suffice to point out that the results are in good agreement with the force field calculations presented in Figures 4 and 5 for aanalogous compounds and in Figure 6 for the same compound, methyl benzoate. Phenyl formate and benzamide exhibit minima displaced from the coplanar conformations ca. ±60° and ±30°, respectively; for methyl benzoate the minimum occurs at $\psi = 0°$, as in Figure 6. For formanilide, however, these calculations place the minimum at $\phi = 0°$, in agreement with the PCILO calculations of Lauprêtre and Monnerie[12] but at variance with the calculations presented in Figure 3. No explanation is apparent for this result of the ab initio calculations. It is incompatible with the X-ray crystallographic data on anilides (Table I), with the possible exception of those for para halogenated derivatives.

The GAUSSIAN-70 calculations yield a maximum of about 5 kcal mol^{-1} for the transverse conformation at $\phi = \pm 90°$. Although large, this barrier is more nearly in accord with expectation than the value indicated by the PCILO calculations.

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Moments of the End-to-End Vectors for *p*-Phenylene Polyamides and Polyesters

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ABSTRACT: Moments of rank 1-4 formed from the components x, y, and z of the chain vector $\mathbf{r}$ and expressed in the coordinate system affixed to the first unit have been calculated as functions of chain length n for *p*-phenylene polyamides of type I, $(-NHC_6H_4CO-)_n$, of type II, $(-NHC_6H_4NH-COC_6H_4CO-)_{n/2}$, and of the corresponding polyesters. Structural data on model compounds furnished the required geometric parameters. Configurational averaging was performed on the basis of the torsional potentials presented in the preceding paper. The persistence vector $\mathbf{a} \equiv \langle \mathbf{r} \rangle$ is dominated by its x component $\langle x \rangle$ along the phenylene axis; the transverse component $\langle y \rangle$ in the plane of this axis and the amide or ester group is negligible owing to the (approximate) mutual independence of torsions about a given phenylene axis; symmetry dictates that $\langle z \rangle \equiv 0$ perpendicular to this plane. The magnitude of the persistence vector depends sensitively on the difference δ between the skeletal bond angles at CO and at N or O. For the respective polyamides, with $\delta = 10°$, $\langle x_\infty \rangle = 410$ and 435 Å; for the polyesters, with $\delta = 7.4°$, $\langle x_\infty \rangle = 740$ and 785 Å. As n increases, the combined effects of departures of successive phenylene axes from parallelity and the random torsions introduce departures from the quasi-rod-like character manifested at comparatively small n. The chains become random coils at very large n (>2000 units for the polyamides). The course of the convergence of the distribution function $W(\mathbf{r})$ to its Gaussian limit, depicted by the higher moments, establishes the scaling factor m relating the number of units to the number of bonds in the corresponding freely jointed model chain. In the limit $1/n \to 0$, $m = 240$ units (1560 Å) for the *p*-phenylene polyamides and 450 units (2900 Å) for the polyesters compared with $m = 20$ (31 Å) for polyethylene.

Moments of the end-to-end vector $\mathbf{r}$ of the *p*-phenylene polyamides and polyesters discussed in the preceding paper[1] are the subject of the investigation reported here. These moments are significant as indexes of the character of the distribution $W(\mathbf{r})$ of vector $\mathbf{r}$. This distribution is determined, in principle, by the moments. Slow convergence of the expansion of $W(\mathbf{r})$ in its moments usually

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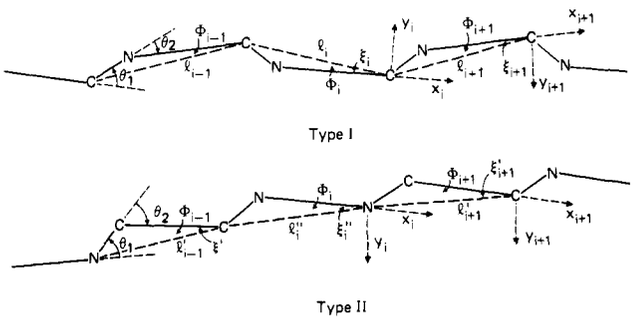

Figure 1. Schematic representation of *p*-phenylene polyamide chains of types I and II in their planar, fully extended configurations. Nitrogen and carbonyl carbons of the amide bonds are indicated by N and C*. Long solid lines represent axes of *p*-phenylene residues. Virtual bonds are represented by dashed lines. Successive amide bonds are cis in the extended form of type I and trans in type II. In the corresponding polyesters O replaces N.

renders actual construction of the distribution in this manner impractical, however.

The moments considered are the configurational averages of the elements of the Cartesian tensors up to fourth rank formed from **r**. They are here expressed in a coordinate system affixed to the first structural unit of the chain, the x axis being taken along the rotation axis of the first phenylene residue and the y axis in the plane defined by this axis and the first amide or ester bond, i.e., the bond of the preceding functional group. Thus, the moments considered are the configurational averages of products $x^{p_x}y^{p_y}z^{p_z}$ where $p_x + p_y + p_z = 1$, 2, 3, or 4. They will be found to reflect the pronounced persistence of these chains in the direction of the phenylene axis, i.e., in the x direction.

Owing to the symmetry of the potentials[1] affecting rotations about the phenylene axes, moments in which p_z is odd vanish. In the absence of correlations between consecutive functional groups, such as may arise from dipole–dipole interactions in the polyamides[1] (see also below), moments with p_y odd must also vanish, apart from the contribution, generally trivial, from the first unit. Thus, the persistence vector **a**, defined as the configurational average of **r** expressed in the coordinate system of the first unit, consists predominantly of $\langle x \rangle$; the component $\langle z \rangle$ is null, and $\langle y \rangle$ is comparatively small, or trivial in the case of particular interest in which rotations of successive functional groups are uncorrelated. In any case, $\langle x \rangle$ and $\langle y \rangle$ converge to finite limits with increase in the number n of structural units (i.e., of phenylene residues). Moments containing even powers of y or of z increase without limit with n, as do those containing even powers of x. These and other characteristics of the moments are demonstrated by the calculations that follow.

