Conformational and Packing Stability of Crystalline Polymers. V. A Method for Calculating Conformational Parameters of Polymer Chains with Glide, Helical, and Translational Symmetries

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ABSTRACT: Mathematical expressions for the conformations of linear polymer chains with glide, helical, and translational symmetries were derived, which are represented only by independent internal rotation angles about skeletal bonds: $(k-1)$ for glide or helical symmetry and $(k-3)$ for translational symmetry only, k being the number of the main chain atoms in the structural unit. For each symmetry, the remaining internal rotation angles are expressed as explicit functions of the independent internal rotation angles. Especially for helical symmetry, one of the helical parameters θ is included as a parameter in the expression of the one remaining internal rotation angle. These equations give simultaneously the space-fixed atomic cartesian coordinates whose Z axis coincides with the molecular axis. The applications of the method derived here were made to several polymers: hypothetical models of the polymethylene chain whose translational unit consists of three or four methylene groups, poly(*tert*-butylethylene oxide), and rubber hydrochloride.

For the structure analyses of polymers by the use of X-ray diffraction and infrared and Raman spectroscopic methods and for energy calculations it is indispensable to describe mathematically conformational models which satisfy definite symmetries and fiber identity periods in terms of bond lengths, bond angles, and internal rotation angles.

For the case of polymer chains with glide symmetry, Ganis and Temussi derived an analytical procedure for the conformation.[1] Recently another treatment was reported in this laboratory[2] by extending Shimanouchi and Mizushima's mathematical treatments.[3] For models of helical polymers, there are mathematical equations derived by Shimanouchi and Mizushima[3] and improved by Miyazawa.[4] According to these papers the helical parameters, *i.e.*, the translation along the helix axis per structural unit d and the rotation angle about the helix axis per structural unit θ, are given explicitly by the equations in terms of bond lengths, bond angles, and internal rotation angles. Moreover Sugeta and Miyazawa reformed the equations to matrix formulas which should be suitable for the electronic computer.[5]

We derived new mathematical equations which can clarify the relationship between the internal coordinates and the conformational parameters. The methods reported in the present paper are applicable to every case of glide, helical, and translational symmetries. In the practical applications of the foregoing methods for each symmetry, the model settings must be carried out by varying all k internal rotation angles with respect to main chain atoms in the structural unit, where the number of main chain atoms in the structural unit is k and the bond lengths and bond angles are held fixed. However, in the present method, the number of variable internal rotation angles is $(k-1)$ for polymers with glide or helical symmetry and $(k-3)$ for the case of translational symmetry only. Therefore the present method reduces the amount of calculation and is especially favorable to the case where k is 3 or more.

Computation of Molecular Parameters

Setting Up the Basic Coordinate System. We assume an extended skeletal polymer chain shown as follows (see Figure 1)

$$\begin{array}{c} \mathrm{M}_1-\mathrm{M}_2-\ldots-\mathrm{M}_{j-1}-\mathrm{M}_j-\mathrm{M}_{j+1}-\ldots \\ r_j \\ \phi_j \\ \tau_j \end{array}$$

where M_j is the jth skeletal atom, r_j is the bond length between M_{j-1} and M_j, ϕ_j is the bond angle between the bonds $\mathrm{M}_{j-1}\mathrm{M}_j$ and $\mathrm{M}_j\mathrm{M}_{j+1}$, and τ_j is the internal rotation angle around the bond $\mathrm{M}_{j-1}\mathrm{M}_j$. The definition of the internal rotation angle is the same as that of ref 2. As shown in Figure 1, a right-handed cartesian coordinate system $\mathbf{x}$ is defined as a basic coordinate system so that the first atom is fixed at the origin, the second atom lies on the x axis, and the third atom is on the xy plane. Here $\mathbf{x}(j)$ is defined as the coordinates of the jth atom in the $\mathbf{x}$ system. The relationship between $\mathbf{x}(j-1)$ and $\mathbf{x}(j)$ can be represented by the following recursion formula

$$\mathbf{x}(j) = \mathrm{A}_2{}^{\phi}\mathrm{T}_{3,j-1}\mathrm{B}_j + \mathbf{x}(j-1) \qquad j \geqq 4 \tag{1}$$

where

$$\mathbf{x}(1) = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \ \mathbf{x}(2) = \begin{bmatrix} r_2 \\ 0 \\ 0 \end{bmatrix},$$

$$\text{and } \mathbf{x}(3) = \begin{bmatrix} -r_3 \cos\phi_2 + r_2 \\ r_3 \sin\phi_2 \\ 0 \end{bmatrix} \tag{2}$$

$$\mathrm{T}_{3,j-1} = \mathrm{A}_3\mathrm{A}_4 \ldots \mathrm{A}_{j-1} \tag{3}$$

$$\mathrm{A}_j = \mathrm{A}_j{}^{\tau}\mathrm{A}_j{}^{\phi} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\tau_j & -\sin\tau_j \\ 0 & \sin\tau_j & \cos\tau_j \end{bmatrix} \times \begin{bmatrix} -\cos\phi_j & -\sin\phi_j & 0 \\ \sin\phi_j & -\cos\phi_j & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ and } \mathrm{B}_j = \begin{bmatrix} r_j \\ 0 \\ 0 \end{bmatrix} \tag{4}$$

Glide Symmetry. The fiber identity period of a polymer chain with glide symmetry consists of two structural units; the number of the main chain atoms in the structural unit is k. By using $(k-1)$ internal rotation angles, the positions of all atoms can be represented in a cartesian coordinate system $\mathbf{X}$, where the Z axis is parallel to the molecular axis and the YZ plane coincides with the glide plane (see Figure 1). Let us show the transformation from the $\mathbf{x}$ system to the $\mathbf{X}$ system.

When the values of $\tau_3, \tau_4, \ldots, \tau_{k+1}$ $(=-\tau_1)$ are assumed as $(k-1)$ independent internal rotation angles, the coordi-

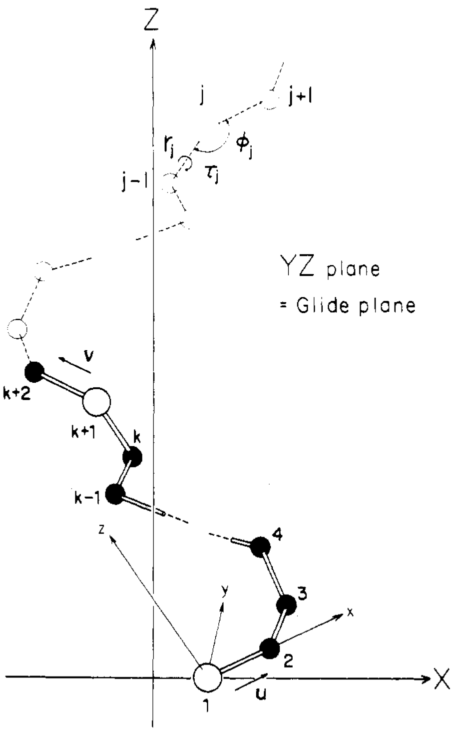


Figure 1. A molecular model with glide symmetry in the basic coordinate system (the **x** system) and in the final coordinate system (the **X** system).

