Structural Studies of Polyethers, $(-(CH_2)_m-O-)_n$. X. Crystal Structure of Poly(ethylene oxide)

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ABSTRACT: The crystal structure of poly(ethylene oxide) was analyzed by X-ray diffraction method. Four (7/2) helical molecules pass through a unit cell with parameters, $a = 8.05$ Å, $b = 13.04$ Å, c(fiber axis) = 19.48 Å, and $\beta = 125.4°$, and the space group, $P2_1/a\text{-}C_{2h}{}^5$. The molecule was found to be appreciably distorted from the molecular model proposed in a previous paper[1] whose symmetry was isomorphous to the point group D_7. For the present analysis, the constrained least-squares method and the least-squares method for helical molecules were utilized.

In a previous paper,[1] a (7/2) helix with symmetry isomorphous to the point group D_7 was proposed for the molecular structure of poly(ethylene oxide) (PEO) by using infrared absorption and X-ray diffraction methods. Here, (7/2) helix means that seven monomeric units turn two times per fiber period. The crystal structure could not, however, be analyzed at that time. On the other hand, Richards[2] tried the crystal structure analysis on the assumption that the molecular symmetry was isomorphous to the point group D_7 and a twofold rotation axis of the molecule was parallel to a twofold screw axis of the lattice, but he did not succeed satisfactorily. In the present paper, the result of detailed crystal structure analysis of PEO is reported.

Experimental Section

Polyox WSR-301 and Polyox Coagulant (Union Carbide Chemicals Co.) were used for the sample. A uniaxially oriented sample was obtained by stretching after quenching of the melt into Dry Ice-methanol.

X-Ray diffraction measurements were made by using Ni-filtered Cu Kα radiation. A specially prepared vacuum camera with diameter 20.0 cm was used for precise measurements of the spacings in addition to the cylindrical cameras of 7.0- and 10.0-cm diameters. The spacings were calibrated by reference to those of aluminum powder. Figure 1 shows the fiber photograph of PEO. The reflection intensities were mainly measured by visual estimation with a standard inensity scale. The integrated intensities of 25 strong reflections were measured by a scintillation counter. The intensities of 205 independent reflections could be measured.

X-Ray Analysis

Unit Cell and Space Group. The unit cell parameters were redetermined by using the vacuum camera of 20-cm diameter as $a = 8.05$ Å, $b = 13.04$ Å, c (fiber axis) = 19.48 Å, and $\beta = 125.4°$. The most probable space group was considered to be $P2_1/a\text{-}C_{2h}{}^5$ from the systematic absences, $h0l$: h = odd, $0k0$: k = odd, and the Patterson function synthesized with the equatorial reflections as Richards reported already.[2] Since there are four general positions in this space group, a molecular chain corresponds to an asymmetric unit.

Trial and Error Procedures. The structure factor of a helical polymer molecule at a crystal site in general crystal systems is given by the following equation according to Cochran, Crick, and Vand[3]

$$F(h,k,l) = \sum_n G_{n,l}(R_h)\ \exp[in(\pm\psi_h + \pi/2)] \times \exp[2\pi i(hx_M + ky_M + lz_M)]\ \exp(\mp in\phi_M) \quad (1)$$

where R_h, ψ_h, and l/c are the cylindrical coordinates of a (hkl) reflection in the reciprocal space, x_M, y_M, and z_M are the fractional coordinates of the origin of the molecule on the helical axis, ϕ_M is the azimuthal angle of the molecule about the helical axis, and the upper and lower signs are to be used for right- and left-handed helices, respectively. In this expression, $G_{n,l}(R_h)$ is given by

$$G_{n,l}(R_h) = u\sum_j f_j J_n(2\pi R_h r_j)\ \exp[i(\mp n\phi_j \pm 2\pi l Z_j/c)] \quad (2)$$

where u is the number of the chemical units per fiber period, r_j, ϕ_j, and Z_j are the cylindrical coordinates of the jth atom, f_j is the atomic scattering factor of the jth atom, J_n is the nth-order Bessel function, and the upper and lower signs are used for up- and down-pointing molecules, respectively. In eq 1 and 2, the order of the Bessel function n is submitted to the following selection rule

$$l = tn + um \qquad (m = 0, \pm1, \pm2, \ldots) \quad (3)$$

where t denotes the number of the turns in the fiber identity period.