Geometric Representation of the Chain

The *p*-phenylene polyamide chains of types I and II are depicted schematically in Figure 1. With replacement of NH by O, these diagrams apply also to the corresponding polyesters. Benzene rings are treated as regular hexagons throughout the analysis and calculations that follow, and all pendent bonds are considered to be directed along axes of the ring. Small deviations of these directions, amounting to as much as 3° according to X-ray crystallographic results,[1-4] are ignored. With these simplifying approximations, the axes of the two rotations, φ and/or ψ, about the bonds adjoining a given phenylene residue are rendered collinear. These two axes and the axis of the intervening phenylene ring are therefore represented in Figure 1 by a single straight line; compare Figure 1 of the preceding paper.[1]

Amide and ester groups are assigned their planar trans configurations. Deviations from these preferred configurations, expressed as the angle of torsion about the partial double bond, are estimated to be on the order of ±5° from the torsional potentials for aromatic amides.[5,6] Values for esters probably are only slightly larger. Deviations of this magnitude may significantly affect the chain dimensions, as Birshtein[7] has shown. Their effect probably is no greater, however, than the limits set by uncertainties in bond angles and by the fluctuations of these angles.[8] In the interests of simplification and in order to avoid obscuring the primary role of the chain geometry, such effects have been disregarded in the present investigation, the amide and ester groups being treated as rigid and planar.

Each unit of the chain is spanned by a virtual bond vector $\mathbf{l}_i$, shown as a dashed line in Figure 1. The virtual bond lies in the plane defined by the phenylene axis and the preceding amide or ester bond. According to the assumptions above, its length l_i and the angle ξ_i that it makes with the phenylene axis in unit i are fixed by geometric parameters, i.e., by bond lengths and bond angles. The direction of a virtual bond, defined in the stated manner and expressed in the coordinate system of the first unit of the chain, depends on the rotations about the phenylene axes of the preceding units but not on rotations about the unit in which the given virtual bond is embedded. The alternative definition of virtual bonds as vectors spanning the phenylene axis and the *succeeding* amide or ester group would render the direction of $\mathbf{l}_i$ dependent on rotations about phenylene axis i.

In chains of type I all virtual bonds are of the same length l. Each joins successive carbonyl carbon atoms. For simplicity, carbonyl groups are assumed to mark the ends of the chain. The chain vector **r** for a molecule comprising n units is then the sum of its n virtual bond vectors.

In chains of type II, two virtual bonds must be distinguished. Those spanning a diacid residue are denoted by $\mathbf{l}'$, and those spanning a diamine or dihydric phenol residue are denoted by $\mathbf{l}''$; see Figure 1. Both join a carbonyl carbon with a nitrogen atom.

The configurations shown in Figure 1, in which the virtual bonds are in planar zigzag array, are the ones of maximum extension. Alternate phenylene axes are parallel in the configurations shown in each of the two types of chains. The angle δ between the directions of consecutive phenylene axes is given by

$$\delta = \theta_1 - \theta_2 = \tau_2 - \tau_1 \qquad (1)$$

where θ_1 and θ_2 are the supplements of the skeletal bond angles τ_1 and τ_2, respectively, at carbonyl and nitrogen. Subject to the assumption of fixed bond angles, this relation is invariant to torsional rotations about the phenylene axes. It applies to chains of both types.

The following bond lengths were chosen for the aromatic polyamides on the basis of crystallographic results cited in the previous paper:[1]

C^{Ph}-C*	1.51 Å
C*-N	1.355 Å
N-C^{Ph}	1.43 Å

where C^{Ph} and C* denote phenyl and carbonyl carbons, respectively. Corresponding values used in calculations on the aromatic polyesters are

C^{Ph}-C*	1.49 Å
C*-O	1.37 Å
O-C^{Ph}	1.41 Å

Table I
Geometrical Parameters

	polyamides	polyesters
	Type I	
θ_1	65.0°	69.1°
θ_2	55.0°	61.7°
δ	10.0°	7.4°
l	6.50 Å	6.44 Å
ξ	9.4°	10.8°
	Type II	
θ_1	65.0°	69.1°
θ_2	55.0°	61.7°
δ	10.0°	7.4°
l'	6.49 Å	6.37 Å
l''	6.51 Å	6.37 Å
l^a	6.28 Å	6.18 Å
ξ'	10.9°	11.6°
ξ''	9.8°	10.9°

[a] See eq 24.

The C^{Ph}–C^{Ph} bond was assigned a length of 1.39 Å.

Values of skeletal bond angle supplements $\theta_1 = \pi - \tau_1$ and $\theta_2 = \pi - \tau_2$ selected on the basis of the crystallographic results examined in the preceding paper[1] are recorded in Table I, together with their differences, δ, for polyamides and polyesters of both types. Also included are the lengths l of the virtual bonds and the angles ξ specifying their directions, as calculated from the stated values assigned to bond lengths and to the skeletal bond angles.

The sum of the two rotations about the phenylene axis of the ith unit is

$$\Phi_i = \zeta_i + \eta_i \tag{2}$$

where ζ_i and η_i are the torsions about the respective bonds pendent to the ith phenylene residue, these rotations being measured in the right-handed sense relative to the planar forms shown in Figure 1. For a polymer of type I, $\zeta_i = \varphi_i$ and $\eta_i = \psi_i$, i.e.,

$$\Phi_i = \varphi_i + \psi_i \tag{3}$$

In a polymer of type II, the rotations about the phenylene axis of the diacid residue are $\zeta_{i-1} = \psi_{i-1;1}$ and $\eta_{i-1} = \psi_{i-1;2}$. Hence

$$\Phi'_{i-1} = \psi_{i-1;1} + \psi_{i-1;2} \tag{4}$$

Similarly for the diamine, or dihydric phenol, residue

$$\Phi''_i = \varphi_{i;1} + \varphi_{i;2} \tag{5}$$

Cartesian coordinate systems are defined for each phenylene residue in the manner shown in Figure 1 and in accordance with previous conventions.[9] The x_i axis is identified with the phenylene axis of unit i. The y_i axis is located in the plane defined by x_{i-1} and x_i; it lies therefore in the plane of unit i, i.e., the plane defined by the phenylene axis and the preceding amide (or ester) bond. The direction of axis y_i is chosen to be acute with axis x_{i-1}. The direction of the z_i axis normal to the plane of the unit completes a right-handed coordinate system.