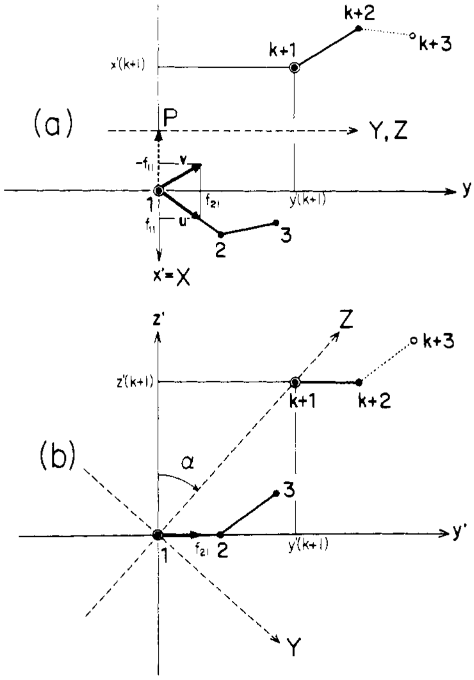


Figure 2. The relationship between the **x'** system and the **X** system in the case of glide symmetry. The **X** system can be obtained by rotating α the **x'** system about the x' axis and translating by **P** along the x' axis. (a) The $x'y'$ projection of the molecular model with glide symmetry and (b) the $y'z'$ projection.

nates of the first, second, . . . , $(k + 2)$th atoms in the **x** system $[\mathbf{x}(1), \mathbf{x}(2), \ldots, \mathbf{x}(k + 2)]$ are determined by the use of eq 1. Here the unit vectors of the bonds $\mathbf{r}_2$ and $\mathbf{r}_{k+2}$ in the **x** system are represented as **u** and **v**, respectively (see Figure 1). A new cartesian coordinate system **x'** is introduced, where the x' and y' axes are parallel to the vectors $\mathbf{u} - \mathbf{v}$ and $\mathbf{u} + \mathbf{v}$, respectively, as shown in Figure 2a. Then the transformation from the **x** system to the **x'** system is given as follows[6]

$$\mathbf{x}'(j) = [(\mathbf{u} - \mathbf{v})/|\mathbf{u} - \mathbf{v}|,\ (\mathbf{u} + \mathbf{v})/|\mathbf{u} + \mathbf{v}|,\ (\mathbf{u} \times \mathbf{v})/|\mathbf{u} \times \mathbf{v}|]\mathbf{x}(j) = \mathbf{F}\mathbf{x}(j) \qquad (5)$$

$$\mathbf{u} = [\mathbf{x}(2) - \mathbf{x}(1)]/r_2 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \text{ and } \mathbf{v} = [\mathbf{x}(k + 2) - \mathbf{x}(k + 1)]/r_{k+2} \qquad (6)$$

where the elements of the **F** matrix are denoted as

$$\mathbf{F} = \begin{bmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{bmatrix} \qquad (7)$$

In Figure 2b, which is the projection on the $y'z'$ plane, the **x'** system is rotated around the x' axis by α so that the Z axis coincides with the direction connecting the first atom to the $(k + 1)$th atom. Next, in Figure 2a, which is the projection on the $x'y'$ plane, the origin is translated along the x' axis by $x'(k + 1)/2$, so that the YZ plane coincides with the glide plane. The matrix **G** and the vector **P** which correspond to the above transformations are as follows.

$$\mathbf{G} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{bmatrix} \text{ and } \mathbf{P} = \begin{bmatrix} x'(k + 1)/2 \\ 0 \\ 0 \end{bmatrix} \qquad (8)$$

$$\begin{aligned} \sin\alpha &= y'(k + 1)/[y'(k + 1)^2 + z'(k + 1)^2]^{1/2} \\ \cos\alpha &= z'(k + 1)/[y'(k + 1)^2 + z'(k + 1)^2]^{1/2} \end{aligned} \qquad (9)$$

Consequently the transformation from the **x** system to the **X** system is given as follows.

$$\mathbf{X}(j) = \mathbf{G}\mathbf{F}\mathbf{x}(j) - \mathbf{P} \qquad (10)$$
$$(j = 1, 2, \ldots, k + 2)$$

The fiber identity period I is a length of twice the Z element of $\mathbf{X}(k + 1)$.

$$I = 2Z(k + 1) \qquad (11)$$

Next the value of one remaining internal rotation angle τ_{k+2} $(= -\tau_2)$ is given in the following way. By using eq 1, the coordinates of the $(k + 3)$th atom in the **x** system are written as

$$\mathbf{x}(k + 3) = \mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1}\mathbf{A}_{k+2}\mathbf{B}_{k+3} + \mathbf{x}(k + 2) \qquad (12)$$

where $\mathbf{A}_{k+2}$ includes the undetermined parameter τ_{k+2}. On the other hand, under glide symmetry, the coordinates of the $(k + 3)$th atom in the **X** system are simply given as

$$\begin{bmatrix} X(k + 3) \\ Y(k + 3) \\ Z(k + 3) \end{bmatrix} = \begin{bmatrix} -X(3) \\ Y(3) \\ Z(3) \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ Z(k + 1) \end{bmatrix} \qquad (13)$$

From eq 10 and 12, we have

$$\begin{aligned} \mathbf{X}(k + 3) &= \mathbf{G}\mathbf{F}\mathbf{x}(k + 3) - \mathbf{P} \\ &= \mathbf{G}\mathbf{F}[\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1}\mathbf{A}_{k+2}\mathbf{B}_{k+3} + \mathbf{x}(k + 2)] - \mathbf{P} \\ &= \mathbf{G}\mathbf{F}(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1})\mathbf{A}_{k+2}\mathbf{B}_{k+3} + \mathbf{X}(k + 2) \end{aligned} \qquad (14)$$

Then

$$\mathbf{A}_{k+2}\mathbf{B}_{k+3} = [\mathbf{G}\mathbf{F}(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1})]^{t}[\mathbf{X}(k + 3) - \mathbf{X}(k + 2)] \qquad (15)$$

