Molecular Vibrations and Structure of High Polymers. II. Helical Parameters of Infinite Polymer Chains as Functions of Bond Lengths, Bond Angles, and Internal Rotation Angles

TATSUO MIYAZAWA, *Institute for Protein Research, Osaka, University, Kitaku, Osaka, Japan*

INTRODUCTION

In the preceding paper[1] a general method of the normal coordinate treatment of infinite helical polymers was described and the dependence of molecular vibrations upon the helical conformations was discussed. The low skeletal frequencies of helical polymers have been found to be very sensitive to the conformational changes, indicating the possibilities of detailed conformational studies of high polymers by means of infrared spectroscopy in the low-frequency region. The selection rule for infrared absorption is closely related with the helical conformation of the polymer, and the helical parameters are the functions of such internal coordinates as the bond lengths, the bond angles, and the internal rotation angles.

The structures of stretched linear polymers have been discussed by Huggins[2] and the interbond angles for likely structure models have been calculated from the observed fiber period. General mathematical expressions for the helical parameters have been derived by Shimanouchi and Mizushima[3] in terms of the bond lengths, the bond angles, and the internal rotation angles. The expressions derived by them apply to any helical polymeric chains and are useful in calculating helical parameters as functions of the internal coordinates.

For most linear polymers the fiber period is readily determined by x-ray diffraction measurements and, if all the chemical units are assumed to be equivalent, likely structure models may be selected from the fiber period. In deducing structure models it appears to be a common practice to use atomic models; however, for more quantitative discussions mathematical equations will be necessary. Therefore, in the present study the mathematical equations derived by Shimanouchi and Mizushima in terms of matrices were modified into more simplified forms in terms of the trigonometric functions of half the bond angles and half the internal rotation angles. The equations thus derived are convenient for the selection of likely helical conformations or the calculation of the internal coordinates from the helical parameters experimentally determined. The equations will be described

for the infinite helical chains of the types $(-M-)_\infty$, $(-M_1-M_2-)_\infty$, $(-M_1-M_2-M_3-)_\infty$, $(-M_1-M_2-M_3-M_4-)_\infty$, $(-M_1-M_2-M_3-M_4-M_5-)_\infty$, and $(-M_1-M_2-M_3-M_4-M_5-M_6-)_\infty$, where M represents the atoms on the backbone chain of the polymer in question.

INTERNAL COORDINATES AND HELICAL PARAMETERS

For an infinite helical polymer the bond lengths. the bond angles, and the internal rotation angles may be taken as the internal coordinates for describing the chain structure. For example, the internal coordinates (Fig. 1):

$$\phi_1 , \qquad \phi_2 , \qquad \phi_3 , \qquad \phi_4 ,$$

$$r_{12} , \qquad r_{23} , \qquad r_{34} , \qquad r_{41} ,$$

$$\tau_{12} , \qquad \tau_{23} , \qquad\qquad \tau_{41} ,$$

are used for the polymer $(-M_1-M_2-M_3-M_4-)_\infty$ where r_{ij} is the bond length of the M_i-M_j bond, ϕ_j is the angle between the M_i-M_j bond and
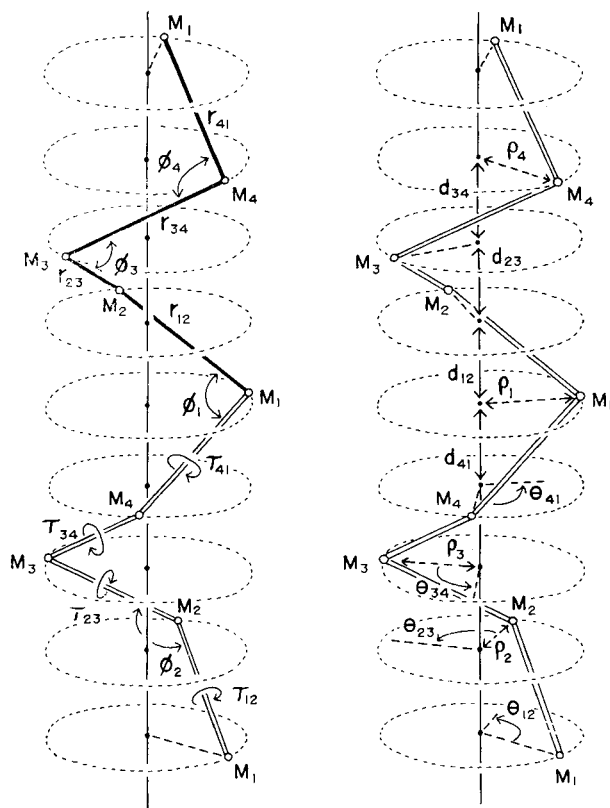

Fig. 1. The internal coordinates, r_{ij}, ϕ_i, τ_{ij}, and the helical parameters, ρ_i, d_{ij}, and θ_{ij} of the helical polymer $(-M_1-M_2-M_3-M_4-)_\infty$.

the M_j—M_k bond, and τ_{ij} is the internal rotation angle about the M_i—M_j bond ($\tau = 0°$ for the *cis* configuration and $\tau = 180°$ for the *trans* configuration).

The helical parameters for describing the structure of infinite helical chain have been defined by Shimanouchi and Mizushima:[3] ρ_i is the distance from the ith atom to the helix axis, and d_{ij} and θ_{ij} are the translation along the axis and the angle of rotation about the axis, respectively, on passing from the ith atom to the succeeding jth atom. For example, the helical parameters (Fig. 1):

$$\rho_1, \qquad \rho_2, \qquad \rho_2, \qquad \rho_4,$$
$$d_{12}, \qquad d_{23}, \qquad d_{34}, \qquad d_{41},$$
$$\theta_{12}, \qquad \theta_{23}, \qquad \theta_{34}, \qquad \theta_{41}, \qquad \theta_{41},$$

are used for the polymer $(-M_1-M_2-M_3-M_4-)_\infty$. The translation ($d$) along the helix axis and the angle θ (in radians) of rotation about the axis, on passing from a given atom of a repeating unit to the corresponding atom of the succeeding unit, are given by:

$$d = d_{12} + d_{23} + \ldots + d_{p-1,p} + d_{p,1} = t/m \tag{1}$$

$$\theta = \theta_{12} + \theta_{23} + \ldots + \theta_{p-1,p} + \theta_{p,1} = 2\pi n/m \tag{2}$$

where m is the number of repeating units and n is the number of helical turns per fiber period t.