The chains in Figure 1 are illustrative of cases in which $\delta > 0$, which condition in fact holds for the polyamides and polyesters. If $\delta < 0$, then according to the stipulations of the preceding paragraph the directions of the y and z axes will be reversed. The algebraic effect of this alteration (see below) may be subsumed by the further stipulation that δ is to be taken positive, i.e., that

$$\delta = |\theta_1 - \theta_2| \tag{1'}$$

The matrix of the transformation of a vector in reference frame $x_{i+1}y_{i+1}z_{i+1}$ to its representation in reference frame $x_iy_iz_i$ is, according to the definitions above,

$$T_i = \begin{vmatrix} \alpha & \beta & 0 \\ \beta\cos\Phi_i & -\alpha\cos\Phi_i & \sin\Phi_i \\ \beta\sin\Phi_i & -\alpha\sin\Phi_i & -\cos\Phi_i \end{vmatrix} \tag{6}$$

where $\alpha = \cos\delta$ and $\beta = \sin\delta$.

The end-to-end vector $\mathbf{r}$ for a chain or n units is

$$\mathbf{r} = \mathbf{l}_1 + \sum_{k=1}^{n-1}\prod_{i=1}^{k}\mathbf{T}_i\mathbf{l}_{k+1} \tag{7}$$

when expressed in the reference frame of the first unit. Each virtual bond is expressed in the coordinate system of the unit it spans; i.e.,

$$\mathbf{l}_k = l_k \begin{vmatrix} u_k \\ v_k \\ 0 \end{vmatrix} \tag{8}$$

where $u_k = \cos\xi_k$ and $v_k = \sin\xi_k$ are the components of a unit vector in the direction of $\mathbf{l}_k$ on the axes x_k and y_k.

The Persistence Vector[10,11]

The average of the end-to-end vector $\mathbf{r}$ over all configurations of the chain consisting of n units, i.e., the persistence vector[10] $\mathbf{a}_n$, is obtained by taking the configurational averages of the serial products of transformations in eq 7. Since, in good approximation, the potentials affecting rotations ζ_i and η_i about the axis of unit i are independent of the rotations in neighboring units of the polymers considered, the transformations comprising each serial product may be averaged separately. Hence, the persistence vector referenced in the coordinate system of the first unit is

$$\mathbf{a}_n \equiv \langle\mathbf{r}\rangle = \mathbf{l}_1 + \sum_{k=1}^{n-1}\prod_{i=1}^{k}\langle\mathbf{T}_i\rangle\mathbf{l}_{k+1} \tag{9}$$

As pointed out in the preceding paper,[1] the torsional potentials affecting Φ_i are symmetric with respect to the planar conformations $\Phi_i = 0$ and π. Hence $\langle\sin\Phi_i\rangle = 0$. Dipolar interactions between neighboring functional groups may cause the potentials at Φ_i and at $\Phi_i \pm \pi$ to differ. To the extent that this difference is significant, $c_i \equiv \langle\cos\Phi_i\rangle$ will depart from zero. The configurational average of the transformation must then be expressed by

$$\langle\mathbf{T}\rangle = \begin{vmatrix} \alpha & \beta & 0 \\ \beta c & -\alpha c & 0 \\ 0 & 0 & -c \end{vmatrix} \tag{10}$$

the serial index i having been dropped.

Since α and β are determined by structural parameters considered to be fixed, only c in eq 10 depends on the torsional potentials. It may be evaluated by numerical integration according to the general relation

$$\langle F(\Phi)\rangle = \int\int \exp[-(E_\zeta + E_\eta + E_\Phi)/kT] \times [F(\Phi)]\,d\zeta\,d\eta \Big/ \int\int \exp[-(E_\zeta + E_\eta + E_\Phi)/kT]\,d\zeta\,d\eta \tag{11}$$

where ζ and η are the torsions about the bonds pendent to the phenylene group; E_ζ and E_η are the potentials associated with these rotations, as discussed in the preceding paper;[1] E_Φ, with $\Phi = \zeta + \eta$, denotes the potential arising from (dipolar) interactions between the adjoining functional groups; and $F(\Phi)$ is any function of Φ. In the present instance, $F(\Phi) = \cos\Phi$. As here expressed, eq 11 comprehends the various trigonometric functions $F(\Phi)$ of Φ which must be averaged in order to evaluate higher moments formed from vector $\mathbf{r}$; cf. seq.

Chains of Type I. In homopolymers of this kind, all units are identical. Hence, only one averaged transfor-

mation matrix $\langle \mathbf{T} \rangle$ is required, serial indexes may be dropped, and the persistence vector reduces to

$$\mathbf{a}_n = \sum_{k=1}^{n} \langle \mathbf{T} \rangle^{k-1}\mathbf{l} = (\mathbf{E} - \langle \mathbf{T} \rangle^n)(\mathbf{E} - \langle \mathbf{T} \rangle)^{-1}\mathbf{l} \quad (12)$$

where $\mathbf{E}$ is the matrix identity. Substituting eq 10 for $\langle \mathbf{T} \rangle$ in the second factor in eq 12, inverting the resulting matrix, and introducing eq 8 for $\mathbf{l}$, we obtain in the limit $n \rightarrow \infty$

$$\mathbf{a}_\infty/l = (1 - \alpha)^{-1}(1 - c)^{-1} \begin{vmatrix} (1 + \alpha c)u + \beta v \\ \beta c u + (1 - \alpha)v \\ 0 \end{vmatrix} \quad (13)$$

For the chains of finite length

$$\mathbf{a}_n = (\boldsymbol{E} - \langle \mathbf{T} \rangle^n)\mathbf{a}_\infty \quad (14)$$

Evaluation of the factor in parentheses in eq 14 is facilitated by diagonalization of $\langle \mathbf{T} \rangle$ as given by eq 10. The eigenvalues are

$$\lambda_{1,2} = (1/2)\alpha(1 - c)[1 \pm (1 + 4c/\alpha^2(1 - c)^2)^{1/2}]$$
$$\lambda_3 = -c \quad (15)$$

and the matrix of eigenvectors, expressed in terms of the eigenvalues, is

$$\mathbf{A} = \begin{vmatrix} 1 & 1 & 0 \\ \dfrac{\lambda_1\lambda_3 - \lambda_2}{(1 + \lambda_3)\beta} & \dfrac{\lambda_2\lambda_3 - \lambda_1}{(1 + \lambda_3)\beta} & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad (16)$$

where

$$\beta^2 = 1 - \alpha^2 = 1 - (\lambda_1 + \lambda_2)^2(1 + \lambda_3)^{-2} \quad (17)$$

Then

$$\mathbf{a}_n = (\mathbf{E} - \mathbf{A}\Lambda^n\boldsymbol{A}^{-1})\mathbf{a}_\infty \quad (18)$$

where $\Lambda = \mathrm{diag}(\lambda_1,\lambda_2,\lambda_3)$ and $\mathbf{a}_\infty$ is given by eq 13.

