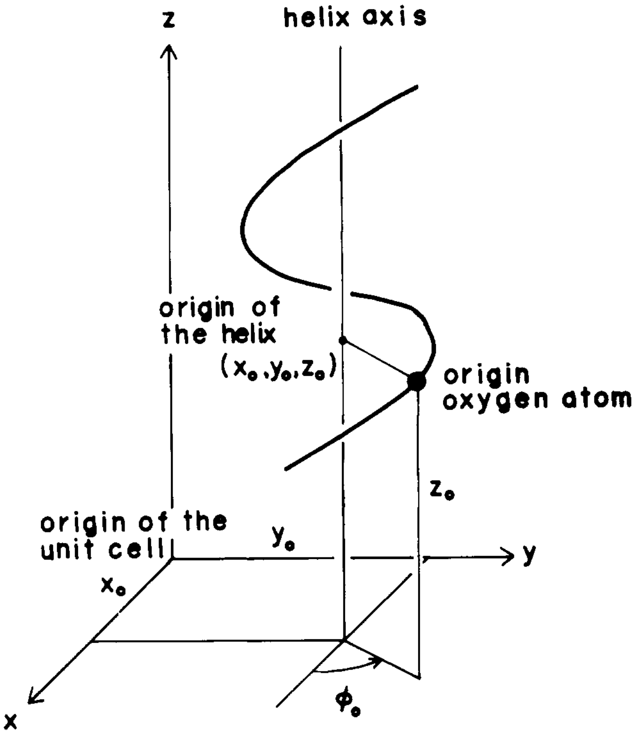


Figure 6. Molecular models of isotactic poly(*tert*-butylethylene oxide): (a) model I (right-handed, upward, and S); (b) model II (right-handed, upward, and R).

Table I
Molecular Coordinates and Atomic Coordinates

Origin of the Helix:	x_o/a 0.250	y_o/a 0.250	z_o/c 0.322	ϕ_o (rad) 0.300
Atom	r (Å)	ϕ (rad)	z (Å)	
O	0.588	0.000	0.000	
C_I	0.858	2.581	0.333	
C_{II}	1.264	3.376	1.581	
C_{III}	2.746	3.168	1.737	
Me_I	3.313	3.366	3.087	
Me_{II}	3.362	2.699	1.793	
Me_{III}	3.550	3.338	0.537	



Bessel functions with the orders, $|n| \leq 9$, were taken into account and the isotropic temperature factor, 5.0 Å^2, was assumed for all atoms. Figure 7 shows the calculated molecular structure factors $[\langle F_M{}^2(R,l/c)\rangle_\psi]^{1/2}$ for models I and II, which are cylindrically averaged. The vertical rods in this figure show the square roots of the relative intensities of the reflections, which were corrected by Lorentz-polarization factors, and divided by the multiplicities and the numbers of the overlapping reflections. The distributions of the calculated intensities for both models agree fairly well with the observed values. Therefore the determination of the molecular model was still difficult only from the molecular structure factor calculations.

Lattice Structure Factor. When the origin of the qth helical chain is displaced from the origin of the lattice to the point (x_q, y_q, z_q) and turned about its axis by the angles ϕ_q as shown by the figure in Table I, the lattice structure factor can be expressed as

$$F_L(h,k,l) = \sum_{q=1}^{4}\sum_{n}^{*}\sum_{j=1}^{7} f_j J_n(2\pi R r_j)\,\exp(iG_{qnj}) \times \exp[2\pi i(hx_q/a + ky_q/b + lz_q/c)] \quad (5)$$

where q and j refer to the molecular chains in a unit cell and the atoms in an asymmetric unit, respectively, and $\Sigma_n{}^*$ means the summation over the n values satisfied by the selection rule (eq 4) in the case of the right-handed helix. In this expression, G_{qnj} can be given as

$$G_{qnj} = n(\psi \mp \phi_j + \pi/2 - \phi_q) \pm 2\pi l z_j/c \quad (6)$$

for the right-handed helix or

$$G_{qnj} = n(-\psi \mp \phi_j + \pi/2 + \phi_q) \pm 2\pi l z_j/c \quad (7)$$

for the left-handed helix, where the upper and lower signs are to be used for the upward and downward helices, respectively.