GENERAL EXPRESSIONS FOR HELICAL PARAMETERS AS FUNCTIONS OF INTERNAL COORDINATES

The general mathematical equations derived by Shimanouchi and Mizushima for the helical parameters, θ, d, and ρ_1, may be expressed in different forms, as shown below. (The notations of r, ϕ, τ, and A and B matrices are different from those used before.[3])

$$\cos(\theta/2) = (1 + a_{11} + a_{22} + a_{33})^{1/2}/2 \tag{3}$$

$$d \sin(\theta/2) = \frac{b_1(a_{13} + a_{31}) + b_2(a_{23} + a_{32}) + b_3(1 - a_{11} - a_{22} + a_{33})}{2(1 - a_{11} - a_{22} + a_{33})^{1/2}} \tag{4}$$

$$2\rho_1^2(1 - \cos\theta) + d^2 = b_1^2 + b_2^2 + b_3^2$$
$$= \text{(distance between } M_1 \text{ atom of}$$
$$\text{a repeating unit and the } M_1 \text{ atom}$$
$$\text{of the succeeding unit)}^2 \tag{5}$$

where a's and b's are the elements of the A and B matrices:

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$
$$= A^\tau_{12} A^\phi_2 A^\tau_{23} A^\phi_3 \ldots A^\phi_{p-1} A^\tau_{p-1,p} A^\phi_p A^\tau_{p,1} A^\phi_1 \tag{6}$$

$$B = \begin{bmatrix} b_1 \\ b_2 \\ b_o \end{bmatrix} = B_{12} + A^\tau{}_{12}A^\phi{}_2 B_{23} + \dots$$

$$+ A^\tau{}_{12}A^\phi{}_2 A^\tau{}_{23}A^\phi{}_3 \dots A^\phi{}_{p-1}B_{p-1,p}$$

$$+ A^\tau{}_{12}A^\phi{}_2 A^\tau{}_{23}A^\phi{}_3 \dots A^\phi{}_{p-1}A^\tau{}_{p-1,p}A^\phi{}_p B_{p,1} \quad (7)$$

and:

$$A^\phi{}_i = \begin{bmatrix} -\cos\phi_i & -\sin\phi_i & 0 \\ \sin\phi_i & -\cos\phi_i & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$A^\tau{}_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos_{ij} & -\sin\tau_{ij} \\ 0 & \sin_{ij} & \cos\tau_{ij} \end{bmatrix}$$

$$B_{ij} = \begin{bmatrix} r_{ij} \\ 0 \\ 0 \end{bmatrix}$$

In calculation of the helical parameters, the A and B matrix elements are calculated by the use of eqs. (6) and (7) and then the values of θ, d, and ρ are calculated successively by the use of eqs. (3), (4), and (5). Though eqs. (3) to (7) apply to any helical polymers, they are not quite convenient for deducing structure models from observed fiber period. For helical polymers made up of repeating units containing a small number of atoms, concise equations may be obtained; thereby the bond angles and internal rotation angles for various structure models may readily be calculated from observed helical parameters such as d and θ. The equations will be described first for the simplest polymer chain $(-M-)_\infty$ and then for more complicated systems.

POLYMER CHAIN $(-M-)_\infty$

For the helical chain $(-M-)_\infty$ consisting of only one kind of atom, the internal coordinates r, ϕ, and τ, and the helical parameters ρ, d, and θ, are not followed by subscripts since their values are identical throughout the chain. For the present case the matrix elements are found to be:

$$1 + a_{11} + a_{22} + a_{33} = (1 + \cos\tau)(1 - \cos\phi)$$

$$1 - a_{11} - a_{22} + a_{33} = (1 + \cos\tau)(1 + \cos\phi)$$

$$b_1 = r$$

$$a_{13} + a_{31} = \sin\tau\sin\phi$$

$$b_2 = b_3 = 0 \quad (8)$$

so that:

$$\cos (\theta/2) = \cos (\tau/2) \sin (\phi/2) \tag{9}$$

$$d \sin (\theta/2) = r \sin (\tau/2) \sin (\phi/2) \tag{10}$$

$$2\rho^2(1 - \cos \theta) + d^2 = r^2 \tag{11}$$

It follows from eqs. (9) and (10) that:

$$\tan (\tau/2) = (d/r) \tan (\theta/2) \tag{12}$$

The internal rotation angle is readily calculated from the values of d/r and θ, and then the calculated value of τ is substituted in eq. (9) to yield the angle ϕ. The angle α between the helix axis and each bond is given by:

$$\cos \alpha = d/r = \sin (\tau/2) \sin (\phi/2)/ \sin (\theta/2) \tag{13}$$

since, as may be seen in Figure 1, the translation d along the helix axis is the projection of the bond length r.

Polyethylene. In polyethylene[4] the carbon chain is in the planar zigzag conformation and has two carbon atoms ($m = 2$) and one turn ($n = 1$) per fiber period of $t = 2.534$ A. The helical parameters and internal coordinates were calculated as shown in Table I, assuming the bond length of $r = 1.54$ A.

Polytetrafluoroethylene. The carbon chain of polytetrafluoroethylene[5] is slightly twisted from the planar zigzag structure and contains thirteen carbon atoms ($m = 13$) and six helical turns ($n = 6$) per fiber period of $t = 16.8$ A. From the helical parameters, d and θ, the bond angle ϕ and the internal rotation angle τ were calculated as shown in Table I, assuming the bond length of $r = 1.54$ A. or $r = 1.56$ A. The angle ϕ was calculated to be greater than the tetrahedral angle, possibly because of the steric repulsion between second neighboring CF_2 groups. The calculated angle τ practically did not change with the assumed value of the bond length.

TABLE I
Data for Various (—M—)$_\infty$ Polymer Structures

Polymer	t, A.	m	n	d, A.	θ	r, A.	ϕ	τ	ρ, A.
Polyethylene	2.534	2	1	1.267	180°	1.54	110.$_6$°	180°	0.43$_8$
Polytetrafluoro-ethylene	16.8	13	6	1.29	166°	$\begin{cases}1.54 \\ 1.56\end{cases}$	114.$_6$° 112.$_4$°	163.$_5$° 163.$_3$°	0.42$_4$ 0.44$_2$
Sulfur	13.7	10	3	1.37	108°	2.02	107°	86°	0.92
Selenium	4.95	3	1	1.65	120°	2.32	105°	102°	0.94
Tellurium	5.91	3	1	1.97	120°	2.86	102°	100°	1.20

Fibrous Sulfur. The structure of fibrous sulfur (ϕ sulfur) was recently studied in detail by x-ray diffraction measurements.[6] The fibrous sulfur has been found to consist of fibrous part (ψ sulfur) and nonfibrous part (γ sulfur).[7] Priss et al. have proposed a model for ψ sulfur, containing ten sulfur atoms and three helical turns per fiber period of 13.7 A. The values of internal coordinates calculated from the helical parameters are shown in

Table I. The internal rotation angle of $\tau = 86°$ agrees with the corresponding values for the molecules of Cl—S—S—Cl[8] and CH_3—S—S—CH_3.[9]

Selenium and Tellurium. In metallic selenium and tellurium[10] the helical chain has a threefold axis and contains three atoms and one turn per fiber period. By assuming the bond lengths[2] r of Se—Se = 2.32 A. and of Te—Te = 2.86 A., the bond angles and the internal rotation angles were calculated as shown in Table I. The calculated values of these angles agree with what would be expected from the present knowledge of structural chemistry.