If the combination of potentials affecting the net torsion Φ is twofold symmetric, as occurs when the dipolar interactions between successive functional groups may be ignored, then $c = 0$ and

$$\langle \mathbf{T} \rangle = \begin{vmatrix} \alpha & \beta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (19)$$

According to the relations above

$$\mathbf{a}_n/l = \begin{vmatrix} \dfrac{u + \beta v - (u + \beta v/\alpha)\alpha^{n-1}}{1 - \alpha} \\ v \\ 0 \end{vmatrix} \quad (20)$$

The limiting value for $n \rightarrow \infty$, obtained by setting $\alpha^{n-1} = 0$ in eq 20, follows also from eq 13 with $c = 0$. Regardless of the value of $n \geq 1$, the y component of $\mathbf{a}_n$ consists only of the contribution vl of the first virtual bond; contributions of all succeeding bonds vanish in consequence of the twofold symmetry of the torsional potentials.

In Figure 2 we show the ratio $\langle x \rangle$ of the x component of the persistence vector $\mathbf{a}_n$ to the length l of the virtual bond plotted against the chain length n for the p-phenylene polyamides (solid line) and polyesters (dashed line) of type I with neglect of interunit correlations, i.e., with $E_\Phi = 0$ and, hence, $c = 0$. The calculations were carried out according to eq 20. In the limit $n \rightarrow \infty$, $\langle x_\infty \rangle/l = 63.1$ for the polyamides and 115.1 for the polyesters. Corresponding values of $\langle x_\infty \rangle$ are 410 and 741 Å, respectively. Values within 1% of the asymptotes are reached at $n \approx 300$ and 550 units for the respective series. The

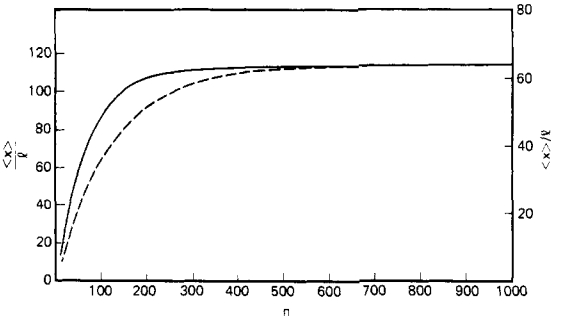

Figure 2. Ratios of persistence lengths $\langle x \rangle$ to the length l of the virtual bond calculated as functions of the number n of units according to eq 20 for polyamides (solid line; ordinate scale on right) and polyesters (dashed line; ordinate scale on left) of type I. The two curves are scaled to converge to the same asymptote.

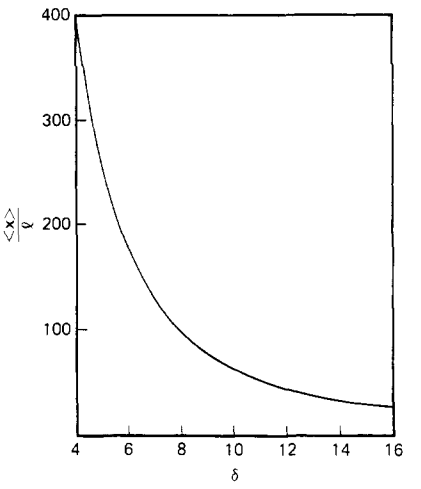

Figure 3. Limiting persistence ratios for chains of type I calculated according to eq 20 with $n = \infty$ as a function of the difference δ between successive rotation axes. Calculations are for fixed $\xi = 9.4°$ for the polyamides. Since the values of the persistence vectors for the polyesters with $\xi = 10.9°$ differ by less than 1% from those for the polyamides for a given value of δ, the curve for the polyesters is not shown separately.

curves are similar in other respects.

The higher asymptote $\langle x_\infty \rangle/l$ and more protracted approach thereto for the polyesters is a direct consequence of the smaller value of δ and the consequent extended range of correlation of the directions of rotation axes. The influence of δ on the persistence vectors[7] is illustrated in Figure 3 where $\langle x_\infty \rangle/l$ is plotted against δ, the value of ξ for the polyamide series being used throughout. This is tantamount to varying θ_1 while fixing θ_2 and all bond lengths. The behavior shown in Figure 3 is essentially (but not exactly) that of a freely rotating chain as a function of its bond angle. Since the values of persistence vectors for polyamides and polyesters of type I differ by less than 1% for the same value of β, results calculated for polyesters are very nearly coincident with those for the polyamide series. Hence, they are not shown separately.

Figure 4 illustrates the effect of a potential dependent upon the mutual orientation of the pendent functional (amide) groups and represented, in approximation, by $E_\Phi = E_\Phi^0(1 - \cos \Phi)$. Values of $E_\Phi^0/kT = {}^1/_4$ and ${}^1/_2$ in conjunction with the potentials E_φ and E_ψ for the amide–phenyl bonds given in the preceding paper yield $c = 0.129$ and 0.252, respectively, by application of eq 11 for a temperature of 300 K. The dipolar interaction between consecutive amide groups may be estimated to fall in the range of these two values chosen for E_Φ^0/kT. The curves in Figure 4 showing $\langle x \rangle/l$ and $\langle y \rangle/l$ as functions of n for

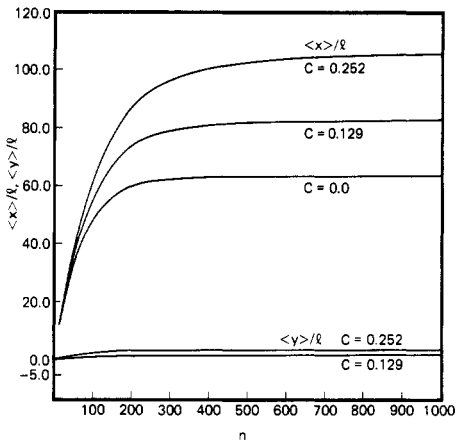

Figure 4. Ratios $\langle x\rangle/l$ and $\langle y\rangle/l$ for polyamide chains of type I calculated as functions of n according to eq 13 and 18 for the values of $c \equiv \langle\cos\Phi\rangle$ indicated and the geometric parameters given in the text.

these values of c were calculated according to eq 13 and 18 for the quoted values of c and the geometric parameters given above. With an increase in c, the limiting ratio $\langle x_\infty\rangle/l$ increases and approach to the limit is more protracted. Values within 1% of the limit are reached at n = 400 and 500 for c = 0.129 and 0.252, respectively, compared with n = 300 for c = 0. The ratio $\langle y_\infty\rangle/l$ increases similarly with c but remains comparatively small. For c = 0 its value is $v \approx -0.16$, independent of $n \geq 1$. These calculations demonstrate effects of the directional correlations between successive units that are implicit in values of $c > 0$.