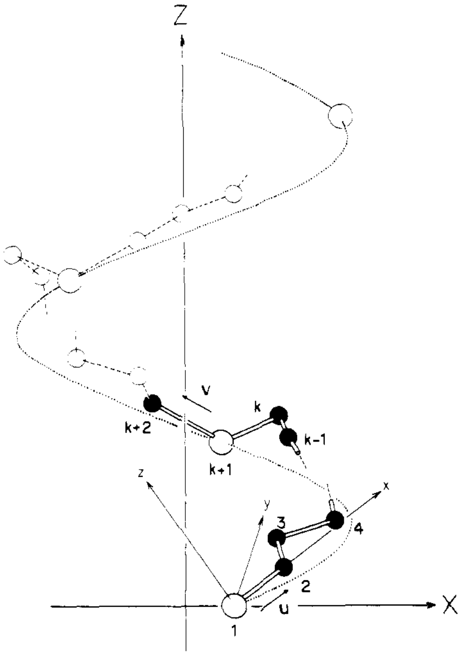


Figure 3. A molecular model with helical symmetry in the basic coordinate system (the **x** system) and in the final coordinate system (the **X** system).

where t denotes the transposed matrix. The right side of eq 15 can be obtained by substituting eq 13 for $\mathbf{X}(k+3)$. We denote the elements of $\{[\mathbf{GF}(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1})]^{t}[\mathbf{X}(k+3) - \mathbf{X}(k+2)]\}/r_{k+3}$ by (ξ, η, ζ). Since the left side of eq 15 can be given by the use of eq 4, the following relationship is found.

$$\mathbf{A}_{k+2}\mathbf{B}_{k+3} = r_{k+3}\begin{bmatrix} -\cos\ \phi_{k+2} \\ \sin\ \phi_{k+2}\cos\ \tau_{k+2} \\ \sin\ \phi_{k+2}\sin\ \tau_{k+2} \end{bmatrix} = r_{k+3}\begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix} \tag{16}$$

Consequently, we have

$$\begin{aligned} \cos\ \tau_{k+2} &= \eta/\sin\ \phi_{k+2} \\ \sin\ \tau_{k+2} &= \zeta/\sin\ \phi_{k+2} \end{aligned} \tag{17}$$

Helical Symmetry (u/t). We consider a linear polymer chain with helical symmetry (u/t) which contains u structural units and t turns in the fiber identity period. Under helical symmetry the number of independent internal rotation angles is $(k-1)$. Let us show the transformation from the **x** system to the **X** system as shown in Figure 3. The Z axis in the **X** system coincides with the helix axis.

As in the case of glide symmetry, the transformation from the first cartesian coordinate system **x** to the **x′** system is carried out by eq 5,[7] where $\tau_{k+1} = \tau_1$. When the angle between the unit vectors **u** and **v** defined in eq 6 is denoted as ψ (see Figure 4), its value is given as

$$\psi = 2\cos^{-1} f_{21} \tag{18}$$

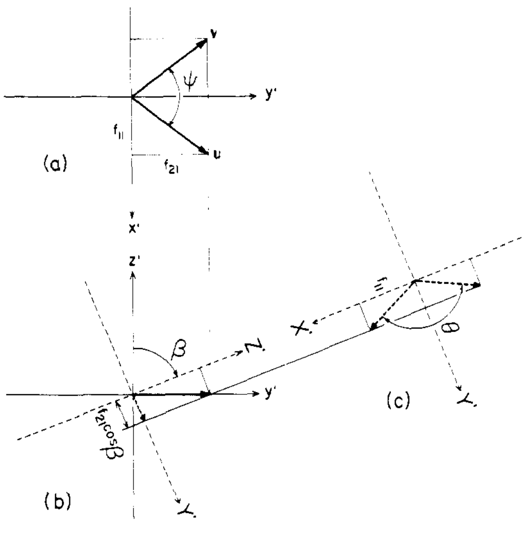


Figure 4. The relationship between the **x′** system and the **X′** system in the case of helical symmetry. The **X′** system can be obtained by rotating β in the **x′** system about the x' axis. (a) The $x'y'$ projection of **u** and **v**, (b) the $y'z'$ projection, and (c) the $X'Y'$ projection.

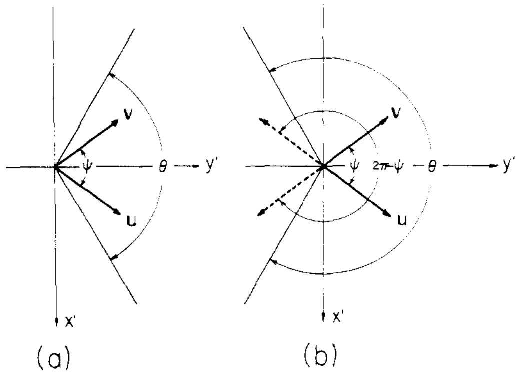


Figure 5. The relationship between ψ (the angle between the unit vectors **u** and **v**) and θ $(=2\pi t/u)$: (a) $0 < \theta < \pi$ and (b) $\pi < \theta < 2\pi$, where always $0 < \psi < \pi$. The case of $\theta = \pi$ corresponds to (2/1) helical symmetry.

Next, by rotating the **x′** system around the x' axis by β, a new cartesian coordinate system **X′** is obtained, where the projection of ψ to the $X'Y'$ plane becomes θ $(=2\pi t/u)$. For θ, there are cases (a) $0 < \theta < \pi$ and (b) $\pi < \theta < 2\pi$ as shown in Figure 5. The case of $\psi = \pi$ corresponds to a (2/1) helix. As can be understood from the definition, **u** and **v** are always in the first and second quadrants of the **x′** system, respectively. This means $0 < \psi < \pi$. If ψ satisfies eq 19, it is possible to make the projection of ψ to the $X'Y'$ plane coincide with θ by rotating the triangle containing ψ around the x' axis.

$$\psi \leqq \theta \leqq 2\pi - \psi \qquad 0 < \psi < \pi \tag{19}$$

The rotation by β is written as

$$\mathbf{H} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\ \beta & -\sin\ \beta \\ 0 & \sin\ \beta & \cos\ \beta \end{bmatrix} \tag{20}$$

$$\beta = \cos^{-1}\,[(f_{11}/f_{21})\cot\ (\theta/2)] \qquad 0 < \beta < \pi \tag{21}$$

Further, the vector **Q** is introduced to transform from the **X′** system to the final cartesian coordinate system **X** (see Figure 9). The elements of **Q** are written as

$$\mathbf{Q} = (^1\!/_2)\begin{bmatrix} 1 & -\cot\ (\theta/2) & 0 \\ \cot\ (\theta/2) & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}\mathbf{HF}\mathbf{x}(k+1) \tag{22}$$

The derivations of eq 21 and 22 are given in Appendix I. Consequently we have

$$\mathbf{X}(j) = \mathbf{HF}\mathbf{x}(j) - \mathbf{Q} \qquad j = 1, 2, \ldots, k+2 \tag{23}$$

The fiber identity period I is

$$I = ud = u|Z(k+1)| \tag{24}$$

The coordinates of the $(k+3)$th atom in the $\mathbf{X}$ system are given by eq 25. Then the value of the remaining internal rotation angle τ_{k+2} $(=\tau_2)$ can be calculated by the same treatment of the case of the glide symmetry

$$\begin{bmatrix} X(k+3) \\ Y(k+3) \\ Z(k+3) \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X(3) \\ Y(3) \\ Z(3) \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ Z(k+1) \end{bmatrix} \tag{25}$$

$$\begin{aligned} \cos\tau_{k+2} &= \eta'/\sin\phi_{k+2} \\ \sin\tau_{k+2} &= \zeta'/\sin\phi_{k+2} \end{aligned} \tag{26}$$

where η' and ζ' are the second and third elements of $\{[\mathbf{HF}(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k+1})]^{\mathrm{t}}[\mathbf{X}(k+3) - \mathbf{X}(k+2)]\}/r_{k+3}$, respectively.