POLYMER CHAIN $(-M_1-M_2-)_\infty$

For the polymer main chain consisting of two kinds of atoms, M_1 and M_2, the mathematical expressions are derived from the elements of the A and B matrices:

$$A = A^\tau_{12}A^\phi_2 A^\tau_{21}A^\phi_1 \tag{14}$$

$$B = B_{12} + A^\tau_{12}A^\phi_2 B_{21} \tag{15}$$

The elements necessary for the calculation of helical parameters are found to be:

$$1 + a_{11} + a_{22} + a_{33} = (1 + \cos\phi_1 \cos\phi_2)(1 + \cos\tau_{12}\cos\tau_{21})$$
$$-\sin\phi_1 \sin\phi_2(\cos\tau_{12} + \cos\tau_{21})$$
$$+\sin\tau_{12} \sin\tau_{21}(\cos\phi_1 + \cos\phi_2) \tag{16}$$

$$1 - a_{11} - a_{22} + a_{33} = (1 - \cos\phi_1 \cos\phi_2)(1 + \cos\tau_{12}\cos\tau_{21})$$
$$+\sin\phi_1 \sin\phi_2(\cos\tau_{12} + \cos\tau_{21})$$
$$+\sin\tau_{12} \sin\tau_{21}(\cos\phi_1 - \cos\phi_2) \tag{17}$$

$$b_1(a_{13} + a_{31}) + b_2(a_{23} + a_{32}) + b_3(1 - a_{11} - a_{22} + a_{33})$$
$$= (r_{12} \sin\tau_{21} + r_{21} \sin\tau_{12}) \sin\phi_1$$
$$+ (r_{12} \cos\tau_{12} \sin\tau_{21} + r_{21} \cos\tau_{21} \sin\tau_{12}) \sin\phi_2$$
$$- (r_{12} \sin\tau_{12} + r_{21} \sin\tau_{21}) \sin\phi_1 \cos\phi_2$$
$$- (r_{12} \sin\tau_{12} \cos\tau_{21} + r_{21} \sin\tau_{21} \cos\tau_{12}) \cos\phi_1 \sin\phi_2 \tag{18}$$

and by extensive factoring eqs. (3) and (4) may ultimately be written in the forms:

$$\cos(\theta/2) = \cos(\tau_{12}/2 + \tau_{21}/2) \sin(\phi_1/2) \sin(\phi_2/2)$$
$$-\cos(\tau_{12}/2 - \tau_{21}/2) \cos(\phi_1/2) \cos(\phi_2/2) \tag{19}$$

$$d \sin(\theta/2)$$
$$= (r_{12} + r_{21}) \sin(\tau_{12}/2 + \tau_{21}/2) \sin(\phi_1/2) \sin(\phi_2/2)$$
$$- (r_{12} - r_{21}) \sin(\tau_{12}/2 - \tau_{21}/2) \cos(\phi_1/2) \cos(\phi_2/2) \tag{20}$$

It is interesting to note that the equations for the helical parameters are expressed in concise forms if they are written in terms of the trigonometric functions of the angles $\phi_i/2$'s and $\tau_{ij}/2$'s. The projections d_{12} and d_{21} of the M_1—M_2 bond and the M_2—M_1 bond on the helix axis are derived from eq. (20), as:

$$d_{12}/r_{12} = \cos \alpha_{12}$$

$$= \left\{ \begin{array}{l} \sin (\tau_{12}/2 + \tau_{21}/2) \sin (\phi_1/2) \sin (\phi_2/2) \\ -\sin (\tau_{12}/2 - \tau_{21}/2) \cos (\phi_1/2) \cos (\phi_2/2) \end{array} \right\} / \sin (\theta/2) \qquad (21)$$

$$d_{21}/r_{21} = \cos \alpha_{21}$$

$$= \left\{ \begin{array}{l} \sin (\tau_{12}/2 + \tau_{21}/2) \sin (\phi_1/2) \sin (\phi_2/2) \\ +\sin (\tau_{12}/2 - \tau_{21}/2) \cos (\phi_1/2) \cos (\phi_2/2) \end{array} \right\} / \sin (\theta/2) \qquad (22)$$

where α_{12} or α_{21} is the angle between the helix axis and the M_1—M_2 bond or the M_2—M_1 bond, respectively. The other helical parameters, ρ_1, ρ_2, θ_{12}, and θ_{21}, are given successively by the use of the following equations:

$$2\rho_1{}^2(1 - \cos \theta) + d^2 = r_{12}{}^2 - 2r_{12}r_{21} \cos \phi_2 + r_{21}{}^2 \qquad (23)$$

$$2\rho_2{}^2(1 - \cos \theta) + d^2 = r_{12}{}^2 - 2r_{12}r_{21} \cos \phi_1 + r_{21}{}^2 \qquad (24)$$

$$2\rho_1\rho_2 \cos \theta_{12} = \rho_1{}^2 + \rho_2{}^2 + d_{12}{}^2 - r_{12}{}^2 \qquad (25)$$

$$2\rho_2\rho_1 \cos \theta_{21} = \rho_2{}^2 + \rho_1{}^2 + d_{21}{}^2 - r_{21}{}^2 \qquad (26)$$

Isotactic Polyolefins. Isotactic polyolefins have helical carbon chains $(-M_1-M_2-)_\infty$ and, since the chain does not have any symmetry elements other than the helix axis, all the internal coordinates are independent variables. The two helical parameters d and θ, have been experimentally determined for the polyolefins listed in Table II. In calculating the bond angles and the internal rotation angles it will be assumed that $r_{12} = r_{21} = r$ and $\phi_1 = \phi_2 = \phi$. Then eqs. (19) and (20) may be rewritten as:

$$d \sin (\theta/2) = 2r \sin^2 (\phi/2) \sin (\tau_{12}/2 + \tau_{21}/2) \qquad (27)$$

$$\cos (\theta/2) = \sin^2 (\phi/2) \cos (\tau_{12}/2 + \tau_{21}/2)$$

$$- \cos^2 (\phi/2) \cos (\tau_{12}/2 - \tau_{21}/2) \qquad (28)$$

Assuming reasonable values of r and ϕ, therefore, the two internal rotation angles can readily be calculated by these equations.