In the case of PEO, the following structure factor equations were obtained by taking into account of the symmetries of the space group $P2_1/a\text{-}C_{2h}{}^5$ and the helical symmetry D_7 of the molecule. Here, z_M and ϕ_M were defined as the height of an oxygen atom and the azimuthal angle between the oxygen atom and the plane parallel to the ac plane, respectively. The crystal structure factor is given by

$h + k$: even

$$F(h,k,l) = 4\sum_n G_{n,l}(R_h)\ \cos[n(\mp\phi_M + \pi/2) + 2\pi(hx_M + lz_M)]\ \cos(\pm n\psi_h + 2\pi k y_M) \quad (4a)$$

$h + k$: odd

$$F(h,k,l) = -4\sum_n G_{n,l}(R_h)\ \sin[n(\mp\phi_M + \pi/2) + 2\pi(hx_M + lz_M)]\ \sin(\pm n\psi_h + 2\pi k y_M) \quad (4b)$$

where the upper signs are used for the right-handed molecule at the position (x_M, y_M, z_M) and the lower signs are used for the left-handed molecule, and $G_{n,l}(R_h)$ is denoted by the following equation when the hydrogen atoms are not taken into account

$$G_{n,l}(R_h) = 7f_O J_n(2\pi R_h r_O) + 14 f_C J_n(2\pi R_h r_C) \times \cos(-n\phi_C + 2\pi l Z_C/c) \quad (5)$$

$$l = 2n + 7m \qquad (m = 0, \pm1, \pm2, \ldots) \quad (6)$$

If only the lowest order Bessel function obtained from eq 6 is taken into account for each layer, the summation with respect to $n(\Sigma_n)$ in eq 4a and 4b can be eliminated. Accordingly, when $G_{n,l}(R_h)$'s are calculated in advance,

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(1) Y. Chatani, H. Tadokoro, T. Yoshihara, and S. Murahashi, *Symp. Polym. Sci., Japan, Tokyo,* Nov 1961, Abstr. 11B-5; H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and S. Murahashi, *Makromol. Chem.*, **73**, 109 (1964).

(2) J. R. Richards, Ph. D. Thesis, University of Pennsylvania, 1961, *Dissertation Abstr.*, **22**, 1029 (1961).

(3) W. Cochran, F. H. C. Crick, and V. Vand, *Acta Crystallogr.*, **5**, 581 (1952).

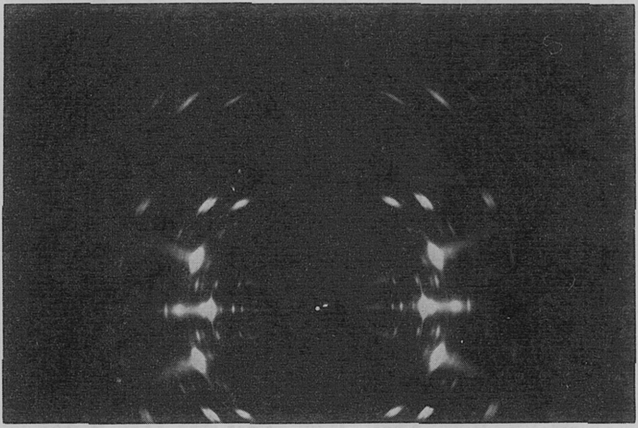


Figure 1. Fiber photograph of PEO taken with the vacuum camera of 20.0-cm diameter. This sample contains a small amount of the planar zigzag modification.

the crystal structure factors can be easily calculated by using $G_{n,l}(R_h)$'s in the same way as the atomic scattering factor in the usual structure factor calculation.