Chains of Type II. The end-to-end vector expressed in the coordinate system for the first unit, which we take to be a diacid residue, is in this case

$$\mathbf{r} = \mathbf{l}_1' + \mathbf{T}_1'\mathbf{l}_2'' + \mathbf{T}_1'\mathbf{T}_2''\mathbf{l}_3' + \mathbf{T}_1'\mathbf{T}_2''\mathbf{T}_3'\mathbf{l}_4'' + \ldots \quad (21)$$

For a homopolymer in which the units are alternately identical, e.g., diacid and diamine, the serial subscripts may be omitted. As for chains of type I, independence of the rotations about successive phenylene axes sanctions separate averaging of the transformations. The persistence vector for a chain having $n/2$ units of each kind, averaged in the coordinate system $x'y'z'$ of the terminal diacid residue, is conveniently expressed as

$$\mathbf{a}_n = 2\sum_{k=1}^{n/2}\langle\mathbf{T}^{(2)}\rangle^{k-1}\bar{\mathbf{l}} \quad (22)$$

where

$$\langle\mathbf{T}^{(2)}\rangle \equiv \langle\mathbf{T}'\mathbf{T}''\rangle = \langle\mathbf{T}'\rangle\langle\mathbf{T}''\rangle \quad (23)$$

and $\bar{\mathbf{l}}$ is the mean virtual bond vector given by

$$2\bar{\mathbf{l}} = \mathbf{l}' + \langle\mathbf{T}'\rangle\mathbf{l}'' \quad (24)$$

Execution of the summation in eq 22 yields

$$\mathbf{a}_n = (\mathbf{E} - \langle\mathbf{T}^{(2)}\rangle^{n/2})\mathbf{a}_\infty \quad (25)$$

where

$$\mathbf{a}_\infty = 2(\mathbf{E} - \langle\mathbf{T}^{(2)}\rangle)^{-1}\bar{\mathbf{l}} \quad (26)$$

The procedures employed above for chains of type I may be applied here as well. If $c' = c'' = 0$, then $\langle\mathbf{T}'\rangle = \langle\mathbf{T}''\rangle$, with $\alpha' = \alpha'' = \alpha$ and $\beta' = \beta'' = \beta$. In this case,

$$\mathbf{a}_n = 2\bar{l}\begin{vmatrix} [\bar{u} + \alpha\beta\bar{v} - (\bar{u} + \beta\bar{v}/\alpha)\alpha^n]/(1-\alpha^2) \\ \bar{v} \\ 0 \end{vmatrix} \quad (27)$$

where $\bar{u}$ and $\bar{v}$ are the x and y components of a unit vector along $\bar{\mathbf{l}}$ in the reference frame of the first virtual bond $\mathbf{l}'$ of the dyad and $\bar{\mathbf{l}}$ is the magnitude of $\bar{\mathbf{l}}$.

Calculations for type II chains carried out according to eq 27 yield results that are greater than those shown in Figure 2 for chains of type I by a factor of 1.06 throughout the range n. They are not presented separately, therefore. Values of $\langle x_\infty\rangle/\bar{l}$ are 67.2 and 121.5 for the polyamide and polyester chains, respectively. Corresponding values of $\langle x_\infty\rangle$ are 422 and 751 Å, respectively.

The Characteristic Ratio

Chains of Type I. For a chain consisting of n identical configurationally independent units, the characteristic ratio is given by

$$C_n \equiv \langle r^2\rangle/nl^2 = \mathbf{u}^{\mathrm{T}}[(\mathbf{E} + \langle\mathbf{T}\rangle)(\mathbf{E} - \langle\mathbf{T}\rangle)^{-1} - 2n^{-1}\langle\mathbf{T}\rangle(\mathbf{E} - \langle\mathbf{T}\rangle^n)(\mathbf{E} - \langle\mathbf{T}\rangle)^{-2}]\mathbf{u} \quad (28)$$

where $\mathbf{u}$ is the unit vector along the virtual bond of length l and $\mathbf{u}^{\mathrm{T}}$ is its transpose. Thus,

$$C_n = C_\infty - \Delta C_n \quad (29)$$

C_∞ and ΔC_n being defined by comparison with the preceding equation.

Substitution of eq 13 for $\langle\mathbf{T}\rangle$ in eq 28 yields

$$C_\infty = \left(\frac{1+c}{1-c}\right)\left[\left(\frac{1+\alpha}{1-\alpha}\right)^{1/2}u + v\right]^2 \quad (30)$$

If $u = 1$ and $v = 0$, this reduces to the well-known result for a single chain consisting of bonds subject to symmetric, mutually independent potentials. ΔC_n may be evaluated by the procedures outlined above.

If $c = 0$ and, hence, $\langle\mathbf{T}\rangle$ is given by eq 19, then the characteristic ratio for the finite chain reduces to the expression

$$C_n = [u((1+\alpha)/(1-\alpha))^{1/2} + v]^2 - (2/n)[(1-\alpha^n)(1-\alpha)^{-2}(\alpha u^2 + \beta uv) - \beta uv + \beta v^2] \quad (31)$$

Characteristic ratios calculated for polyamides of type I are shown in Figure 5 where they are plotted against n. The upper solid curve was calculated for c = 0.252 according to eq 28–30; the lower solid curve, calculated according to eq 31, represents chains in which the rotations and ψ about a given phenylene axis are uncorrelated, i.e., for which $c = 0$. Geometric parameters δ and ξ given in Table I were used in these calculations. The limiting value of C_∞ is 123.6.

Corresponding results for the type I polyester series, calculated for $c = 0$ with the use of eq 31, are shown by the solid curve in Figure 6. In the limit $x \to \infty$, C_∞ = 225.

