Conformational Averages over All Possible Skeletal Rotations. Poly(oxymethylene)

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ABSTRACT: A matrix algorithm for the statistical-mechanical treatment of an unperturbed ····-A–B–A–B–··· polymer chain with energy correlation between first-neighboring skeletal rotations φ_n is described. It is based on the Fourier expansion of the $w(\varphi_n\varphi_{n+1})$ Boltzmann statistical weight and accounts for all skeletal rotations (asr scheme). Calculations of the chain partition function and of the mean-square end-to-end distance have been carried out for poly(oxymethylene) at different temperatures, the conformational energy being evaluated by using two distinct sets of non-bonded interaction parameters. The results of the unperturbed dimensions are in satisfactory agreement with experimental data. In addition, if the same energy data are used, the results are rather close to those obtained by the less sophisticated rotational isomeric state (ris) scheme usually adopted. The ris scheme is shown to be also adequate for the calculation of the average intramolecular conformational energy, if the torsional oscillation about skeletal bonds is taken into account in the harmonic approximation. The results show that the intramolecular contribution accounts for about 15% of the heat of melting.

In a previous paper a theory was proposed by one of us for dealing with the classical statistical mechanics of polymer chains with first-neighbor interactions, accounting for all possible skeletal rotations (asr scheme),[1] in contrast to the usual rotational isomeric state (ris) approach.[2] The *asr scheme is based upon a matrix representation of the* Fourier coefficients of the conformational statistical weight as well as of the functions to be averaged, expressed in terms of the rotation angles. Calculations were carried out for the unperturbed polyethylene chain according both to the asr and to the ris schemes: although the mean-square end-to-end distance did not show a difference larger than about 5% between the two methods, a *substantial difference was found in the average conformational energy.*[1] As it will be shown in the following, the discrepancy may be well accounted for if the potential energy connected with the torsional oscillations about skeletal bonds is evaluated in the assumption that single bonds behave as independent harmonic oscillators.

In principle, within the usual assumptions of classical statistical mechanics, which involve factorization of the overall partition function into its kinetic and conformational components, the asr approach is exact. In practice, the double Fourier series representing the statistical weight associated with neighboring rotations must be truncated somewhere, and this introduces some degree of approximation. However, in the case of polyethylene (PE) it was possible to verify that at normal temperature the results become virtually insensitive to increasing Fourier expansion at relatively moderate levels (*i.e.*, no Fourier terms containing cos $m\varphi$ or sin $m\varphi$ with m larger than about 10 are needed, φ being the rotation angle),[1] which allows the problem to be easily tackled with normal capacity computers. Furthermore, in all the cases where the energy barriers between the minima are of the same order as or lower than PE (about 3 kcal/mol), a Fourier expansion of the same degree should be sufficient to get virtually exact results at normal temperatures. In contrast, the ris approximation should be expected as progressively inadequate, at least in principle, with the lowering of the energy barriers and/or the flattening of the minima. An indication in this sense may be found in the results obtained by one of us[3] for the unperturbed dimensions of *cis*-1,4-polybutadiene, where the ris scheme appears to *represent a relatively poor approximation due to the flat*ness of the potential energy function associated with neighboring rotations.[4] Other polymer chains where the ris scheme should be expected to give relatively inadequate answers are those characterized by a strong energy of interaction between adjacent rotations. For these polymers, such as isotactic polypropylene which has also been investigated by us,[5] the definition of the rotational isomeric states may be difficult if the location of the energy minima of any rotation angle depends on the values of the adjacent rotations, which makes the asr method recommendable.

A fuller discussion of the relative merits of the asr and ris approaches is given in the accompanying paper.[5]

The purpose of this paper is twofold. First the asr scheme will be extended to cover the case of an ····-A–B–A–B–··· polymer chain. Secondly, some results obtained for poly(oxymethylene) (POM) will be reported, concerning both the unperturbed dimensions and the average conformational energy in solution. The figures obtained from the asr and the ris schemes using the same energy parameters will be compared between themselves as well as with the experimental data. The calculations carried out previously by Flory and Mark on the unperturbed dimensions of POM[6] will also be discussed in comparison with our results. Previous results obtained for PE with both types of calculation will also be considered.[1]

asr Scheme for an -[A–B-]$_N$ Polymer Chain. Let i be the serial index of the general -[A–B–] monomer unit. We will distinguish between even and odd skeletal bonds ac-

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(1) G. Allegra and A. Immirzi, *Makromol. Chem.*, **124**, 70, (1969).