Polypropylene. In isotactic polypropylene or poly-1-butene the helical main chain contains three ($m = 3$) repeating units, —CH_2—CH—, and one turn ($n = 1$) per fiber period of $t = 6.50$ A.[11] By assuming the bond length of $r = 1.54$ A. and the bond angle of $\phi = 110°$ the internal rotation angles were calculated to be $\tau_{12} = 197°$ and $\tau_{21} = -67°$, although considerations of steric repulsions among nonbonded carbon atoms would favor the angle τ_{12} smaller than 180°. Therefore the internal rotation angles were assumed to be $\tau_{12} = 180°$ and $\tau_{21} = -60°$ instead, and the bond angle was calculated

TABLE II
Structural Data for Various Isotactic Polyolefins

Polymer	t, A.	m	n	d, A.	θ	r, A.[a]	ϕ^{a}	τ_{12}	τ_{21}	ρ, A.
Polypropylene	6.50	3	1	2.16_7	120.0°	1.54	$\begin{cases}110° \\ 114°\end{cases}$	$\begin{matrix}197° \\ 180°\end{matrix}$	$\begin{matrix}-67° \\ -60°\end{matrix}$	$\begin{matrix}0.75 \\ 0.81\end{matrix}$
Poly-4-methyl-1-pentene	13.85	7	2	1.97_9	102.9°	1.54	114°	162°	−71°	1.06
Poly-m-methyl-styrene	21.74	11	3	1.97_6	98.2°	1.54	114°	164°	−76°	1.10
Poly-o-methyl-styrene	8.10	4	1	2.02_5	90.0°	$\begin{cases}1.54 \\ 1.56\end{cases}$	$\begin{matrix}114° \\ 114°\end{matrix}$	$\begin{matrix}169° \\ 167°\end{matrix}$	$\begin{matrix}-86° \\ -85°\end{matrix}$	$\begin{matrix}1.13 \\ 1.17\end{matrix}$

[a] It has been assumed that $r_{12} = r_{21}$ and $\phi_1 = \phi_2$.

to be $\phi = 114°$. This value is somewhat greater than the tetrahedral angle; however, it may well be taken as a reasonable value.

Poly-4-methyl-1-pentene. In isotactic poly-4-methyl-1-pentene the helical chain has seven repeating units and two turns per fiber period of $t = 13.85$ A.[11] By assuming the bond length of $r = 1.54$ A. and the bond angle of $\phi = 114°$, the internal rotation angles were calculated as shown in Table II. As an example of the use of eqs. (21)–(26) other helical parameters of this polymer were calculated:

$$\rho_1 = \rho_2 = 1.06_2 \text{ A.}$$
$$d_{12} = 0.46_6 \text{ A. and } d_{21} = 1.51_3 \text{ A.}$$
$$\theta_{12} = 87.4° \text{ and } \theta_{21} = 15.5°$$

It may be remarked that $\theta_{12} + \theta_{21} = 102.9° = \theta$, as required.

Poly-m-methylstyrene. The helical chain of isotactic poly-m-methylstyrene[11] has eleven units and three turns per fiber period of $t = 21.74$ A. Assuming the bond length of $r = 1.54$ A. and the bond angle of $\phi = 114°$ the internal rotation angles were calculated as shown in Table II.

Poly-o-methylstyrene. In poly-o-methylstyrene[11] the helical chain has four units and one turn per fiber period of $t = 8.10$ A. For this polymer the internal rotation angles were calculated by assuming the bond length of $r = 1.54$ A. or 1.56 A., as shown in Table II. The calculated values of the angles τ_{12} and τ_{12} did not change much with the assumed value of the bond length.

Polyoxymethylene. The fiber period of polyoxymethylene has been measured at 17.3 A.[12] and the structure model deduced by Huggins[2] has been confirmed by a recent x-ray diffraction measurement.[13] The Huggins model contains nine repeating units ($—CH_2—O—$) and five turns of the helix per fiber period and it is thought to belong to the dihedral group. It follows, then, that $r_{12} = r_{21}$ and $\tau_{12} = \tau_{21}$ and eqs. (19) and (20) may be written as:

$$\cos(\theta/2) = \sin(\phi_1/2) \sin(\phi_2/2) \cos\tau - \cos(\phi_1/2) \cos(\phi_2/2) \tag{30}$$

$$d \sin(\theta/2) = 2r \sin(\phi_1/2) \sin(\phi_2/2) \sin\tau \tag{31}$$

If we also assume that $\phi_1 = \phi_2$, then eqs. (30) and (31) are reduced to the same form as (9) and (10):

$$\cos (\theta/4) = \cos (\tau/2) \sin (\phi/2) \tag{32}$$

$$(d/2) \sin (\theta/4) = r \sin (\tau/2) \sin (\phi/2) \tag{33}$$

By assuming the bond length of $r = 1.43$ A., the helical parameters and the internal coordinates of Huggins' model were calculated as $d = 2d_{12} = 2d_{21} = 1.92_2$ A., $2\theta_{12} = 2\theta_{21} = 200°$, $\rho_1 = \rho_2 = 0.69_1$ A., $\alpha_{12} = \alpha_{21} = 48°$, $\phi_1 = \phi_2 = 110°52'$, and $\tau = 77°24'$. Actually, however, the angles ϕ_1 and ϕ_2 may be different from each other. Experimental data sufficient for estimating the difference are not available. In order to see the applicability of the approximate equations (32) and (33), the angle ϕ_1 was tentatively taken to be $112°52'$ and the angles ϕ_2 and τ were calculated to be $108°58'$ and $77°26'$, respectively. It may be remarked that the angle τ is essentially independent from the difference $\phi_1 - \phi_2$ and that the value of $(\phi_1 + \phi_2)/2 = 110°55'$ is practically equal to the value of $\phi = 110°52'$ calculated on the assumption of $\phi_1 = \phi_2$. With this assumption, therefore, likely structure models of the polymer $(\text{—M}_1\text{—M}_2\text{—})_\infty$ may be deduced only from the helical parameter d.

Polyisobutylene. The helical chain of polyisobutylene has eight repeating units, $\text{—CH}_2\text{—C(CH}_3)_2\text{—}$, per fiber period of $t = 18.63$ A.[14] The model proposed by Fuller et al.[14] contains seven turns ($n = 7$) per fiber period, so that $d = 2.328$ A. and $\theta = 315°$. On the assumption of $\phi_1 = \phi_2$ the internal coordinates were calculated as $r = 1.54$ A. (assumed), $\phi = 100.0°$, and $\tau = 150.5°$, and this model does not appear to be likely since the calculated value of ϕ is much smaller than the normal C—C—C angle of about $110°$. In fact, the model containing five turns per fiber period (so that $\theta = 225°$) was deduced by Liquori from the x-ray diffraction measurements.[16] The internal coordinates and helical parameters for this model were calculated to be $r = 1.54$ A. (assumed), $\phi = 114°$, $\tau = 97°$, $\rho = 0.61$ A., and $\alpha = 41°$. In view of the calculated angle of ϕ, this model is a reasonable one. The internal rotation angle, however, is appreciably different from the normal value of ca. $60°$, probably owing to the large steric repulsion among the methyl groups of adjacent repeating units.