The systematic absence ($hk0$ when h or k is odd) was observed on the equatorial line, and the comparison between the calculated molecular structure factors for both models and the observed structure factors per chain gave a good agreement for the equatorial reflections as shown in Figure 7. Therefore the origins of four helical chains can be considered to locate in the unit cell, having the relation of I, II, III, and IV as shown in Figure 8.

The characteristic systematic absence ($hk9$ when h or k is even) was observed on the 9th layer line, for example, the 009 reflection was not observed although the 0018 re-

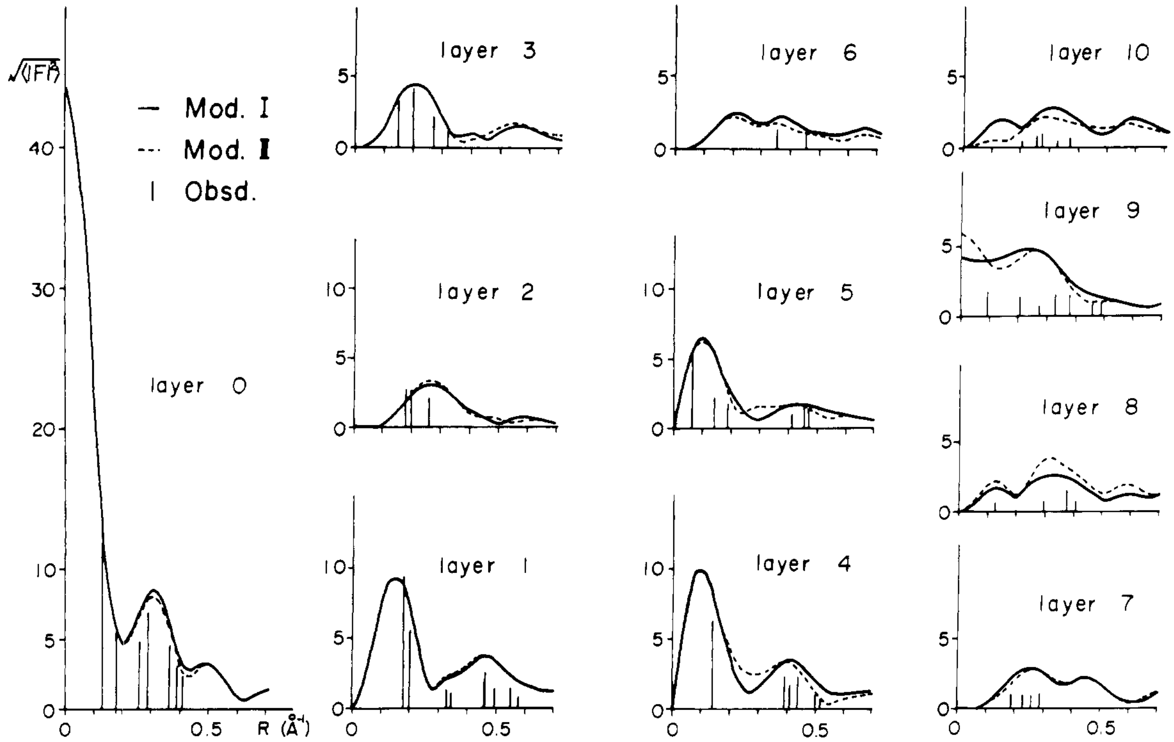


Figure 7. Comparison between the square roots of the observed relative intensities and the calculated molecular structure factors for models I and II: solid line, calculated value of model I; broken line, calculated value of model II; vertical rod, observed value.