By using the molecular parameters reported in the previous paper ($r_O = 0.527$ Å, $\phi_O = 0.0°$, $Z_O = 0.0$ Å, $r_C = 1.569$ Å, $\phi_C = 30.6°$, and $Z_C = 0.854$ Å),[1] $G_{n,l}(R_h)$'s were calculated according to eq 5, and the determination of the molecular position was tried by using eq 4a and 4b. At first, the molecular position ($x_M = 0.225$, $y_M = 0.131$ or 0.369, and $z_M = 0.016$ or -0.016) was obtained by calculating the structure factors for the reflections on the equator and the seventh layer, starting from the values given by the Patterson synthesis. Subsequently, by using the reflections on the fourth layer, $y_M = 0.369$ and $z_M = -0.016$ were determined for the right-handed molecule and four values for ϕ_M (76, 166, 256, and 346°) were possible. The two values (76 and 256°) for ϕ_M were excluded from the structure factor calculation of the second layer. Consequently, two models were obtained with respect to the azimuthal angle about the helical axis, model I ($x_M = 0.225$, $y_M = 0.369$, $z_M = -0.016$, $\phi_M = 166°$) and model II ($x_M = 0.225$, $y_M = 0.369$, $z_M = -0.016$, $\phi_M = 346°$). When the structure factor calculation was made for the reflections on the first, third, and fifth layers by using the two models, the results gave poor agreement between the calculated and observed structure factors, and two models were indistinguishable.

Least-Squares Refinement under Helical Symmetry D_7. In the trial and error procedures, good agreement between the calculated and observed structure factors was not obtained for the first, third, and fifth layer lines. This was considered to be owing to inaccuracy of the molecular model and the molecular position at this stage. The program of the least-squares method on the basis of the Fourier transform of a helical polymer by Cochran, Crick, and Vand[3] was written in Fortran where a part of the structure factor calculation was made according to the appendix, and was applied to the refinement of the molecular structure and the molecular position.

The refinement started from models I and II. Here, Bessel functions having the order less than the seventh were taken into consideration. The refinement starting from model I converged into the discrepancy factor

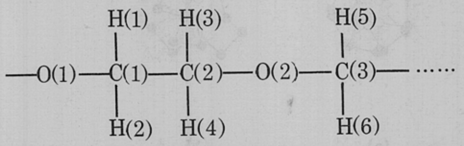
$$R(=\Sigma|\sqrt{I_o} - \sqrt{I_c}|/\Sigma\sqrt{I_o}) = 34.6\%$$

and model II converged into 37.4%. The both discrepancy factors were too poor to determine which model is correct. These unsatisfactory results by the refinement should be considered to be caused by the distortion of the molecule from the exact helical symmetry D_7.

Table I
Parameters Obtained by the Constrained Least-Squares Refinement

			Std Dev
Fractional coordinates of the O(1) atom	x	0.0640	0.003
	y	0.3656	0.003
	z	−0.0424	0.002
Eulerian angles (deg)	θ	−39.0	2.4
	ϕ	−145.4	3.1
	χ	2.5	1.9
Internal rotation angles about the skeletal atoms (deg)	C(1)–C(2)	57.0	4.9
	C(2)–O(2)	193.8	3.2
	O(2)–C(3)	188.8	3.3
	C(3)–C(4)	67.8	4.5
	C(4)–O(3)	182.9	2.7
	O(3)–C(5)	174.1	3.3
	C(5)–C(6)	74.2	4.3
	C(6)–O(4)	204.3	3.1
	O(4)–C(7)	182.8	3.0
	C(7)–C(8)	49.0	4.2
	C(8)–O(5)	180.3	3.2
	O(5)–C(9)	193.9	2.9
	C(9)–C(10)	91.8	4.5
	C(10)–O(6)	186.2	2.9
	O(6)–C(11)	180.3	3.1
	C(11)–C(12)	60.2	4.0
	C(12)–O(7)	182.0	3.2
	O(7)–C(13)	190.5	3.0
	C(13)–C(14)[b]	199.1	4.5
Overall isotropic temperature parameter (Å^2)	B	8.36	0.3