Special Case (1/0). Translational Symmetry Only. We consider the special helical symmetry in which the number of turns is zero (1/0) ($u = 1$ and $t = 0$). In this case, the number of independent internal rotation angles is $(k-3)$.

When the values of $(k-3)$ independent internal rotation angles $\tau_3, \tau_4, \ldots, \tau_{k-1}$ are assumed, the coordinates of the main chain atoms $\mathbf{x}(1), \mathbf{x}(2), \ldots, \mathbf{x}(k)$ are readily determined by the use of eq 1, where the elements of $(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})$ become apparent.

$$\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \tag{27}$$

$$(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})\mathbf{A}_k = \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} \tag{28}$$

Although eq 28 includes the undetermined parameter τ_k, the elements of $\mathbf{r}_{k+2}$ in the $\mathbf{x}$ system can be expressed by the following

$$\mathbf{r}_{k+2} = \mathbf{x}(k+2) - \mathbf{x}(k+1) = (\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})\mathbf{A}_k\mathbf{A}_{k+1}\mathbf{B}_{k+2} \tag{29}$$

where $\mathbf{A}_{k+1}$ contains the undetermined parameter τ_{k+1} $(=\tau_1)$. By the translational symmetry, the bond vector $\mathbf{r}_{k+2}$ is parallel to the bond vector $\mathbf{r}_2$ $(=\mathbf{B}_2)$. Then we have

$$(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})\mathbf{A}_k\mathbf{A}_{k+1}\mathbf{B}_{k+2} = \mathbf{r}_2 = \mathbf{B}_2 \tag{30}$$

Accordingly

$$\mathbf{A}_{k+1}\begin{bmatrix} r_{k+2} \\ 0 \\ 0 \end{bmatrix} = [(\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})\mathbf{A}_k]^{\mathrm{t}}\begin{bmatrix} r_2 \\ 0 \\ 0 \end{bmatrix} \tag{31}$$

Since $r_{k+2} = r_2$, eq 31 is rewritten as eq 32 by using eq 28.

$$\begin{bmatrix} -\cos\phi_{k+1} \\ \sin\phi_{k+1}\cos\tau_{k+1} \\ \sin\phi_{k+1}\sin\tau_{k+1} \end{bmatrix} = \begin{bmatrix} b_{11} \\ b_{12} \\ b_{13} \end{bmatrix} \tag{32}$$

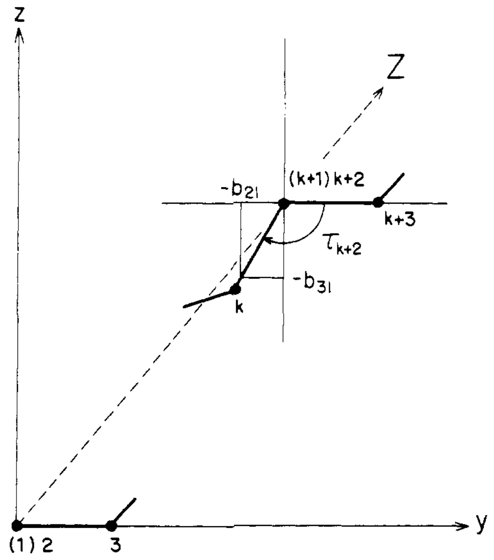


Figure 6. The *yz* projection of the molecular model with the translational symmetry only, where $\mathbf{x}(k+3) = \mathbf{x}(k+1) + \mathbf{x}(3)$.

From eq 27, 28, and 32, the value of b_{11} is given as

$$b_{11} = -\cos\phi_{k+1} = -a_{11}\cos\phi_k + a_{12}\sin\phi_k\cos\tau_k + a_{13}\sin\phi_k\sin\tau_k \tag{33}$$

By resolving this quadratic equation of τ_k, we have[8]

$$\begin{aligned} \cos\tau_k &= [a_{12} \pm a_{13}(1 - a_{11}{}^2 - \rho^2)^{1/2}]/(1 - a_{11}{}^2) \\ \sin\tau_k &= [a_{13} \mp a_{12}(1 - a_{11}{}^2 - \rho^2)^{1/2}]/(1 - a_{11}{}^2) \end{aligned} \tag{34}$$

$$\rho = (-\cos\phi_{k+1} + a_{11}\cos\phi_k)/\sin\phi_k \tag{35}$$

Since the discriminant should not be less than zero for a nontrivial value of τ_k, the following condition arises.

$$D = (1 - a_{11}{}^2 - \rho^2) \geqq 0 \tag{36}$$

It is noted that the first assumed $(k-3)$ internal rotation angles are not entirely independent of each other and eq 36 should be satisfied. At this stage, the elements of $(\mathbf{A}_2{}^{\phi}\cdot\mathbf{T}_{3,k-1})\mathbf{A}_k$ (eq 28) become apparent by substituting the value of τ_k obtained from eq 34. Then the value of τ_{k+1} $(=\tau_1)$ can be calculated by eq 32.

$$\begin{aligned} \cos\tau_{k+1} &= b_{12}/\sin\phi_{k+1} \\ \sin\tau_{k+1} &= b_{13}/\sin\phi_{k+1} \end{aligned} \tag{37}$$

By using eq 1 and 28, the bond vector $\mathbf{r}_{k+1}$ in the $\mathbf{x}$ system is expressed as

$$\mathbf{r}_{k+1} = \mathbf{x}(k+1) - \mathbf{x}(k) = (\mathbf{A}_2{}^{\phi}\mathbf{T}_{3,k-1})\mathbf{A}_k\mathbf{B}_{k+1} = r_{k+1}\begin{bmatrix} b_{11} \\ b_{21} \\ b_{31} \end{bmatrix} \tag{38}$$

The coordinates of the $(k+3)$th atom should be $\mathbf{x}(k+1) + \mathbf{x}(3)$. The *yz* projection of the molecular model is shown in Figure 6. From this figure, it is understandable that the value of τ_{k+2} $(=\tau_2)$ is given by eq 39.

$$\begin{aligned} \cos(2\pi - \tau_{k+2}) &= -b_{21}/(b_{21}{}^2 + b_{31}{}^2)^{1/2} \\ \sin(2\pi - \tau_{k+2}) &= -b_{31}/(b_{21}{}^2 + b_{31}{}^2)^{1/2} \end{aligned} \tag{39}$$

The equations derived here, which are applicable to any linear polymer chain, are convenient for computation with an electronic computer. In Appendix II are shown the flow charts of the programs aiming to calculate the possible sets of the internal rotation angles and the atomic cartesian coordinates satisfying molecular symmetries and the fiber identity period.