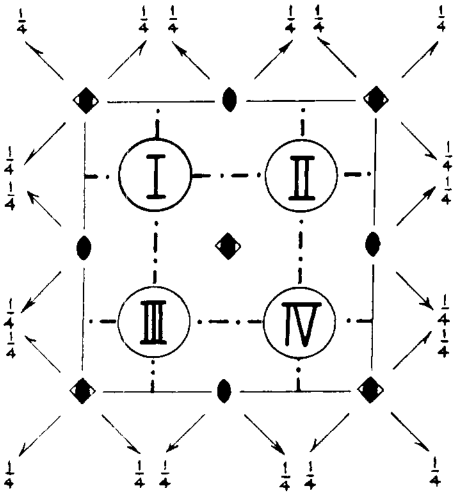


Figure 8. Way of the packing of helices for the space group $P\bar{4}n2\text{-}D_{2d}{}^8$.

flection could be observed clearly. At this stage, only the 0th order Bessel function was taken into account for the 9th layer line, since the contribution of the Bessel functions with the orders, $|n| \geq 9$, is negligibly small in the present sample. The possible space group satisfying the systematic absence of the equatorial and 9th layer lines is $P4_2\text{-}C_4{}^3$ alone in the space groups belonging to the tetragonal system with four general equivalent positions. In the case of this space group, the intensities of the observable *hk*9 reflections (h = odd and k = odd) can be given by

$$I(h,k,9) = \left[4\sum_{j=1}^{7} f_j J_0(2\pi R r_j)\cos(18\pi z_j/c)\right]^2 + \left[4\sum_{j=1}^{7} f_j J_0(2\pi R r_j)\sin(18\pi z_j/c)\right]^2 \quad (8)$$

Accordingly, if the space group is $P4_2\text{-}C_4{}^3$, the lattice structure factor per chain of the observable *hk*9 reflection should be almost identical with the molecular structure factor $[\langle F_M{}^2(R,9/c)\rangle_\psi]^{1/2}$. But the agreement between the calculated molecular structure factors and the observed values is not so satisfactory, as shown in Figure 7.

Here the possibility was extended to the tetragonal space groups with more than four general equivalent positions, and furthermore the possible space group was examined in detail by taking into account the additional systematic absence ($h0l$ when $h + l$ = odd and $0kl$ when $k + l$ = odd). In consequence, the acceptable space group was found to be $P\bar{4}n2\text{-}D_{2d}{}^8$. The symmetry elements of the space group are shown in Figure 8. This space group has eight general equivalent positions, but the molecular chain does not have any symmetry existing in the space group. Therefore, the manner of packing of the chains should be restricted as follows: in Figure 8, if the right-handed helices are located at the positions I and IV, the left-handed helices are at the positions II and III, and pairs of the upward and downward isomorphous helices correlated by the twofold rotation axis at $z = c/4$ or $z = 3c/4$ must exist at the definite positions with the probability of ½, respectively. In the case of this space group, the intensities of the *hk*9 reflections with h = odd and k = odd can be expressed by

$$I_L(h,k,9) = \left[4\sum_{j=1}^{7} f_j J_0(2\pi R r_j)\sin\left[18\pi(z_0 + z_j)/c\right]\right] \quad (9)$$

where z_0 is the height of the origin oxygen atom from the origin of the unit cell. The value of z_0 was adjusted by trial so as to give a good agreement between the calculated and observed intensities. The structure factors of five reflections on the 9th layer line are given against $z_0 - (1/4)c$ in Figure 9. The solid and broken lines correspond to the calculated structure factors of models I and II, respectively. The vertical rods show the observed values and are drawn in the positions at which the best agreement is