[a] The atoms are numbered as



$$—\mathrm{O(1)}—\underset{\mathrm{H(2)}}{\overset{\mathrm{H(1)}}{\mathrm{C(1)}}}—\underset{\mathrm{H(4)}}{\overset{\mathrm{H(3)}}{\mathrm{C(2)}}}—\mathrm{O(2)}—\underset{\mathrm{H(6)}}{\overset{\mathrm{H(5)}}{\mathrm{C(3)}}}—\cdots\cdots$$

[b] The angle about the bond C(13)–C(14) indicates the dihedral angle O(7)–C(13)–C(14)–H(28). [c] The following parameters were held constant during the refinement: bond length: C–C = 1.54 Å, C–O = 1.43 Å, C–H = 1.09 Å; bond angle: O–C–C = 110°, C–O–C = 112°, H–C–H = 109.5°. The dihedral angle y_m–O(1)–C(1)–C(2) was chosen to be 39.0°, where the y_m axis is the y axis of the coordinate system fixed on the molecule.[5]

Constrained Least-Squares Refinement Free from the Helical Symmetry D_7. After the refinement under the helical symmetry D_7, the least-squares refinement of the crystal structure was made without a constraint of the helical symmetry D_7. If the usual least-squares method was applied to PEO, the number of variables become over 65 even if only the skeletal atoms were taken into account. Therefore, the constrained least-squares method[4,5] was applied to the refinement of the crystal structure, where the bond lengths (C–O, 1.43 Å; C–C, 1.54 Å; and C–H, 1.09 Å) and the bond angles (O–C–C, 110.0°; C–O–C, 112.0°; and H–C–H, 109.5°) were fixed. The number of adjustable parameters was reduced to 28 (Table I) and the four constraining conditions were used. The refinement starting from model I converged to the discrepancy factor 15.7%, but model II did not improve (34.1%). Therefore, the crystal structure refined from model I was found to be correct. The crystal structure is shown in Figure 2 and the molecular structure is shown in Figure 3 along with the

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(4) S. Arnott and A. J. Wonacott, *Polymer*, 7, 157 (1966).

(5) Y. Takahashi, T. Sato, H. Tadokoro, and Y. Tanaka, *J. Polym. Sci., Part A-1*, 11, 233 (1973).

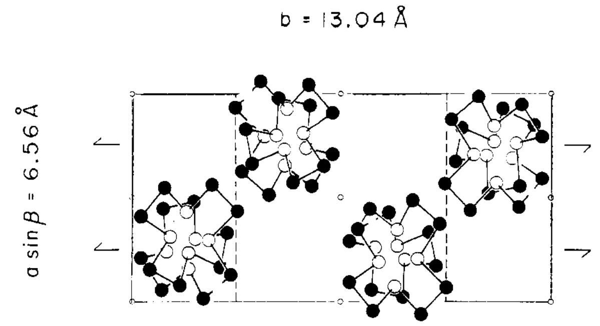

Figure 2. Crystal structure of PEO.

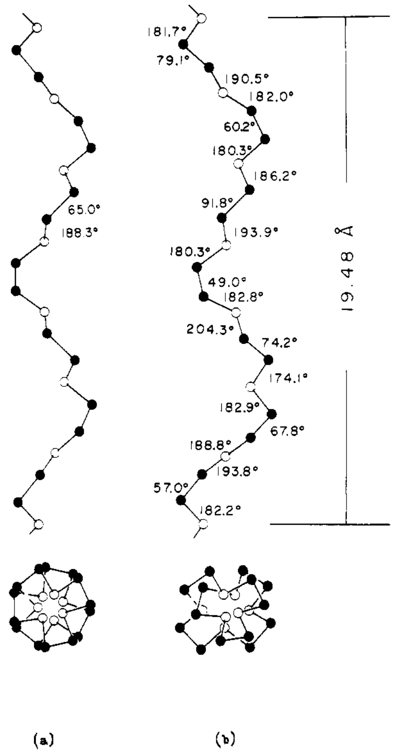

Figure 3. (a) Molecular model of PEO with the helical symmetry D_7 and (b) molecular structure of PEO. The figures give the internal rotation angles.