Applications

We applied the methods derived in the preceding sections to the following cases: (a) hypothetical models of the polymethylene chain whose fiber identity period consists of three or four methylene groups [for simplicity, these polymers are called polytrimethylene and polytetramethylene, respectively], (b) poly(*tert*-butylethylene oxide), and (c) rubber hydrochloride. The conformational energies for case c were calculated only for the possible conformations satisfying the observed fiber identity period (I_0) and molecular symmetry. The bond lengths and bond angles used in the present paper are as follows: C–C = 1.54 Å, C–H = 1.09 Å, C–O = 1.43 Å, C–Cl = 1.73 Å, and all the bond angles are tetrahedral. The methyl group of rubber hydrochloride was assumed to be in the staggered form.

Polytrimethylene. Here we assume polytrimethylene with only translational symmetry, the fiber identity period of which consists of three methylene groups (k = 3).

$$[-\underset{\tau_1}{CH_2(1)}-\underset{\tau_2}{CH_2(2)}-\underset{\tau_3}{CH_2(3)}-]_n$$

The independent internal rotation angles should be zero, because (k − 3) angles are independent. From eq 27, we have a $a_{11} = 1/3$, $a_{12} = -8^{1/2}/3$, and $a_{13} = 0$. Then eq 34, 37, and 39 give $\tau_3 = \pm 104°29'$ ($\cos\tau_3 = -1/4$ and $\sin\tau_3 = \pm 15^{1/2}/4$) and $\tau_3 = \tau_4$ $(=\tau_1) = \tau_5$ $(=\tau_2)$. Thus, polytrimethylene can take only two threefold helical conformations (right- and left-handed helices) in order to have translational symmetry.

Polytetramethylene. For this polymer we consider three cases, *i.e.*, glide, twofold helix, and translation only. For the cases with glide and twofold helical symmetries, the main chain atoms of the structural unit are 2 (=k) and the number of independent internal rotation angles (k − 1) becomes 1. On the other hand, for the case with only translational symmetry, the number of main chain atoms of the fiber identity period is 4 (=k) and the number of independent internal rotation angles (k − 3) becomes 1. The sets of internal rotation angles for these cases are classified as follows.

	τ_1	τ_2	τ_3	τ_4
	$[-CH_2(1)$ −	$CH_2(2)$ −	$CH_2(3)$ −	$CH_2(4)-]_n$
glide	A	B	−A	−B
twofold helix	A	B	A	B
only translation	A	B	C	D

In the case of glide symmetry, the elements of **F**, **G**, and **P** (eq 7 and 8) are obtained by assuming the value of τ_3 $(=-\tau_1)$. Then the values of (ξ, η, ζ) are given and the remaining internal rotation angle τ_4 $(=-\tau_2)$ can be calculated from eq 17. For any value of τ_3 except 180°, τ_4 is always 180°, and τ_4 can take any value for τ_3 = 180°. In other words, under glide symmetry, one of the two internal rotation angles is always 180° and the other one can take an arbitrary value. The relationship between τ_3 $(=-\tau_1)$ and τ_4 $(=-\tau_2)$ under glide symmetry is illustrated by the bold solid line in Figure 7. In the case of the twofold helix, the elements of **F**, **H**, and **Q** (eq 7, 20, and 22) are obtained for each value of τ_3 $(=\tau_1)$. Then we calculate the values of (ξ', η', ζ'), and the remaining internal rotation angle τ_4 $(=\tau_2)$ is given by eq 26. There is always a solution of τ_4 for any value of τ_3, since the twofold helix ($\theta = \pi$) always satisfies eq 19. The special case (**v** parallel to **u**) corresponds to that of τ_3 = 180°, where τ_4 satisfying the twofold helical symmetry is never present because the model cannot but take the glide or translational symmetry only. The relationship between τ_3 $(=\tau_1)$ and τ_4 $(=\tau_2)$ under the two-fold helical symmetry is shown by the bold broken line in Figure 7. For the case with only translational symmetry, the structural unit (=the fiber identity period) coincides with four methylene groups. There are two values of τ_4 for each value of τ_3 by eq 34. For each of these values of τ_4, we can calculate the two remaining internal rotation angles τ_5 $(=\tau_1)$ and τ_6 $(=\tau_2)$ from eq 37 and 39. Accordingly there are two sets of four internal rotation angles for each value of τ_3. These two sets correspond to the conformations with glide and twofold helical symmetries.

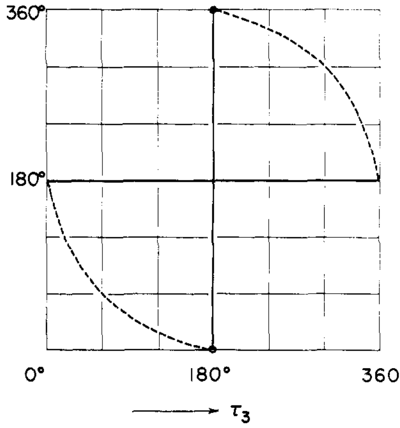
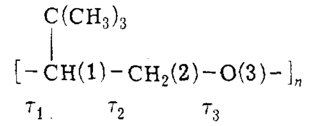


Figure 7. The relationship between τ_3 and τ_4 of polytetramethylene under glide symmetry (bold solid line) and twofold helical symmetry (bold broken line).