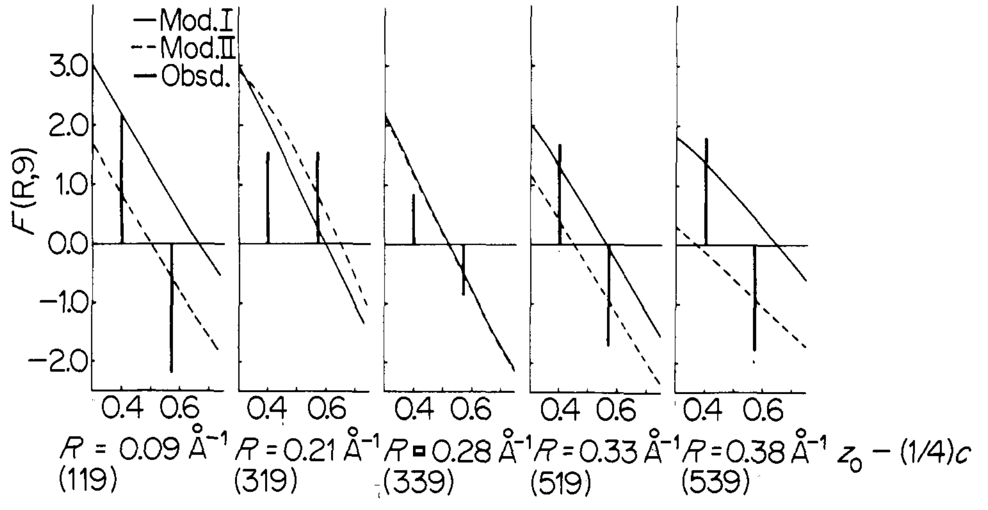


Figure 9. Determination of z_0 values by the comparison between the calculated and observed structure factors of five reflections of the 9th layer line. The calculated structure factors of models I and II are plotted against $z_0 - (1/4)c$ with the solid and broken lines, respectively. The vertical rods show the observed values and are drawn on the positions, to which the best agreements are given for models I and II. The signs of the observed values are conveniently chosen.

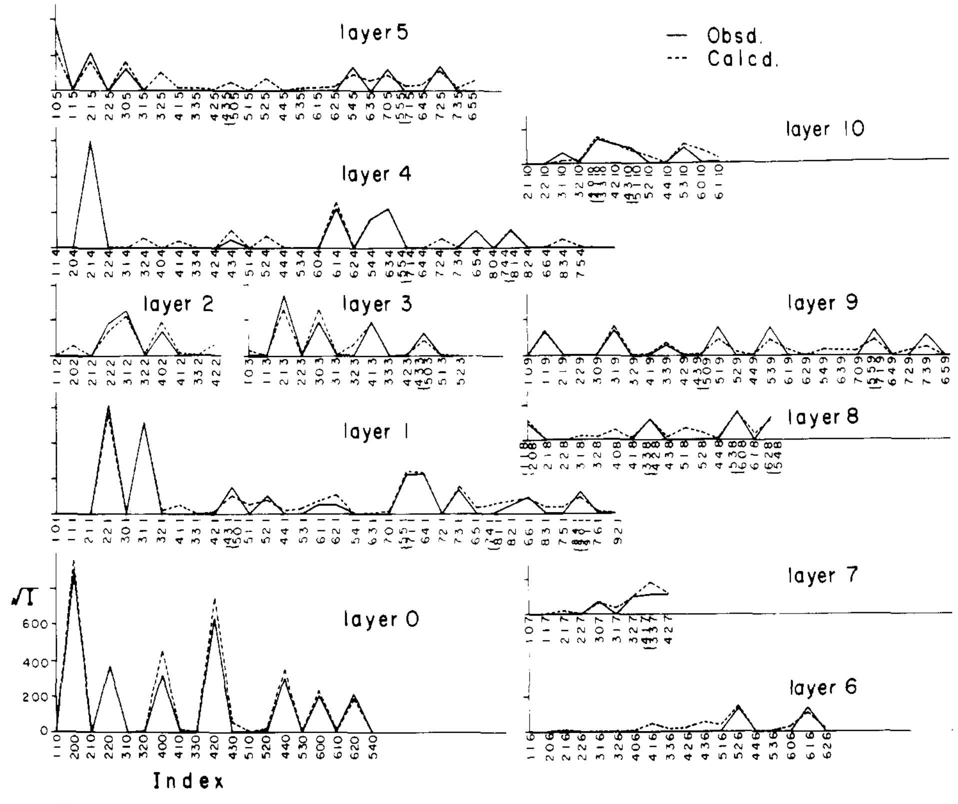


Figure 10. Comparison between the observed and calculated structure factors of isotactic poly(*tert*-butylethylene oxide). The observed structure factors, $(I_o)^{1/2}$, were put on the same scale as the calculated structure factors, $(I_c)^{1/2}$ [= $(mF_c^2)^{1/2}$], by setting $\Sigma k(I_o)^{1/2} = \Sigma(mF_c^2)^{1/2}$, where k is the scale factor and m is the multiplicity. $(I_c)^{1/2}$ of the reflections which overlap on the X-ray photograph are $(\Sigma mF_c^2)^{1/2}$.