Table II
Fractional Coordinates of PEO

	x	y	z
O(1)	0.064	0.366	−0.042
C(1)	−0.070	0.313	−0.028
C(2)	0.055	0.250	0.053
O(2)	0.194	0.315	0.123
C(3)	0.345	0.257	0.195
C(4)	0.469	0.329	0.272
O(3)	0.343	0.367	0.296
C(5)	0.449	0.438	0.364
C(6)	0.302	0.485	0.382
O(4)	0.254	0.412	0.423
C(7)	0.063	0.433	0.409
C(8)	0.025	0.355	0.458
O(5)	0.201	0.347	0.543
C(9)	0.172	0.275	0.591
C(10)	0.340	0.289	0.685
O(6)	0.274	0.359	0.722
C(11)	0.433	0.382	0.807
C(12)	0.355	0.457	0.843
O(7)	0.188	0.413	0.840
C(13)	0.105	0.481	0.870
C(14)	−0.045	0.423	0.881
H(1)	−0.162	0.369	−0.023
H(2)	−0.169	0.263	−0.081
H(3)	−0.048	0.214	0.065
H(4)	0.140	0.191	0.046
H(5)	0.270	0.199	0.209
H(6)	0.446	0.220	0.183
H(7)	0.596	0.287	0.324
H(8)	0.526	0.393	0.256
H(9)	0.571	0.398	0.420
H(10)	0.514	0.499	0.348
H(11)	0.373	0.552	0.422
H(12)	0.162	0.508	0.322
H(13)	0.066	0.510	0.431
H(14)	−0.058	0.427	0.342
H(15)	−0.105	0.380	0.457
H(16)	−0.008	0.280	0.428
H(17)	0.024	0.288	0.579
H(18)	0.179	0.198	0.572
H(19)	0.374	0.215	0.717
H(20)	0.477	0.319	0.694
H(21)	0.484	0.312	0.844
H(22)	0.561	0.417	0.810
H(23)	0.477	0.475	0.909
H(24)	0.304	0.528	0.806
H(25)	0.228	0.512	0.931
H(26)	0.026	0.543	0.825
H(27)	−0.138	0.371	0.828
H(28)	−0.144	0.478	0.883

molecular model having the helical symmetry D_7. The final atomic parameters refined by the constrained least-squares method and in the fractional coordinates are given in Tables I and II, respectively. Table III gives the comparison between the calculated and observed structure factors. (See paragraph at end of text regarding supplementary material.)

Discussion

The internal rotation angles about the skeletal bonds are given in Figure 3. Considerable distortion from the helical symmetry D_7 is appreciated by the figure, but the conformation of PEO is essentially the (7/2) helix and consists of TTG sequences, since the seven monomeric units turn two times per fiber period and the average values of the internal rotation angles about the C–O and C–C bonds are 186.0 and 68.4°, respectively. Distortion from the helical symmetry was also found in the case of poly(isobutylene),[6] but it is not so large as PEO. In the case of poly(*tert*-butylethylene oxide),[7] a satisfactory result (R = 16%) was obtained by the analysis under the helical symmetry. Since PEO has no large side group in comparison with the polymers mentioned above, it is considered that the molecular chain of PEO is more flexible and the intermolecular forces act to the main-chain atoms more strongly. Consequently, the large distortion of the PEO molecule may be attributed to the flexibility of the molecular chain and the intermolecular forces. On the other hand, PEO takes the planar zigzag conformation[8] and also takes various conformations in the crystalline complexes with urea,[9] thiourea,[10] and $HgCl_2$.[11,12] This fact may also suggest the flexibility of the PEO molecule.

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(6) T. Tanaka, Y. Chatani, and H. Tadokoro, *J. Polym. Sci., Part A-1*, to be published.