Poly(*tert*-butylethylene oxide). As a more general application of the present treatment to the helical polymer (u/t), we treated poly(*tert*-butylethylene oxide), the crystal structure of which was determined in this laboratory.[9] This polymer has a (9/4) helical structure with the fiber identity period 24.65 Å. The numbering of internal rotation angles of the main chain is denoted as follows (k = 3).



$$[-\underset{\tau_1}{\overset{\overset{C(CH_3)_3}{|}}{CH(1)}}-\underset{\tau_2}{CH_2(2)}-\underset{\tau_3}{O(3)}-]_n$$

In the previous paper[10] we used the molecular parameter equations given by Miyazawa[4] in order to obtain the sets of internal rotation angles which satisfy the (9/4) helical symmetry and the fiber identity period 24.65 Å, where we had to vary practically all three internal rotation angles (τ_1, τ_2, and τ_3) although these are not independent of each other. According to the present method, the sets of three internal rotation angles with (9/4) helical symmetry can be obtained by assuming only two variables [τ_3 and τ_4 $(=\tau_1)$]. The decrease of variables from 3 to 2 enables considerable reduction of the amount of calculation (see Appendix II). Furthermore, since τ_5 $(=\tau_2)$ can be calculated by using τ_3, τ_4, and θ, the conformations with these internal rotation angles strictly maintain helical symmetry. For the left-handed helix of this polymer, u = 9 and t = 5 ($\theta = 10\pi/9$) for practical convenience. Varying τ_3 and τ_4 from 0 to 360°, we can calculate the elements of **F** in eq 7. At this stage the assumed values of τ_3 and τ_4 are omitted if the angle ψ does not satisfy eq 19 and furthermore if $9|Z(4)|$ in eq 24 is not within tolerance of the observed fiber identity period 24.65 Å. Then the remaining internal rotation angle τ_5 $(=\tau_2)$ can be calculated from eq 26. The thus obtained possible sets of

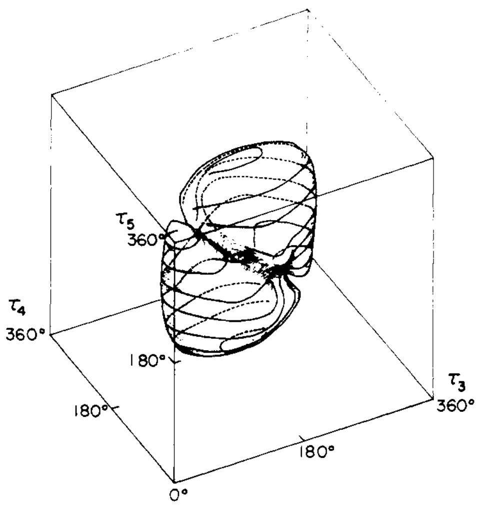


Figure 8. The perspective view of the closed surface showing the relationship between τ_3, τ_4, and τ_5 of rubber hydrochloride under glide symmetry and fiber identity period 8.95 Å.

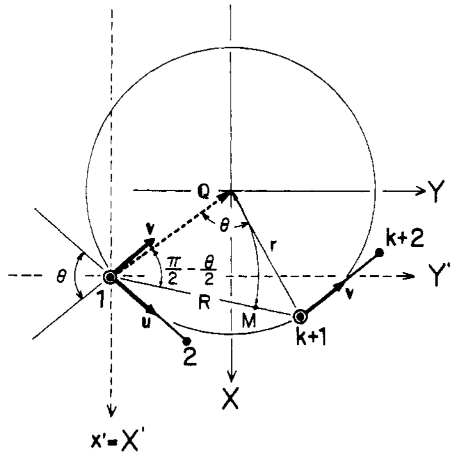
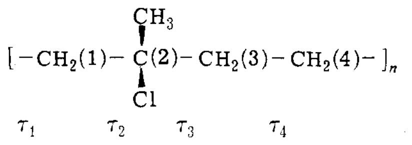


Figure 9. The relationship between the **X'** system and the **X** system. The **X** system can be obtained by translating the **X'** system by **Q** on the $X'Y'$ plane.

internal rotation angles are on the two closed curves in a cube defined by the three-dimensional cartesian coordinates τ_1 $(=\tau_4)$, τ_2 $(=\tau_5)$, and τ_3, each covering from 0 to 360°. The result obtained by using the present method coincides with that in the previous paper.[10]

Rubber Hydrochloride. According to the structure analysis of rubber hydrochloride by Bunn and Garner,[11] the molecular chain with syndiotactic configuration has a glide plane as its only element of symmetry with the fiber identity period 8.95 Å. The internal rotation angles of the main chain are as follows (k = 4).



$$\underset{\tau_1}{[-\mathrm{CH_2(1)}-}\ \underset{\tau_2}{\overset{\mathrm{CH_3}}{\underset{\mathrm{Cl}}{\mathrm{C(2)}}}}-\underset{\tau_3}{\mathrm{CH_2(3)}}-\underset{\tau_4}{\mathrm{CH_2(4)}-]_n}$$

The internal rotation angles of the subsequent structural unit are given by changing the signs of the above four internal rotation angles, where C(6) has the opposite steric configuration to C(2). Under glide symmetry, the number of independent internal rotation angles is 3. Varying three independent internal rotation angles τ_3, τ_4, and τ_5 $(=-\tau_1)$ from 0 to 360°, the sets of τ_3, τ_4, and τ_5 are obtained under glide symmetry and the fiber identity period 8.95 Å. The sets of τ_3, τ_4, and τ_5 $(=-\tau_1)$ are on the closed surface in a cube defined by the three-dimensional cartesian coordinates τ_3, τ_4, and τ_5, each covering from 0 to 360° as shown schematically in Figure 8. We could perform readily the energy calculation of an isolated polymer chain for all the possible conformations with these internal rotation angles, since the coordinates of the main chain atoms are simultaneously given in the **X** system, where the Z axis is parallel to the molecular axis and the YZ plane coincides with the glide plane. The calculations covered all the atom pairs within five structural units for the van der Waals interactions and the point dipole pairs within 12 structural units.[12] As listed in Table I, four stable conformations were obtained. The model I found to be the most stable by the present energy calculation is essentially the same as the structure determined by X-ray analysis.[11]

Table I
The Energetically Stable Conformations of Rubber Hydrochloride with the Fiber Identity Period 8.95 Å and Glide Symmetry

	τ_1, deg	τ_2, deg	τ_3, deg	τ_4, deg	E^a
I	169	67	169	173	−5.8
II	176	−79	177	176	−5.2
III	180	−178	77	−178	−4.4
IV	180	−178	−73	−178	−4.2

[a] kcal/mol mu.

Conclusion

The merits of the present method are the following.

(1) The equations are expressed only by independent internal rotation angles: $(k-1)$ for the polymers with glide or helical symmetry and $(k-3)$ for those with translational symmetry only. For each symmetry, the remaining internal rotation angles are explicitly represented as functions of the independent internal rotation angles. This means favorable reduction of the amount of practical calculation (see Appendix II).

(2) According to the methods reported so far, the helical models with the parameters d and θ should be calculated approximately by trial and graphically. In the present method the value of θ is included in the expression of the remaining internal rotation angle as a parameter. This means that the conformations strictly maintain helical symmetry. But the value of d should be obtained by the foregoing methods.

(3) The calculation for the set of internal rotation angles satisfying the molecular symmetry and fiber identity period gives simultaneously the space-fixed atomic cartesian coordinates whose Z axis coincides with the molecular axis, and, if the polymer chain has glide symmetry, the YZ plane corresponds to the glide plane.