POLYMER CHAIN $(\text{—M}_1\text{—M}_2\text{—M}_2\text{—})_\infty$

For the polymer chain consisting of three kinds of atoms, the mathematical expressions were derived from the elements of the A and B matrices:

$$A = A^\tau_{12} A^\phi_2 A^\tau_{23} A^\phi_3 A^\tau_{31} A^\phi_1 \tag{34}$$

$$B = B_{12} + A^\tau_{12} A^\phi_2 B_{23} + A^\tau_{12} A^\phi_2 A^\tau_{23} A^\phi_3 B_{31} \tag{35}$$

The description of the mathematical derivations carried out in the present study would take too much space and therefore only the final results will be presented here.

$\cos (\theta/2)$

$$
\begin{aligned}
= \quad &\cos (+\ \tau_{12}/2 + \tau_{23}/2 + \tau_{31}/2)\ \sin (\phi_1/2)\ \sin (\phi_2/2)\ \sin (\phi_3/2) \\
&-\cos (-\ \tau_{12}/2 + \tau_{23}/2 + \tau_{31}/2)\ \cos (\phi_1/2)\ \cos (\phi_2/2)\ \sin (\phi_3/2) \\
&-\cos (+\ \tau_{12}/2 - \tau_{23}/2 + \tau_{31}/2)\ \sin (\phi_1/2)\ \cos (\phi_2/2)\ \cos (\phi_3/2) \\
&-\cos (+\ \tau_{12}/2 + \tau_{23}/2 - \tau_{31}/2)\ \cos (\phi_1/2)\ \sin (\phi_2/2)\ \cos (\phi_3/2)
\end{aligned}
\tag{36}
$$

$d \sin (\theta/2)$

$$
\begin{aligned}
= \quad &(+\ r_{12} + r_{23} + r_{31})\ \sin (+\ \tau_{12}/2 + \tau_{23}/2 + \tau_{31}/2) \\
&\qquad\qquad\qquad \sin (\phi_1/2)\ \sin (\phi_2/2)\ \sin (\phi_3/2) \\
&-(-\ r_{12} + r_{23} + r_{31})\ \sin (-\ \tau_{12}/2 + \tau_{23}/2 + \tau_{31}/2) \\
&\qquad\qquad\qquad \cos (\phi_1/2)\ \cos (\phi_2/2)\ \sin (\phi_3/2) \\
&-(+\ r_{12} - r_{23} + r_{31})\ \sin (+\ \tau_{12}/2 - \tau_{23}/2 + \tau_{31}/2) \\
&\qquad\qquad\qquad \sin (\phi_1/2)\ \cos (\phi_2/2)\ \cos (\phi_3/2) \\
&-(+\ r_{12} + r_{23} - r_{31})\ \sin (+\ \tau_{12}/2 + \tau_{23}/2 - \tau_{31}/2) \\
&\qquad\qquad\qquad \cos (\phi_1/2)\ \sin (\phi_2/2)\ \cos (\phi_3/2) \\
= \quad &r_{12} \cos \alpha_{12} \sin (\theta/2) + r_{23} \cos \alpha_{23} \sin (\theta/2) \\
&\qquad\qquad\qquad + r_{21} \cos \alpha_{31} \sin (\theta/2) \tag{37}
\end{aligned}
$$

$$
\begin{aligned}
2\rho_1{}^2(1 - \cos \theta) + d^2 \\
= \ &r_{12}{}^2 + r_{23}{}^2 + r_{21}{}^2 - 2r_{23}\ (r_{12} \cos \phi_2 + r_{31} \cos \phi_2) \\
&+ 2r_{12}r_{31}\ (\cos \phi_2 \cos \phi_3 - \sin \phi_2 \sin \phi_3 \cos \tau_{23}) \tag{38}
\end{aligned}
$$

$$
d_{12} = r_{12} \cos \alpha_{12} \tag{39}
$$

$$
2\rho_1\rho_2 \cos \theta_{12} = \rho_1{}^2 + \rho_2{}^2 + d_{12}{}^2 - r_{12}{}^2 \tag{40}
$$

The equation for other helical parameters, ρ_2, ρ_3, d_{23}, d_{31}, θ_{23}, or θ_{31}, may be obtained by displacements of the terms of the corresponding equation according to the rule of cyclic changes $1 \rightarrow 2$, $2 \rightarrow 3$, and $3 \rightarrow 1$ of the subscripts.

Polypeptides. Polypeptides or poly-α-amino acids have been known to take various helical conformations, depending upon the environment. For example, polyglycine has two crystalline forms:[17] polyglycine I is in the antiparallel-chain extended form[18] with a twofold screw axis (fiber axis) and polyglycine II is in a helical conformation with a threefold screw axis (fiber axis).[19] Poly-L-alanine[20] exists either in the α helix[21] or in the extended form. β-Keratin is considered to be in the parallel-chain extended form.[18] The values of the bond lengths and bond angles for polypeptides ($-C_\alpha HR$ $-CO-NH-)_\infty$ have been given by Pauling and Corey:[22] $r_{12}(C_\alpha-C)$ $= 1.53$ A., $r_{23}(C-N) = 1.32$ A., $r_{31}(N-C_\alpha) = 1.47$ A., $\phi_1(N-C_\alpha-C)$ $= 110°$, $\phi_2(C_\alpha-C-N) = 114°$, and $\phi_3(C-N-C_\alpha) = 123°$, and the in-

ternal rotation angle about the CO—NH bond has been established to be $\tau_{23} = 180°$. In substituting these values, eqs. (36) and (37) were written as:

$$\cos(\theta/2) = -0.817 \sin(\tau_{12}/2 + \tau_{31}/2) - 0.045 \sin(\tau_{12}/2 - \tau_{31}/2)$$

$$d \sin(\theta/2) = 2.967 \cos(\tau_{12}/2 + \tau_{31}/2) - 0.664 \cos(\tau_{12}/2 - \tau_{31}/2)$$

and the internal rotation angles $\tau_{12}(C_\alpha—C)$ and $\tau_{31}(N—C_\alpha)$ were calculated as shown in Table III.