Chains of Type II. In this case eq 28 is replaced by

$$C_n \equiv \langle r^2\rangle/n\bar{l}^2 = 2\mathbf{u}^{\mathrm{T}}[(\mathbf{E} + \langle\mathbf{T}^{(2)}\rangle) \times (\mathbf{E} - \langle\mathbf{T}^{(2)}\rangle)^{-1} - 4n^{-1}\langle\mathbf{T}^{(2)}\rangle(\mathbf{E} - \langle\mathbf{T}^{(2)}\rangle^{n/2})(\mathbf{E} - \langle\mathbf{T}^{(2)}\rangle)^{-2}]\mathbf{u} \quad (32)$$

where the mean virtual bond length $\bar{l}$ is defined by eq 24. If $c = 0$,

$$C_n = \frac{1+\alpha^2}{1-\alpha^2}\bar{u}^2 + \frac{2\alpha}{\beta}\bar{u}\bar{v} + \bar{v}^2 - \frac{4}{n}\left[\frac{\alpha^2(1-\alpha^n)}{(1-\alpha^2)^2}\right] + \left(\bar{u}^2 + \frac{\beta}{\alpha}\bar{u}\bar{v}\right) \quad (33)$$

Calculations carried out according to this equation show that the characteristic ratios for type II chains are 6%

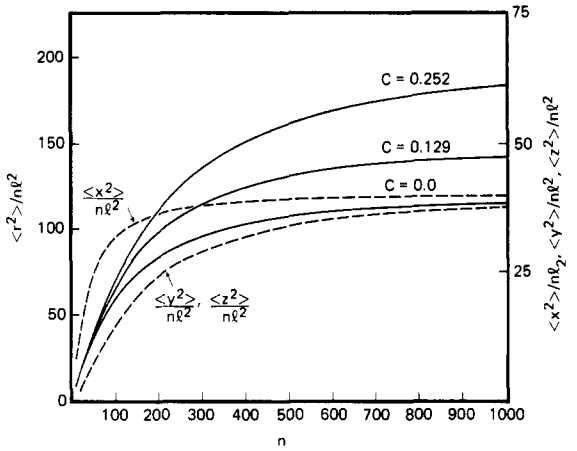

Figure 5. Characteristic ratios (solid curves) and second moment ratios (dashed curves) for polyamides of type I plotted against n. The solid curves represent characteristic ratios calculated from eq 28–31 for the values of c indicated. Dashed curves for the moments $\langle x^2\rangle/nl^2$, $\langle y^2\rangle/nl^2$, and $\langle z^2\rangle/nl^2$ were calculated also with $c = 0$, using procedures published previously.[12,13] Asymptotes of the curve for $c = 0$ are rendered coincident through choice of ordinate scales differing by a factor of 3.

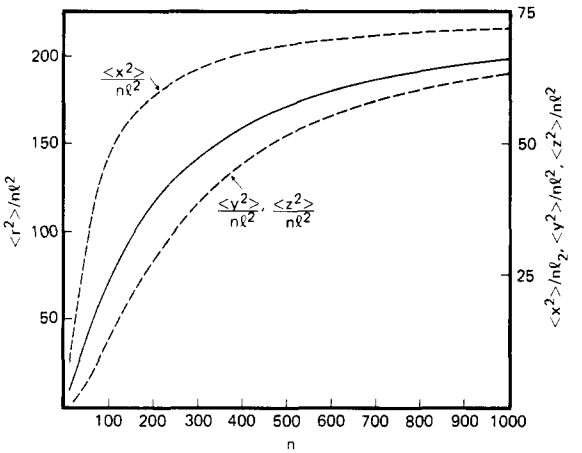

Figure 6. Characteristic ratios (solid curves) and second moment ratios (dashed curves) for polyesters of type I plotted against n for $c = 0$; see legend to Figure 5.

greater than the corresponding characteristic ratios of type I chains.

Moments of Cartesian Tensors Formed from the Chain Vector r

Moments of the Cartesian tensors formed from **r** were calculated by methods previously published.[11-14] These moments, being the configurational averages of the elements of the tensors, may be expressed generically by $\langle x^{p_x}y^{p_y}z^{p_z}\rangle$, where the sum $p_x + p_y + p_z = p$ is the rank of the tensor. Averages of products of sines and cosines of Φ of rank $\leq p$ are required for their evaluation.[11-13] Equation 11 was used for this purpose, the torsional potentials $E(\varphi)$ and $E(\psi)$ being taken from the preceding paper.[1] Moments containing odd powers of z are null in consequence of the symmetry of the torsional potentials. If $c = 0$, those containing odd powers of y also are null, apart from the trivial contribution of the first unit. Calculations that follow are limited to this case.

The Second Moments. Under the conditions stated, only the diagonal elements $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ of the second moment tensor are nonzero. Expressed as dimensionless ratios through division by nl^2, the progression of these moments with n is portrayed by the dashed curves in Figures 5 and 6; they are referred to the ordinate axes on the right. The torsional potentials $E(\varphi)$ and $E(\psi)$ allow similar deviations in the two directions transverse to the phenylene axis. Hence, $\langle y^2\rangle$ and $\langle z^2\rangle$ rapidly merge to the same curve as n increases. They are therefore represented by the same dashed line in Figure 5 and in Figure 6. In the limit $x \to \infty$ each of the moments converges to $C_n/3$. Coincidence with the curve for C_n in this limit has been achieved deliberately through expansion of the right-hand ordinate scale by a factor of 3.

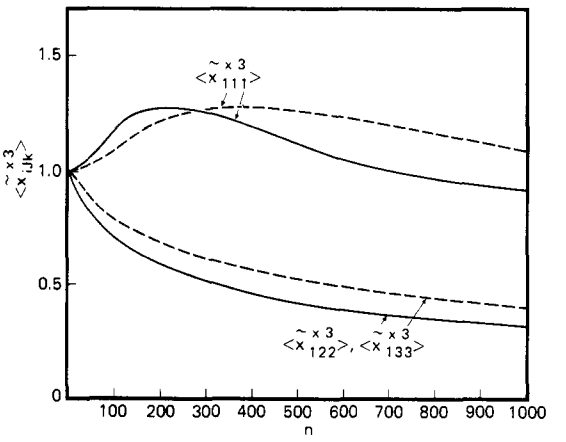

Figure 7. Reduced third moments for polyamides (solid curves) and polyesters (dashed curves) plotted against n.