Appendix I

The elements of the $X'Y'$ projection of **u** are $(f_{11}, f_{21}\cos\beta, 0)$ as shown in Figure 4c. The angle between the $X'Y'$ projection of **u** and the Y' axis should be $\theta/2$. Then the following relationship is obtained by considering the scalar product.

$$[f_{11}, f_{21}\cos\beta,\ 0]\begin{bmatrix}0\\1\\0\end{bmatrix} = (f_{11}^2 + f_{21}^2\cos^2\beta)^{1/2}\ 1\ \cos(\theta/2)$$

$$\cos^2\beta = (f_{11}/f_{21})^2[\cos(\theta/2)/\sin(\theta/2)]^2$$

$$0 < \beta < \pi$$

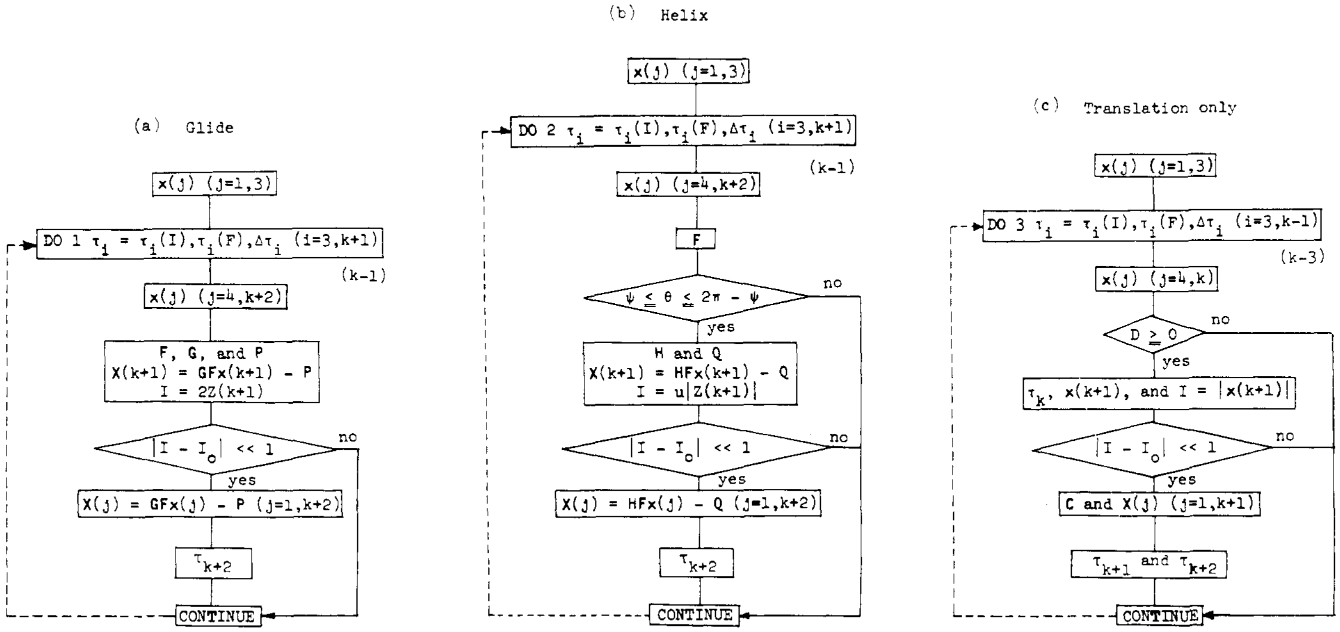


Figure 10. The flow charts of the programs for electronic computer: (a) glide symmetry, (b) helical symmetry, and (c) translational symmetry only.

If $0 < \theta \leq \pi$, $\cos(\theta/2) \geq 0$ and $\cos\beta \geq 0$, and if $\pi < \theta < 2\pi$, $\cos(\theta/2) < 0$ and $\cos\beta < 0$, and always f_{11}, f_{21}, and $\sin(\theta/2) > 0$. Therefore, we have eq 21.

The **X** system is obtained by translating the **X'** system by **Q** on the $X'Y'$ plane as shown in Figure 9. By using the coordinates of the $(k+1)$th atom in the **X'** system, $\mathbf{X}'(k+1)$ $[=\mathbf{HFx}(k+1)]$, the helix radius r is given as follows.

$$r = R/[2\sin(\theta/2)]$$

where

$$R = [X'(k+1)^2 + Y'(k+1)^2]^{1/2}$$

In Figure 9, the point M is defined so that the point M is on the $X'Y'$ projection of the line connecting the first and $(k+1)$th atoms and the distance from the first atom to the point M is r. Therefore the coordinates of the point M in the **X'** system are $[rX'(k+1)/R,\ rY'(k+1)/R,\ 0]$. The point M can be made to coincide with the origin of the **X** system by rotating around the Z' axis by $(\pi/2 - \theta/2)$. Then the elements of the vector **Q** are represented as

$$\mathbf{Q} = \begin{bmatrix} \cos(\pi/2 - \theta/2) & -\sin(\pi/2 - \theta/2) & 0 \\ \sin(\pi/2 - \theta/2) & \cos(\pi/2 - \theta/2) & 0 \\ 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} rX'(k+1)/R \\ rY'(k+1)/R \\ 0 \end{bmatrix}$$

$$= (1/2)\begin{bmatrix} 0 & -\cot(\theta/2) & 0 \\ \cot(\theta/2) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \mathbf{HFx}(k+1)$$

Appendix II

A compact program was made, which is intended to calculate the possible sets of internal rotation angles and atomic coordinates satisfying the molecular symmetry and fiber identity period for any k. In Figure 10 the flow chart of the program for each case is shown.

Furthermore, the conformational energies can be computed for all the possible conformations by changing the internal rotation angles around single bonds in an isolated polymer chain under the conditions of molecular symmetry and fiber identity period. In executing the "DO" statement, if $N_i = \{[\tau_i(F) - \tau_i(I)]/\Delta\tau_i\} + 1$ [the initial value $\tau_i(I)$, the final value $\tau_i(F)$, and the increment $\Delta\tau_i$] and N_i is common for any i $(=N)$, we must calculate practically N^k times operations in the use of the foregoing methods. If the present method is used, it may be sufficient only to calculate N^{k-1} or N^{k-3} times operations for the glide and helix or the translation only, respectively. So the number of calculations decreases by $1/N$ times of N^k times operation (if the translation only, by $1/N^3$ times).