given for models I and II. The signs of the observed values are conveniently chosen. The best agreement was found at $z_0 - (1/4)c = 0.40$ Å for model I and at $z_0 - (1/4)c = 0.57$ Å for model II. Figure 9 shows better agreement for model I than model II.

Structure Factor Calculation. The crystal structure factors (space group $P\bar{4}n2$-D_{2d}^8) were calculated by eq 5, 6, and 7 for models I and II. In these calculations, the rotation angles, ϕ_0, which is defined as the angle between the a axis and the radial direction of the origin oxygen atom, was examined in the vicinity of z_0 determined from the comparison with the intensities of the 9th layer line by trial and error method. The contribution of the hydrogen atoms was not taken into account. As the result, the discrepancy factor R $(=\Sigma|(I_o)^{1/2} - (I_c)^{1/2}|/\Sigma(I_o)^{1/2}$ of the observed independent 57 reflections was 19% for model I and 27% for model II. The refinement by the least-squares method reduced the discrepancy factor to 16% only for model I, while an apparent reduction could not be found for model II. Accordingly model I may be considered to be an acceptable molecular model. The final coordinates are listed in Table I, and the agreement between the observed and calculated structure factors is shown in Figure 10. The isotropic temperature factor was 9.6 Å^2 for all atoms.

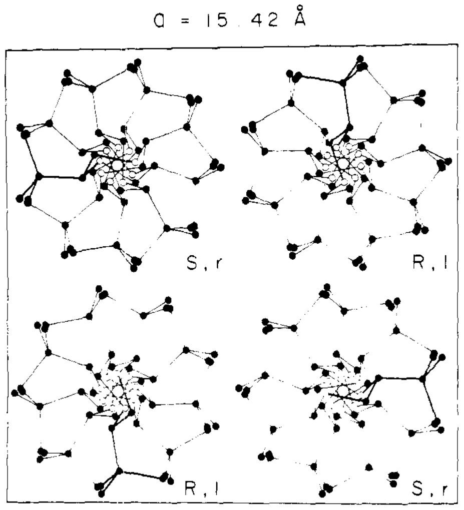


Figure 11. Crystal structure of isotactic poly(*tert*-butylethylene oxide) modification I. Only the upward helices are illustrated for simplicity; R, rectus; S, sinister; r, right handed; l, left handed.

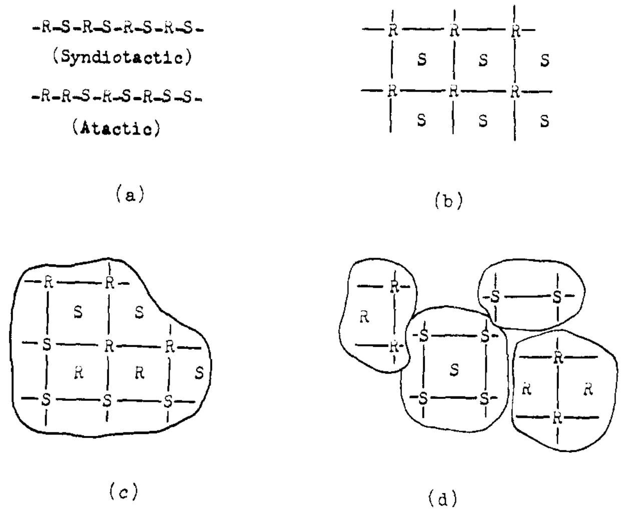


Figure 12. Way of the optical compensation of racemic polymers: (a) intramolecular compensation: syndiotactic and atactic; (b) compensation in a unit cell; (c) compensation in a crystallite; (d) intercrystallite compensation. R and S show rectus and sinister monomeric units, respectively, in the case (a), and rectus and sinister polymer chains in the cases, b, c, and d.