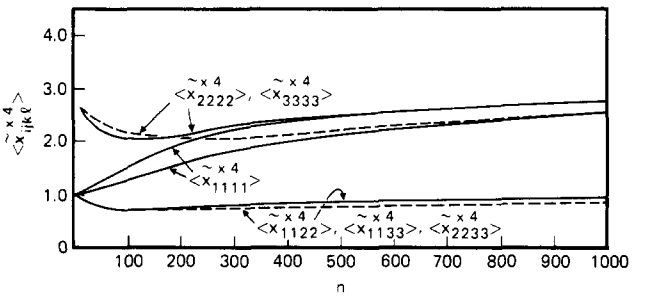

Figure 8. Reduced fourth moments for polyamides (solid curves) and polyesters (dashed curves) plotted against n.

Calculations for chains of type II yield second moments that, like the first moments, exceed the corresponding moments for chains of type I by about 6%.

Higher Moments. Third and fourth moments reduced according to the following prescription

$$\langle \tilde{x}^{p_x}\tilde{y}^{p_y}\tilde{z}^{p_z}\rangle = \frac{\langle x^{p_x}y^{p_y}z^{p_z}\rangle}{\langle x^2\rangle^{p_x/2}\langle y^2\rangle^{p_y/2}\langle z^2\rangle^{p_z/2}} \qquad (34)$$

are presented in Figures 7 and 8, respectively, for the polyamides (solid curves) and polyesters (dashed curves) of type I with $c = 0$. Calculations of third and fourth moments for chains of type II yield the same values when reduced according to eq 34. Convergence to the asymptotes for infinite chains is very slow for all components of the third and fourth moments. The third moments, which indicate the skewness of the distribution $W(\mathbf{r})$ of the chain vectors, approach their limits of zero only for very long chains. The three main components of the averaged fourth order tensor, namely $\langle \tilde{x}_{1111}\rangle$, $\langle \tilde{x}_{2222}\rangle$, and $\langle \tilde{x}_{3333}\rangle$, attain 88% of their limiting values at $n = 800$. At the same chain length the other three components, $\langle \tilde{x}_{1122}\rangle$, $\langle \tilde{x}_{1133}\rangle$, and $\langle \tilde{x}_{2233}\rangle$, reach 90% of their limiting values for $n \to \infty$.

Correlation with the Freely Jointed Chain in the Gaussian Limit. The even moments for a freely jointed model chain of n' bonds can be scaled to those of the real chain of n bonds by resort to the relation $n' = n/m$, where m is the scaling ratio defined as the number of real bonds

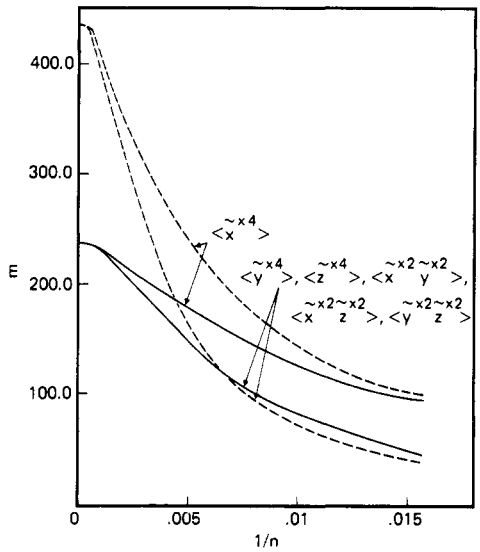

Figure 9. Scaling ratio m plotted against $1/n$ for polyamides (solid curves) and polyesters (dashed curves) calculated according to eq 35.

Table II
Comparison of Parameters Characterizing Chain Extension

	polyamides (I)	polyesters (I)	polyethylene
$\langle x_\infty \rangle / l$	63	115	3.75
$\langle x_\infty \rangle$, Å	410	740	5.75
b/l	124	225	5.35
b, Å	803	1450	8.20
m	240	450	20[a]
ml, Å	1560	2900	31[a]

[a] From ref 13 and 14.

that are equivalent to one bond of the model. Following the derivations given in ref 13, the number m can be deduced from the relation

$$m = nK^{-1}\left[\langle \tilde{x}^{p_x} \tilde{y}^{p_y} \tilde{z}^{p_z} \rangle_0 - \langle \tilde{x}^{p_x} \tilde{y}^{p_y} \tilde{z}^{p_z} \rangle \right] \qquad (35)$$

where the subscript 0 denotes the moments in the Gaussian limit, and $K = {}^6/_5$ and ${}^2/_5$ for the homogeneous and the nonhomogeneous components of the fourth moments, respectively.[13,18] Values of m thus obtained are plotted for polyamides (solid lines) and polyesters (dashed lines) against $1/n$ in Figure 9. For each component of the fourth moment tensor, they converge approximately to the same limit of 240 structural units for the polyamide series and 450 for the polyesters. This result demonstrates that the spatial distribution becomes uniformly isotropic in the limit $1/n \rightarrow 0$, i.e., the high anisotropy of chains of moderate length eventually vanishes when the chains become very long.

Summary of Results of Calculations and Comparison with Experiment

In Table II we list parameters deduced from the foregoing calculations for polyamides and polyesters of type I. Those for the corresponding polymers of type II are omitted since they parallel those for type I. Values for polyethylene chains are given in the last column for comparison. Lengths b of the Kuhn segment are calculated from the characteristic ratios and maximum lengths r_{max} according to the relations

$$n^* b^2 = C_\infty n l^2 \qquad n^* b = r_{max} \qquad (36)$$

n^* being the number of Kuhn segments in a chain of n real bonds. The length r_{max} at full extension is identified with nl for the p-phenylene chains, the small difference between l and its projection on the rectilinear axis of the fully extended planar zigzag being ignored. For the polymethylene chain we let $r_{max} = nl'$ where $l' = 1.27$ Å is the projection of the C–C bond on the axis of the fully extended chain. It follows from eq 36 that $b/l = C_\infty$ for the p-phenylene amide and ester chains.

For a chain that conforms to the freely jointed model, the three quantities $\langle x_\infty \rangle$, b, and ml (or ml') should be equal. They will be seen to be widely disparate for each of the real chains included in Table II. For polyamides and polyesters they are approximately in the ratio 1:2:4. Obviously, the freely jointed chain fails to afford a universal representation of the spatial characteristics of real chains.

The chains here considered should conform satisfactorily to the Porod–Kratky persistent chain model. The quantities in the first two rows of Table II may therefore appropriately be compared with persistences evaluated from experimental results treated according to this model. Arpin and Strazielle[16] investigated the polyamides of types I and II in 96% sulfuric acid. From molecular weights and radii of gyration determined by light scattering they found persistence lengths of 400–600 Å for type I and 200 Å for type II. Analysis of the intrinsic viscosity gave 400 and 150 Å, respectively. Flow birefringence measurements of Tsvetkov[17] yielded persistences of 320 and 200 Å for the respective Kuhn segments. Applying the same method, Arpin and Strazielle[16] confirmed the latter value.