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(6) The matrix **F** becomes undetermined in the following two cases: (a) the unit vector **v** is parallel to **u** and (b) **v** is antiparallel to **u.** However, the transformation from the **x** system to the **X** system is readily found out. In a, any plane which passes the midpoint between the first and $(k+1)$th atoms and is parallel to **v** (=**u**) can be the glide plane. In b, the glide plane passes the midpoint between the first and $(k+1)$th atoms and is parallel to the yz plane.
(7) When the unit vector **v** is parallel to the unit vector **u,** the model cannot take any helical symmetry except for (1/0) symmetry, *i.e.,* the translational symmetry.
(8) There are two special cases (a) $a_{11} = 1$ and ϕ_1 $(=\phi_{k+1}) = \phi_k$ and (b) $a_{11} = -1$ and $\phi_1 + \phi_k = \pi$, where $a_{12} = a_{13} = 0$ because eq 27 is the orthogonal matrix. Therefore τ_k can take an arbitrary value. In a, the unit vectors **u** and **v** and the bond vector $\mathbf{r}_k$ are parallel to each other. In b, $\mathbf{r}_k$ is antiparallel to **u** and **v.** Of course, **v** is parallel to **u.**
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(12) The conformational energy of an isolated polymer chain was computed by taking into account the internal rotation barriers, the nonbonded interactions, and the dipole–dipole interactions, where the bond lengths and bond angles were held fixed. The sinusoidal type function was used for the internal rotation barrier. The height of the barrier V_0 was assumed to be 2.8 kcal/mol for the C–C bond.[13] For the nonbonded interaction, we used Lennard-Jones 6-12 type potential functions, of which coefficients were calculated by using the Slater–Kirkwood equations. The parameters listed in Table 1 of ref 14 were used except for the chlorine atom [$\alpha = 2.30(\text{Å}^3)$, $N_{eff} = 16.0$, and van der Waals radius = 1.75 Å].[15,16,17] The electrostatic interactions were calculated by as-

suming that point dipoles exist at the midpoints of polar bonds. The C–Cl bond moment is 2.0 D.[18] The dielectric constant was assumed to be 4.0.[19]

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Proton and Carbon-13 Nuclear Magnetic Resonance Studies of Poly(vinyl acetate)

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ABSTRACT: Two poly(vinyl alcohol) samples of known stereoregularity were converted to poly(vinyl acetate) by acetylation. The 220-MHz proton resonance spectra and 22.6-MHz carbon-13 Fourier transform noise-decoupled spectra of the acetylated products were obtained in a variety of solvents. By examining the acetoxy methyl proton spectra in nitromethane solution, we have deduced triad and pentad tacticity. The stereochemical sequence distributions in terms of triads and tetrads were determined from the methylene carbon spectra in perdeuterated 1,1,2,2-tetrachloroethane solution at 120°.

Poly(vinyl acetate), PVAc, was one of the first examples used by many authors to illustrate the utility of high resolution proton nmr method for tacticity determination.[2a] Bovey and coworkers reported that the resonances due to the acetoxy methyl protons in different stereoregular sequences of PVAc can be readily resolved.[2b] However, Ramey and Messick showed that the spectral features of these methyl protons are dependent on the solvents.[3] By carrying out a systematic study on model compounds, Fujii, *et al.*,[4] were able to make unambiguous spectral assignments for PVAc. Recently, Abe and Nishioka further demonstrated that the line widths of the acetoxy methyl proton peaks are not uniform and can vary significantly with different solvents.[5] In two recent papers the carbon-13 spectra of PVAc were reported but no detailed spectral analysis was given.[6,7]

In this work, two poly(vinyl alcohol) samples, PVA, of known stereoregularity were converted to PVAc by acetylation. The 220-MHz proton and 22.6-MHz noise-decoupled Fourier transform carbon-13 spectra of the derived acetylated products were obtained in a variety of solvents. From the observed spectra we have deduced the tacticities of the PVAc samples in terms of triad, tetrad, and pentad placements.

Experimental Section

The PVA samples used in this work were those reported previously, *i.e*, an atactic and a highly isotactic polymer.[8] These samples were converted into PVAc by acetylation in pyridine with acetic anhydride.[9] Infrared absorption of hydroxyl groups (~3400 cm^{-1}) was used to monitor the extent of acetylation. The derived products were found to have degrees of esterification in excess of 99.5% in both cases.

For proton measurements the nmr sample solutions were prepared to contain 5 wt % of PVAc. A small amount of hexamethyldisiloxane (HMDS) was added as internal reference. Proton spectra were recorded on a Varian HR-220 nmr spectrometer equipped with a variable temperature probe. The spectra were calibrated by the audiomodulation technique.

The carbon-13 spectra were obtained using a Bruker HFX-90 nmr spectrometer equipped with a Digilab nmr 3 Fourier transform accessory. The spectrometer was operated at 22.63 MHz with proton noise decoupling and a time-shared deuterium lock. Our spectral measurement procedure was in accordance with that described in the previous papers.[7,8] In this study samples were examined as 10% solutions in 10-mm tubes at elevated temperatures. All the carbon chemical shift values were reported with respect to the internal reference HMDS.

Peak areas were determined by using (i) integration, (ii) a Du Pont 310 Curve Resolver, and (iii) a planimeter.

Results and Discussion

I. Proton Resonance Spectra. From the 100-MHz spectra of an atactic PVAc in deuterated chloroform ($CDCl_3$) and carbon tetrachloride (CCL_4) solutions, Abe and Nishioka showed that the line widths of the triplet acetoxy methyl proton resonances are not constant.[5] More surprisingly, these methyl protons in nitromethane solution were found to exhibit a six-line spectrum. They attributed these observations to the pentad tacticity effects but did not attempt a detailed analysis of the nitromethane solution spectrum.[5] In the present study we have examined the 220-MHz spectra of the PVAc samples dissolved in a variety of solvents. Some examples are depicted in Figure 1 and the proton chemical shifts are summarized in Table I. Generally speaking, the spectral feature of the acetoxy methyl protons of the atactic polymer can be described by (i) a relatively broad singlet (in benzene, chlorobenzenes, 1-chloronaphthalene, and hexafluoroacetone deuterate), (ii) a triplet (in most of the other solvents), and (iii) a triplet with fine structures (in nitromethane and nitroethane). From the singlet acetoxy proton spectra, it is seen that the solvent shielding increases from hexafluoroacetone deuterate < 1-chloronaphthalene < *o*-dichlorobenzene < benzene. With the exception of the fluorinated solvent, the observed diamagnetic shielding effect appears to be inversely related to the molecular size of the solvent. On the other hand the shielding of the triplet acetoxy methyl protons increases from nitrobenzene < methanol, $CDCl_3$ < perdeuterated 1,1,2,2-tetrachloroethane ($CDCl_2CDCl_2$), methylene chloride < CCl_4 < perdeuterated dimethyl sulfoxide (DMSO-d_6). In this case the observed trends cannot be simply correlated with the polarity or with the size of the solvent molecule.

Since more than three peaks were observed for the acetoxy protons in the nitromethane solution spectra, we have attempted to analyze these lines in terms of configurational sequences longer than triad placements. In Figure 2 the