In this analysis, the numerical calculations were performed by using a NEAC 2200 Model 500 digital computer installed in Osaka university.

Results and Discussion

Crystal Structure. The crystal structure of the racemic isotactic poly(*tert*-butylethylene oxide) is illustrated in Figure 11. The molecular chains at the upper left and lower right positions are right-handed *S* helices and those at the upper right and lower left positions are left-handed *R* helices. This crystal structure is considered to be statistically disordered, consisting of a random mixture of upward and downward helices of 1:1 ratio. In this crystal structure, the positions of the C_{III} atoms of the side groups are not so much different between the upward and downward helices. Therefore, although the positions of the main chain atoms belonging to the upward and downward helices are much different, the side groups occupy nearly the same positions in the lattice, resulting in a good overall packing of molecules. It may be considered that the chain packing is essentially governed by intermolecular interactions among the side groups.[28]

Statistical Disorder and the Systematic Absence. In the present study, it was found that the crystal structure of poly(*tert*-butylethylene oxide) has a statistical disorder in the up and down sense of the isomorphous helical chains. There are other isotactic polymers having a statistical disorder of this type; for example, polypropylene,[29] poly(1-butene),[30] polystyrene,[31] polyacetaldehyde,[32] poly(3-methyl-1-butene),[33] poly(4-methyl-1,3-pentadiene),[34] and poly(4-methyl-1-pentene).[35] In the case of isotactic poly(*tert*-butylethylene oxide), the existence of a statistically disordered structure must necessarily be introduced from the requirements of the space group $P\bar{4}n2\text{-}D_{2d}{}^{8}$. The same situation was encountered in the determination of the space group for isotactic poly(4-methyl-1,3-pentadiene)[34] ($I\bar{4}c2\text{-}D_{2d}{}^{10}$) and isotactic poly(4-methyl-1-pentene)[35] ($P\bar{4}b2\text{-}D_{2d}{}^{7}$), and these space groups lead to statistically disordered structures. The crystal structures of these three kinds of isotactic polymers belong to the tetragonal system and there are twofold rotation axes perpendicular to the fiber axis correlating a pair of the isomorphous chains with each other. Therefore, it is considered that the crystal structure of isotactic poly(*tert*-butylethylene oxide) is similar to those of isotactic poly(4-methyl-1,3-pentadiene) and isotactic poly(4-methyl-1-pentene) from this point of view.

Structure of the Racemic Polymer. Here, the structure of the racemic poly(*tert*-butylethylene oxide) will be discussed from the viewpoint of achieving the optical compensation. Four possible structural models[6] are considered as shown schematically in Figure 12. In the case of (a), *R* and *S* monomeric units exist in a molecular chain, randomly (atactic polymer) or alternately (syndiotactic polymer). On the other hand, a polymer chain is optically active in itself in the case of the isotactic polymer chain. In the case of (b), the same number of *R* and *S* polymer chains pass through the unit cell. In the case of (c), *R* and *S* polymer chains exist in a crystallite with 1:1 statistical ratio, and so the optical compensation occurs in a crystallite. In the last case, (d), the bulk sample of the racemic polymer consists of two kinds of crystallites, each composed only of *R* polymer chains or only of *S* polymer chains. That is, the optical compensation occurs between the same amounts of *R* crystallites and *S* crystallites.

As the result of the crystal structure analysis of isotactic poly(*tert*-butylethylene oxide) modification I, it is found that two *R* polymer chains and two *S* polymer chains exist at definite positions in the unit cell. Therefore the unit cell is optically inactive and the type of optical compensation corresponds to case (b). That is in contrast to the cases of isotactic poly(propylene sulfide)[6] and isotactic poly(propylene oxide).[4] The former corresponds to the case (d), and the latter to the case (c) or (d).

Appendix

A Proposal Concerning the Notations of the Types of Helical Polymers. The notation (*u*/*t*) has been used conventionally as the expression of the type of the helical

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polymer where u is the number of the monomeric units and t is the turn number of the helix in the identity period. Actually, in the case of polyoxymethylene,[36] nine monomeric units are contained and the helix turns five times in the identity period, and so the type of the helix can be demonstrated to be (9/5).