TABLE III
Structural Data for Various Conformations of Polypeptides

Conformation	t, A.	m	n	d, A.	θ	$\tau(C_\alpha—C)$	$\tau(N—C_\alpha)$
α Helix	27	18	5	1.5	100°	−47°	−58°
Polyglycine II	9.3	3	1	3.1	120°	−144°	+76°
Parallel-chain extended	6.5	2	1	3.2$_5$	180°	+112°	−118°
Antiparallel-chain extended	7.0	2	1	3.5	180°	+145°	−142°

It may be seen that the polypeptides which assume the α helical conformation are in the stable *gauche* configurations ($\tau = \sim \pm 60°$) about the $C_\alpha—C$ and $N—C_\alpha$ bonds. The $C_\alpha—C$ and $N—C_\alpha$ bonds of the antiparallel-chain extended conformation are twisted from the trans configuration ($\tau = 180°$) by the angles of 30–40°, probably in order to favor the formation of strong interchain hydrogen bonds. The $C_\alpha—C$ and $N—C_\alpha$ bonds of the parallel-chain extended conformation are in the eclipsed configuration ($\tau = \sim \pm120°$) and this conformation is considered less stable than the antiparallel-chain extended conformation as far as the internal rotation potentials are concerned. In fact, β-keratin is the only polypeptide that has been suggested to be in the parallel-chain extended conformation.[18] The infrared spectra (1700–1500 cm.$^{-1}$) of all the other polypeptides or protein in the extended form have been found to be in accord with the antiparallel-chain extended conformation.[23,24]

Polyethylene Glycol. The x-ray diffraction studies of polyethylene glycol, $(—CH_2—O—CH_2—)_\infty$, have been reported by Sauter[25] and more recently by Walter and Reding,[26] and the fiber period has been found to be $t = 19.25$ A. A structure model containing nine repeating units has been proposed by Sauter. Infrared spectra of this polymer have been studied by Davison[27] and a model containing nine units and three turns per fiber period has been put forward, although the actual fiber period of this model would be one third of the observed value. Coexistence of the *trans* and *gauche* configurations of the $O—CH_2—CH_2—O$ groups has been concluded by Miyake,[28] from his vibrational assignment of the infrared spectra. More recently, however, the infrared studies as well as the approximate normal coordinate treatment have led the present author to conclude that this

polymer is made up of only the *gauche* configuration ($\tau = {\sim}60°$)[1]. An attempt was made to deduce a likely structure model of polyethylene glycol from the observed fiber period, with the assumption of the same bond angles and same internal rotation angles throughout the chain. Then eqs. (36) and (37) may be ultimately written as:

$$\cos (\theta/6) = \cos (\tau/2) \sin (\phi/2) \tag{41}$$

$$d \sin (\theta/6) = (r_{12} + r_{23} + r_{31}) \sin (\tau/2) \sin (\phi/2) \tag{42}$$

and by assuming the bond lengths of $r(CH_2{-}CH_2) = 1.54$ A. and $r(CH_2{-}O) = 1.43$ A., the angles ϕ and τ were calculated for reasonable sets of m (number of repeating units) and n (number of turns per fiber period).

The structure models having the angle $105° < \phi < 120°$, and the angle $40° < \tau < 90°$ (nearly *gauche*) or $140° < \tau < 180°$, were looked for and only three were found, as shown in Table IV. It may be remarked that likely structure models containing nine units per fiber period have not been found. Of the three models listed in Table IV, model III appears to be a likely one in view of the bond angle ϕ and the internal rotation angle τ. The helical parameters for model III were calculated as $d(O{-}CH_2) = 0.89$ A., $d(CH_2{-}CH_2) = 0.96$ A., $\rho(O) = 0.87$ A., $\rho(CH_2) = 0.83$ A., $\theta(O{-}CH_2) = 82°$, and $\theta(CH_2{-}CH_2) = 93°$.

TABLE IV
Structural Data for Models of Polyethylene Glycol

Model	m	n	d, A.	θ	ϕ	τ
I	8	5	2.41	225°	119°	46°
II	6	5	3.21	300°	117°	82°
III	7	5	2.75	257°	116°	60°

POLYMER CHAIN $(-M_1{-}M_2{-}M_2{-}M_4{-})_\infty$

For the polymer chain consisting of the repeating units $-M_1{-}M_2{-}M_3{-}M_4{-}$, the mathematical equations analogous to (36) and (37) were constructed and were numerically ascertained to be valid. In expressing these equations the trigonometric functions will be abbreviated as (for examples):

$$C(-12 + 23 + 34 + 41): \cos (-\tau_{12}/2 + \tau_{23}/2 + \tau_{34}/2 + \tau_{41}/2)$$

$$S(+12 - 23 - 34 + 41): \sin (+\tau_{12}/2 - \tau_{23}/2 - \tau_{34}/2 + \tau_{41}/2)$$

$$C(2): \cos (\phi_2/2)$$

$$S(3): \sin (\phi_3/2)$$

$$\cos (\theta/2) = \quad C(+ 12 + 23 + 34 + 41)S(1)S(2)S(3)S(4)$$
$$-C(- 12 + 23 + 34 + 41)C(1)C(2)S(3)S(4)$$
$$-C(+ 12 - 23 + 34 + 41)S(1)C(2)C(3)S(4)$$
$$-C(+ 12 + 23 - 34 + 41)S(1)S(2)C(3)C(4)$$
$$-C(+ 12 + 23 + 34 - 41)C(1)S(2)S(3)C(4)$$
$$-C(- 12 - 23 + 34 + 41)C(1)S(2)C(3)S(4)$$
$$-C(+ 12 - 23 - 34 + 41)S(1)C(2)S(3)C(4)$$
$$+C(- 12 + 23 - 34 + 41)C(1)C(2)C(3)C(4) \qquad (43)$$

$$d \sin (\theta/2) = (+ r_{12} + r_{23} + r_{34} + r_{41})S(+ 12 + 23 + 34 + 41)$$
$$S(1)S(2)S(3)S(4)$$
$$-(- r_{12} + r_{23} + r_{34} + r_{41})S(- 12 + 23 + 34 + 41)$$
$$C(1)C(2)S(3)S(4)$$
$$-(+ r_{12} - r_{23} + r_{34} + r_{41})S(+ 12 - 23 + 34 + 41)$$
$$S(1)C(2)C(3)S(4)$$
$$-(+ r_{12} + r_{23} - r_{34} + r_{41})S(+ 12 + 23 - 34 + 41)$$
$$S(1)S(2)C(3)C(4)$$
$$-(+ r_{12} + r_{23} + r_{34} - r_{41})S(+ 12 + 23 + 34 - 41)$$
$$C(1)S(2)S(3)C(4)$$
$$-(- r_{12} - r_{23} + r_{34} + r_{41})S(- 12 - 23 + 34 + 41)$$
$$C(1)S(2)C(3)S(4)$$
$$-(+ r_{12} - r_{23} - r_{34} + r_{41})S(+ 12 - 23 - 34 + 41)$$
$$S(1)C(2)S(3)C(4)$$
$$+(- r_{12} + r_{23} - r_{34} + r_{41})S(- 12 + 23 - 34 + 41)$$
$$C(1)C(2)C(3)C(4) \qquad (44)$$