(7) H. Sakakihara, Y. Takahashi, H. Tadokoro, N. Oguni, and H. Tani, *Macromolecules*, **6**, 205 (1973).

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(9) H. Tadokoro, T. Yoshihara, Y. Chatani, and S. Murahashi, *J. Polym. Sci., Part B*, **2**, 363 (1963).

(10) R. Iwamoto and H. Tadokoro, unpublished data, referred in: H. Tadokoro, *Macromol. Rev.*, **1**, 119 (1966).

Table IV
Closest intermolecular Distances

$\mathrm{C}\cdots\mathrm{C} \geq 3.50$ Å
$\mathrm{C}\cdots\mathrm{O} \geq 3.58$ Å
$\mathrm{C}\cdots\mathrm{H} \geq 2.63$ Å
$\mathrm{O}\cdots\mathrm{O} \geq 4.03$ Å
$\mathrm{O}\cdots\mathrm{H} \geq 2.62$ Å
$\mathrm{H}\cdots\mathrm{H} \geq 1.96$ Å

The intermolecular distances within 4.5 Å were calculated for all pairs of atoms and the closest intermolecular distances of C···C, C···O, C···H, O···O, O···H, and H···H are given in Table IV. The van der Waals radii of C, O, and H atoms are generally accepted to be 1.7–1.8 Å, 1.4–1.5 Å, and 1.0–1.2 Å, respectively. Although the distances given in Table IV are mostly reasonable in comparison with the sums of the van der Waals radii, the distances of C···H and H···H are a little too short. These C···H and H···H distances are, however, considered to be permissible from the assumption during the analysis, especially the position of the hydrogen atoms, and from the insufficient accuracy of the present analysis, mainly caused by the difficulty of the intensity measurement.

Appendix

Structure Factor for a Crystal Composed of Helical Molecules. Structure factor for a crystal composed of helical molecules is calculated by summing eq 1 and 2 over all molecules in a unit cell. Before summation, it is necessary to determine the position $\mathbf{x}_M$ (expressed by the fractional coordinates), the azimuthal angle ϕ_M, and the helix sense, *i.e.*, the helix hand (right or left handed) and the direction (upward or downward), of the molecule transformed by the symmetry operation of the space group. The molecular position $\mathbf{x}_M'$ after transformation is easily calculated by the following equation in the same way as the usual structure factor calculation

$$\mathbf{x}_M' = \mathbf{S}\mathbf{x}_M + \mathbf{L} \tag{7}$$

where **S** and **L** are the symmetry operation matrix and vector, respectively, which are given in International Tables for X-Ray Crystallography, Vol. I. The azimuthal angle and helix sense cannot, however, be obtained directly from the symmetry operation matrix and vector. Accordingly, they are determined by the following procedures after transformation to Cartesian coordinate system.

At first, a right-handed Cartesian coordinate system **X** is set so that the origin is on that of the fractional coordinate system, the *Z* axis coincides with the *c* axis of the unit cell, *i.e.*, the fiber axis, and the *X* axis is on the *ac* plane. The Cartesian coordinates $\mathbf{X}_M$ of the molecule are related to the fractional coordinates $\mathbf{x}_M$ by the matrix **C**

$$\mathbf{x}_M = \mathbf{C}\mathbf{X}_M \tag{8}$$

Accordingly, the Cartesian coordinates $\mathbf{X}_M'$ after transformation are given by

$$\mathbf{X}_M' = \mathbf{C}^{-1}\mathbf{S}\mathbf{C}\mathbf{X}_M + \mathbf{C}^{-1}\mathbf{L} = \mathbf{R}\mathbf{X}_M + \mathbf{C}^{-1}\mathbf{L}$$
$$\mathbf{R} = \mathbf{C}^{-1}\mathbf{S}\mathbf{C} \tag{9}$$

where $\mathbf{C}^{-1}$ is the inverse matrix of **C**, and **R** is the orthogonal symmetry operation matrix. Here, the matrices $\mathbf{C}$, $\mathbf{C}^{-1}$, $\mathbf{S}$, and $\mathbf{R}$ correspond to the matrices $[\boldsymbol{\beta}]$, $[\boldsymbol{\alpha}]$, $[\mathbf{P}]$, and $[\boldsymbol{\rho}]$, respectively, which are used in International Tables for X-Ray Crystallography, Vol. II, p 62.