But in the complex case where it is difficult to decide the turn number t visually by tracing along the main chain atoms, the type of the helix cannot be designated by the notation described above. Therefore, in such cases the helix may be defined as right-handed when the rotation angle between any atom and the equivalent atom of the subsequent monomeric unit, ϕ_u, is smaller than 180° in the right-handed cylindrical coordinate system. The types of helical polymers may be denoted by use of ϕ_u of the right-handed helix. An example of this case is that of poly(*tert*-butylethylene oxide). ϕ_u of the right-handed helix is 160° and nine monomeric units are contained in the identity period, that is, $u = 9$ and $t = 4$ $[(160^\circ \times 9)/2\pi]$. Accordingly the type of poly(*tert*-butylethylene oxide) can be shown as (9/4).

Furthermore, we should note that the conventional nomenclature is to be preferred to the present proposal, if there is no complex situation of the type just mentioned.

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Small-Angle X-Ray Diffraction Study of Chlorinated Polyethylene Crystallized from Melt

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ABSTRACT: As model compounds of semicrystalline copolymers we prepared samples of linear polyethylene chlorinated in solution to various extents (0.5–4.2 wt % chlorine). The partitioning of chlorine atoms between the amorphous and crystalline phases of these copolymers, crystallized from melt, was studied by a low-angle X-ray scattering technique. The chlorine atom can be utilized as a convenient probe because of its high contrast in both electron and mass densities. The total scattering power of the sample was obtained by integration of the observed X-ray intensity. Both the scattering power and the mass density of the sample can be expressed as functions of the degree of crystallinity and the partition coefficient of chlorine in the two phases. From the observed values of the scattering power and mass density, the latter two quantities were evaluated. The degrees of crystallinity thus obtained agree well with the values determined independently from the heats of fusion. The partition coefficient of chlorine, *i.e.*, the ratio of concentration of chlorine in the crystalline phase to that in the amorphous phase, is around 0.15 but decreases somewhat with increasing concentration of chlorine in the copolymer.

When a small amount of comonomer units is introduced into a linear homopolymer, one obtains a copolymer which still crystallizes into a semicrystalline structure resembling that of the homopolymer. It has frequently been surmized that, when crystallization of such a copolymer is performed extremely slowly, all the noncrystallizable comonomer units are rejected completely from the crystalline lattice. It is not certain, however, whether such a complete rejection can be achieved in any copolymer that has been crystallized with a rate attainable in practice. There are at least two kinds of experimental evidence that suggest that the rejection of comonomer units is not complete. One is that the unit cell dimensions of the crystalline lattice of copolymers, determined by X-ray diffraction, are frequently much larger than those of the corresponding homopolymer. The effect has been reported widely[1-6] for copolymers of polyethylene and branched polyethylene. The second line of evidence comes from the study of melting temperatures. The early theory by Flory,[7] relating the melting point of a copolymer to its composition, is based on the assumption of complete rejection of comonomers. The prediction of the theory, however, has been found in a number of copolymer series[8-11] to underestimate the degree of melting point depression due to the comonomer units. The extent of deviation from the theory has also been shown to depend on the size of the comonomer unit.[10,11]

In this work we apply the technique of small-angle X-ray diffraction to obtain a direct measure of the amount of comonomer units incorporated into the crystalline phase. As a model of random copolymers, we employ a series of samples of linear polyethylene chlorinated in solution to various extents. Chlorinated polyethylene was earlier employed as a model copolymers by Killian and coworkers.[4,12] The degree of chlorination in our samples was kept fairly low and at most to a few chlorine atoms per 100 carbons. Chlorinated polyethylene offers several advantages over other copolymers for the present purpose. First, the chlorination reaction performed in solution allows placement of chlorine atoms at random positions along the polyethylene chain. This random placement of chlorine atoms in our samples was confirmed by high-resolution nmr study.[13] Secondly, the chlorination reaction is

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