If like bond angles and like internal rotation angles are assumed throughout the chain, eqs. (43) and (44) are simplified:

$$\cos (\theta/8) = \cos (\tau/2) \sin (\phi/2) \qquad (45)$$

$$d \sin (\theta/8) = (r_{12} + r_{23} + r_{34} + r_{41}) \sin (\tau/2) \sin (\phi/2) \qquad (46)$$

Syndiotactic Polypropylene. The helical chain conformation of syndiotactic polypropylene has been studied by x-ray diffraction measurements and a structure model has been proposed.[11] This model contains two repeating units

$$\overset{\quad\quad CH_3 \quad\quad\quad\quad\quad \overset{r_{34}\quad r_{41}}{}}{-CH_2-\underset{}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-}$$
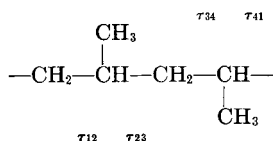
$$\underset{r_{12}\quad r_{23}}{}$$

and one turn per fiber period of $t = 7.3$ A. so that $d = 3.65$ A. and $\theta = 180°$. Twofold axes pass through the methylene groups and intersect the fiber axis (twofold axis) at right angle; therefore $r_{12} = r_{41}$, $r_{23} = r_{34}$, $\phi_2 = \phi_4$, $\tau_{12} = \tau_{41}$, and $\tau_{23} = \tau_{34}$. If we assume that $r_{12} = r_{23}$ and $\phi_1 = \phi_2 = \phi_4$, then eqs. (43) and (44) may be written as:

$$\cos (\theta/2) = \cos (\tau_{12} + \tau_{23}) \sin^4 (\phi/2) + \cos^4 (\phi/2)$$

$$- [2 \cos \tau_{12} + 2 \cos \tau_{23} + \cos (\tau_{12} - \tau_{23}) + 1]$$

$$\sin^2 (\phi/2) \cos^2 (\phi/2) \quad (47)$$

$$d \sin (\theta/2) = 4r \sin (\tau_{12} + \tau_{23}) \sin^4 (\phi/2)$$

$$- 4r (\sin \tau_{12} + \sin \tau_{23}) \sin^2 (\phi/2) \cos^2 (\phi/2) \quad (48)$$

Assuming the bond length of $r = 1.54$ A. and the angle of $\phi = 114°$ as calculated for isotactic polypropylene, the internal rotation angles of syndiotactic polypropylene were calculated to be $\tau_{12} = 171°$ and $\tau_{23} = -57°$.

POLYMER CHAIN $(-M_1-M_2-M_3-M_4-M_5-)_\infty$

For the polymer chain $(-M_1-M_2-M_3-M_4-M_5-)_\infty$ the equations for the helical parameters d and θ were constructed as shown below and were numerically confirmed:

$\cos (\theta/2)$

$= C(+ 12 + 23 + 34 + 45 + 51)S(1)S(2)S(3)S(4)S(5)$

$$+ \left[\begin{cases} -C(- 12 + 23 + 34 + 45 + 51)C(1)C(2)S(3)S(4)S(5) \\ -C(- 12 - 23 + 34 + 45 + 51)C(1)S(2)C(3)S(4)S(5) \\ +C(- 12 + 23 - 34 + 45 + 51)C(1)C(2)C(3)C(4)S(5) \end{cases} \right.$$

and the other four corresponding terms obtained by the rule of cyclic changes of subscripts $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4, 4 \rightarrow 5, 5 \rightarrow 1$

$$(49)$$

$d \sin (\theta/2)$

$= (+ r_{12} + r_{23} + r_{34} + r_{45} + r_{51})S(+ 12 + 23 + 34 + 45 + 51)$
$$S(1)S(2)S(3)S(4)S(5)$$

$$\left[\begin{cases} -(- r_{12} + r_{23} + r_{34} + r_{45} + r_{51})S(- 12 + 23 + 34 + 45 + 51) \\ \qquad\qquad C(1)C(2)S(3)S(4)S(5) \\ -(- r_{12} - r_{23} + r_{34} + r_{45} + r_{51})S(- 12 - 23 + 34 + 45 + 51) \\ \qquad\qquad C(1)S(2)C(3)S(4)S(5) \\ +(- r_{12} + r_{23} - r_{34} + r_{45} + r_{51})S(- 12 + 23 - 34 + 45 + 51) \\ \qquad\qquad C(1)C(2)C(3)C(4)S(5) \end{cases} \right.$$

and the other four corresponding terms obtained by the rule of cyclic changes of subscripts

$$(50)$$

For example, cellulose has the backbone chain $(-C-C-C-C-CO-)_\infty$ or $(-C-C-O-C-CO-)_\infty$ and here eqs. (49) and (50) may be applied.

If the polymer in question has like bond angles and like internal rotation angles throughout the chain, then eqs. (49) and (50) may be rewritten:

$$\cos(\theta/10) = \cos(\tau/2)\sin(\phi/2) \tag{51}$$

$$d\sin(\theta/10) = (r_{12} + r_{23} + r_{34} + r_{45} + r_{51})\sin(\tau/2)\sin(\phi/2) \tag{52}$$

POLYMER CHAIN $(-M_1-M_2-M_3-M_4-M_5-M_6-)_\infty$

For the polymer chain consisting of repeating units, $-M_1-M_2-M_3-M_4-M_5-M_6-$, the equations for the helical parameters were constructed and were numerically checked:

$$
\begin{aligned}
\cos(\theta/2) = &\; C(+12 + 23 + 34 + 45 + 56 + 61) \\
&\qquad S(1)S(2)S(3)S(4)S(5)S(6) \\[4pt]
&-C(-12 + 23 - 34 + 45 - 56 + 61) \\
&\qquad C(1)C(2)C(3)C(4)C(5)C(6) \\[4pt]
&+\left[\left\{
\begin{array}{l}
-C(-12 + 23 + 34 + 45 + 56 + 61) \\
\qquad C(1)C(2)S(3)S(4)S(5)S(6) \\
-C(-12 - 23 + 34 + 45 + 56 + 61) \\
\qquad C(1)S(2)C(3)S(4)S(5)S(6) \\
+C(-12 + 23 - 34 + 45 + 56 + 61) \\
\qquad C(1)C(2)C(3)C(4)S(5)S(6) \\
+C(-12 - 23 + 34 - 45 + 56 + 61) \\
\qquad C(1)S(2)C(3)C(4)C(5)S(6)
\end{array}
\right\}
\right. \\
&\quad \text{and the other five corresponding terms ob-} \\
&\quad \text{tained by the rule of cyclic changes of sub-} \\
&\quad \left. \text{scripts } 1 \to 2, 2 \to 3, 3 \to 4, 4 \to 5, 5 \to 6, 6 \to 1 \right] \\[4pt]
&+\left[\left\{
\begin{array}{l}
C(-12 + 23 + 34 - 45 + 56 + 61)C(1)C \\
\qquad (2)S(3)C(4)C(5)S(6) \\
-C(-12 - 23 - 34 + 45 + 56 + 61)C(1) \\
\qquad S(2)S(3)C(4)S(5)S(6)
\end{array}
\right\}
\right. \\
&\quad \text{and the other two corresponding terms ob-} \\
&\quad \text{tained by the rule of cyclic changes of sub-} \\
&\quad \left. \text{scripts} \right]
\end{aligned}
\tag{53}
$$

The equation for the helical parameter d will not be described here; however, it is readily constructed by referring to eqs. (49), (50), and (53).