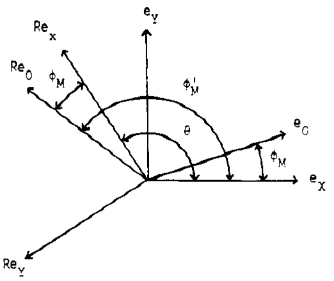

Figure 4. Relation among unit vectors.

The azimuthal angle ϕ_M is given by (Figure 4)

$$\cos\phi_M = \mathbf{e}_0\cdot\mathbf{e}_X \tag{10a}$$

$$\sin\phi_M = \mathbf{e}_0\cdot\mathbf{e}_Y \tag{10b}$$

where $\mathbf{e}_X$, $\mathbf{e}_Y$, $\mathbf{e}_Z$ are the unit vectors along the *X*, *Y*, and *Z* axes of the Cartesian coordinate system, respectively, and $\mathbf{e}_0$ is the unit vector pointing from the origin of the molecule to the atom chosen for indicating the azimuthal angle. The azimuthal angle ϕ_M' of the molecule after transformation **R** is given by,

$$\begin{aligned}\cos\phi_M' &= \mathbf{Re}_0\cdot\mathbf{e}_X\\ &= (\mathbf{Re}_0\cdot\mathbf{Re}_X)(\mathbf{Re}_X\cdot\mathbf{e}_X) + (\mathbf{Re}_0\cdot\mathbf{Re}_Y)(\mathbf{Re}_Y\cdot\mathbf{e}_X)\end{aligned} \tag{11a}$$

$$\begin{aligned}\sin\phi_M' &= \mathbf{Re}_0\cdot\mathbf{e}_Y\\ &= (\mathbf{Re}_0\cdot\mathbf{Re}_X)(\mathbf{Re}_X\cdot\mathbf{e}_Y) + (\mathbf{Re}_0\cdot\mathbf{Re}_Y)(\mathbf{Re}_Y\cdot\mathbf{e}_Y)\end{aligned} \tag{11b}$$

Consequently, by defining the angle between the vectors $\mathbf{e}_X$ and $\mathbf{Re}_X$ as θ, the angle ϕ_M' is given by the following equation

$$\phi_M' = \pm\phi_M + \theta \tag{12}$$

where θ is obtained by

$$\cos\theta = \mathbf{Re}_X\cdot\mathbf{e}_X \tag{13a}$$

$$\sin\theta = \mathbf{Re}_X\cdot\mathbf{e}_Y \tag{13b}$$

and the sign of ϕ_M in eq 12 is determined by the sign of the following equation

$$\pm\cos\theta = \mathbf{Re}_Y\cdot\mathbf{e}_Y \tag{14}$$

The direction and helix hand of the molecule after transformation are determined by the signs of the following equations

$$\pm 1 = \mathbf{Re}_Z\cdot\mathbf{e}_Z \tag{15}$$

$$\pm 1 = (\mathbf{Re}_X \times \mathbf{Re}_Y)\cdot\mathbf{Re}_Z \tag{16}$$

When the sign in eq 15 (or eq 16) is positive, the direction (or helix hand) of the molecule after transformation is the same as the original one, and when the sign in eq 15 (or eq 16) is negative, the direction (or helix hand) is opposite.

These procedures were used in the programs of the structure factor calculation and the least squares method for helical polymers, which were also applied to poly(*tert*-butylethylene oxide).[7]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number MACRO-73-672.

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(12) M. Yokoyama, H. Ishihara, R. Iwamoto, and H. Tadokoro, *Macromolecules*, **2**, 184 (1969).