Our calculated persistence lengths $\langle x_\infty \rangle$ should be regarded as upper bounds. Allowance for torsional fluctuations about the amide and ester bonds should lower them appreciably.[7] Bond angle bending will affect them likewise, although to a smaller degree. Estimation of these effects according to the methods of Birshtein[7,8] suggests a reduction on the order of 25–40% for the polyamides. When adjusted in this manner, the calculations fall within the range observed for polyamides of types I and II. Theory fails, however, to account for the difference between the persistences observed for polymers of the two types.

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(18) Yoon and Flory[13] derived the scaling ratio m from reduced moments of the "displacement vector" $\rho = \mathbf{r} - \mathbf{a}$, instead of from the reduced moments of the chain vector $\mathbf{r}$ itself, as in eq 35. In as much as the reduced displacement vector defined by $\rho = \langle\rho\rho^{T}\rangle^{-1/2}\rho$ converges to the reduced chain vector $\tilde{\mathbf{r}}$ in the limit $1/n \rightarrow 0$, these alternative procedures must lead to the same value of the scaling ratio m.

Unperturbed Dimensions of Amylose in Binary Water/Dimethyl Sulfoxide Mixtures‡

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ABSTRACT: The unperturbed dimensions of amylose have been determined in the mixed solvent water/dimethyl sulfoxide (Me_2SO) over the range of Me_2SO volume fraction (Φ_{Me_2SO}) from 0.30 to 0.90. The molecular weight, second virial coefficient, and mean square radius of gyration were measured for 11 different values of Φ_{Me_2SO} by light scattering. Intrinsic viscosities have been determined in the same solvent mixtures. The excluded volume expansion factor was evaluated from the observed molecular weights, virial coefficients, and polymer chain dimensions with the modified Flory–Krigbaum–Orofino theory and the Yamakawa–Tanaka theory and used in conjunction with chain dimensions from both light scattering and intrinsic viscosity to calculate the unperturbed dimensions. In the mixed solvent the unperturbed mean-square end-to-end distance declines from its value in water to about 80% of this value at $\Phi_{Me_2SO} = 0.60$; further variation for $\Phi_{Me_2SO} > 0.60$ cannot be ascertained with confidence. The observed effect of specific solvation on the unperturbed dimensions is discussed in terms of changes in the preferred conformational isomers for rotations about the chemical bonds of the glycosidic linkage.

The dilute solution behavior of most common polysaccharides has now been analyzed in terms of more or less realistic molecular models, and a framework for rationalizing solution properties in terms of molecular structure and conformation has been established.[1,2] No member of the class has received more attention than amylose, the linear α-1,4-glucan component of starch,[3] and a good understanding of the molecular basis for its aqueous solution characteristics has emerged.[4-6] As yet no detailed model has been presented for the influence of specific solvation effects on the unperturbed dimensions of amylose or any other polysaccharide, although it is widely recognized that the polar character of these polymers and their common solvents makes likely an important influence of strong solvation on the conformational energy surface of the chain.[7] It is as part of an effort to understand the role of specific solvation in polysaccharide solution behavior that the studies reported here were undertaken.

Figure 1 shows a conventional conformational energy map[7,8] for the dimeric amylose chain segment "maltose". The maltose unit is shown as an inset on the map, and the glycosidic linkage torsion angles φ and ψ are defined; conventions for the zero and positive sense of rotation are given elsewhere.[2,7] The map shown, although correct for *aqueous* amylose in its major features, does not reflect any explicit accounting of solvation effects and has not been refined to conform to any measured solution characteristics of amylose.[2,7]

Amylose has been studied extensively in H_2O and dimethyl sulfoxide (Me_2SO) solution, and its properties in the binary solvent H_2O/Me_2SO have also been investigated. Metastable solutions of amylose in water can be prepared, from which amylose in the B-crystalline modification precipitates in a process known as retrogradation.[9-13] The rate of retrogradation displays a strong dependence on mean molecular weight and molecular weight distribution.[9,12] In favorable cases it has therefore been possible to investigate the solution characteristics of amylose in water and in aqueous salt solutions. It is widely believed that aqueous 0.33 M KCl is a Θ solvent for the polymer[3,14] in which the characteristic ratio $C_\infty \equiv \langle r^2\rangle_0/xL^2 \simeq 5$, where $\langle r^2\rangle_0$ is the mean-square unperturbed end-to-end distance, x is the degree of polymerization, and L is the length of the virtual bond (4.25 Å)[8] connecting successive glycosidic oxygens. Molecular models for aqueous amylosic chains are well developed and suggest that the dissolved polymer is a mobile random coil with a tortuous backbone trajectory that nevertheless displays at any instant considerable irregular short-range helical structure.[6]

In contrast to water, Me_2SO is a good solvent for amylose, and the intrinsic viscosity, radius of gyration, and second virial coefficient are considerably larger for a given amylose sample in Me_2SO than in H_2O solution.[11,15-19] Fujii et al.[19] conclude from studies of the chain length dependence of the intrinsic viscosity, radius of gyration, virial coefficient, and sedimentation coefficient of amylose fractions that the molecular conformation of the polymer in Me_2SO is stiff and "predominantly helical, in contrast to that of the same polymer in aqueous solutions of simple electrolyte". Proton magnetic resonance (^1H NMR) and infrared spectroscopic studies of amylose and model compounds[20] reveal the presence in Me_2SO solution of an interresidue hydrogen bond between hydroxyls OH(2) and OH(3′). St. Jacques et al. infer from further ^1H NMR studies[21] that OH(3′) is the proton donor in this interaction and conclude that the favored conformations of the glycosidic linkage torsion angles φ and ψ (see Figure 1) are such as to confer on the chain "substantial right-handed helical character in this solvent". Maltose conformations with positive values of φ and ψ in the vicinity of the position marked Z on the energy map in Figure 1 are implied by this proposal.[21]

Molecular models for aqueous amylosic chains, on the other hand, are unanimous in their implication that the residual helical character in this medium has predominantly left chirality.[4-6,22,23] The lowest energy conformation in Figure 1, for example, is in the field of left helical states

‡ Dedicated to Professor Paul J. Flory on the occasion of his 70th birthday.

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