Deoxyribonucleic acid or ribonucleic acid has the backbone chain $(-CH-CH_2-O-P-O-CH-)_\infty$ and eq. (53) may be applied.

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Addendum

Since the writing of the present paper, the helical conformations of poly(ethylene glycol) have been studied more extensively. By assuming the interbond angle of $\phi = 111°$, the structure models having the angles of $150° < \tau < 210°$ or $45° < |\tau| < 85°$ have been looked for. Excepting the models containing more than ten chemical units per fiber period, only two models (IV and V) have been found. The internal rotation angles are: for the model IV (m = 9, n = 2), $\tau(O—CH_2) = 178°$ and $\tau(CH_2—CH_2) = 47°$; for the model V (m = 7, n = 2), $\tau(O—CH_2) = 191.5°$ and $\tau(CH_2—CH_2) = 60°$. In view of the angles τ and ϕ, the model V appears to be the most likely one.[29] The helical parameters for the model V are: $d(O—CH_2) = 0.83$A., $d(CH_2—CH_2) = 1.09$A., $\rho(O) = 0.56$A., $\rho(CH_2) = 1.60$A., $\theta(O—CH_2) = 31.5°$, and $\theta(CH_2—CH_2) = 40°$.

Synopsis

Helical conformations of infinite polymer chains may be described by the helical parameters including ρ_i (the distance of the ith atom from the helix axis), d_{ij} (the translation along the axis), and θ_{ij} (the angle of rotation about the axis on passing from the ith atom to the jth). For the polymer main chain ($—M—$)∞, ($—M_1—M_2—$)∞, ($—M_1—M_2—M_3—$)∞, ($—M_1—M_2—M_3—M_4—$)∞, ($—M_1—M_2—M_3—M_4—M_5—$)∞, or ($—M_1—M_2—M_3—M_4—M_5—M_6—$)∞ concise mathematical equations for the helical parameters are given in terms of the internal coordinates, such as the bond lengths, the bond angles, and the internal rotation angles. These equations are useful in calculating the internal coordinates and in selecting likely structure models from the helical parameters experimentally determined. The internal coordinates and helical parameters of polyethylene, polytetrafluoroethylene, sulfur, selenium, tellurium, isotactic polypropylene, poly-4-methyl-1-pentene, poly-m-methylstyrene, poly-o-methylstyrene, polyoxymethylene, polyisobutylene, polypeptides (α helix, parallel-chain, or antiparallel-chain extended form), polyglycine II, polyethylene glycol, and syndiotactic polypropylene were calculated and were used for discussing the structure of these helical polymers.

Résumé

Les conformations hélicoïdales de chaînes polymériques infinies peuvent être décrites par les paramètres comprenant ρ_i (la distance du i^e atome de l'axe hélicoïdal), d_{ij} (la translation au long de l'axe), et θ_{ij} (l'angle de rotation autour de l'axe en passant de l'i^e atome au j^e). Pour la chaîne polymérique principale, ($—M—$) ∞, ($—M_1—M_2—$) ∞, ($—M_1—M_2—M_3—$) ∞, ($—M_1—M_2—M_3—M_4—$) ∞, ($—M_1—M_2—M_3—M_4—M_5—$) ∞, ou ($—M_1—M_2—M_3—M_4—M_5—M_6—$) ∞, des équations mathématiques concises pour les paramètres hélicoïdaux sont données en termes de coordonnées internes, comme les longueurs des liaisons, les angles de liaisons, et les angles de rotation interne. Ces équations sont utiles pour calculer les coordonnées internes et pour choisir des modèles de structure vraisemblables à partir des paramètres hélicoïdaux déterminés expérimentalement. Les coordonnées internes et les paramètres hélicoïdaux du polyéthylène, polytétrafluoroéthylène, soufre, sélénium, tellure, polypropylène isotactique, poly-4-méthyl-pentène-1, poly-m-méthylstyrène, poly-o-méthylstyrène, polyoxyméthylène, polyisobutylène, polypeptides (α hélice, chaîne parallèle, ou forme à chaîne antiparallèle étendue), polyglycine II, polyéthylène glycol, et du polypropylène syndiotactique furent calculés et furent utilisés pour discuter de la structure de ces polymères hélicoïdaux.

Zusammenfassung

Die Helixkonformation unendlicher Polymerketten kann durch die Helixparameter ρ_i (der Abstand des i-ten Atoms von der Schraubenachse), d_{ij} (die Translation entlang der Achse) und θ_{ij} (der Rotationswinkel um die Achse, wenn man vom i-ten zum j-ten Atom geht) beschrieben werden. Für die Polymerhauptkette, ($—M—$)∞, ($—M_1—M_2—$) ∞, ($—M_1—M_2—M_3$) ∞, ($—M_1—M_2—M_3—M_4—$) ∞, ($—M_1—M_2—M_3—M_4—M_5—$) ∞ oder ($—M_1—M_2—M_3—M_4—M_5—M_6—$) ∞, werden strenge mathematische Gleichungen für die Helixparameter als Funktion der inneren Koordinaten, wie Bindungslängen, Bindungswinkel und innere Rotationswinkel angegeben. Diese Gleichungen sind zur Berechnung der inneren Koordinaten und zur Auswahl geeigneter Strukturmodelle mittels der experimentell bestimmten Helixparametern geeignet. Es wurden die inneren Koordinaten und Helixparameter von Polyäthylen, Polytetrafluoräthylen, Schwefel, Selen, Tellur, isotaktischem Polypropylen, Poly-4-methylpenten-1, Poly-m-methylstyrol, Poly-o-methylstyrol, Polyoxymethylen, Polyisobutylen, Polypeptiden (α-Helix, gestreckte Form mit parallelen oder antiparallelen Ketten), Polyglycin II, Polyäthylenglykol und syndiotaktischem Polypropylen berechnet und zur Diskussion der Struktur dieser Helixpolymeren verwendet.