(2) (a) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954; (b) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Translated from the Russian Edition, Serge N. Timasheff and M. J. Timasheff, Ed., Interscience, New York, N. Y., 1963; (c) T. M. Birhstein and O. B. Ptitsyn, in "Conformations of Macromolecules," Translated from the 1964 Russian Edition, S. N. Timasheff and M. J. Timasheff, Ed., Interscience, New York, N. Y., 1966; (d) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, Chapter V and references quoted therein.

(3) G. Allegra, *Makromol. Chem.*, **110**, 58 (1967).

(4) T. Ishikawa and K. Nagai (*J. Polym. Sci., Part A-2*, **7**, 1123 (1969)) have criticized the transcription of the continuum energy plot to the rotational state scheme, adopted by one of us for the case of *cis*-1,4-polybutadiene (G. Allegra, ref 3 of this list). Their argument was that some conformations, corresponding to "saddle" points in the plot, would have a smaller area than that of the minimum conformations. Actually, the angular intervals between consecutive energy levels along the coordinate of positive curvature at the saddle points are closely similar to the corresponding intervals around the true minima. Since this seems to be the only criterion allowing any comparison in size between the true minima and the saddle points, the statement of the Japanese authors does not seem to be well justified.

(5) G. Allegra, M. Calligaris, L. Randaccio, and G. Moraglio, *Macromolecules*, **6**, 397 (1973).

(6) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).

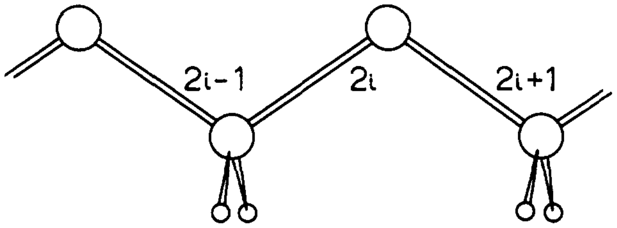
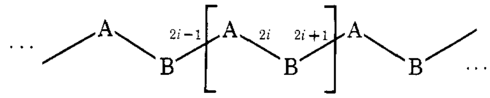


Figure 1. Schematic representation of the poly(oxymethylene) chain in the zigzag planar conformation.

cording to (see also Figure 1)



In the hypothesis of energy interaction involving first neighboring rotations only, the intramolecular energy associated with a given conformation of a chain containing N monomer units is expressed as

$$E(\varphi_1\varphi_2\cdots\varphi_{2N}) = \sum_{i=1}^{N}\{E^{(1)}(\varphi_{2i-1}\varphi_{2i}) + E^{(2)}(\varphi_{2i}\varphi_{2i+1})\} \quad (1)$$

where φ_n is the rotation angle around the nth skeletal bond (we will assume φ = 180° for the trans conformation). $E^{(1)}$ and $E^{(2)}$ are energy functions pertaining to the two different bond pairs associated with the monomer unit under consideration. They include the intrinsic rotational potentials as well as the non-bonded interaction energies depending on the rotation angles. Non-bonded interactions involving side groups may be accounted for provided they may be assumed as rigidly connected with the skeletal atoms. Equation 1 implies that attention is restricted to the interactions between atoms, or atomic groups, separated by not more than four bonds. It also implies equivalence of all the monomer units, which may be physically obtained only if the terminal units are connected in a ringlike way (*i.e.*, $\varphi_{2N+1} \equiv \varphi_1$, $\varphi_{2N+2} \equiv \varphi_2$, and so on).[7]

According to eq 1, the conformational partition function of the chain is

$$\begin{aligned} Z &= \int\cdots\int_0^{2\pi} \exp[-E(\varphi_1\cdots\varphi_{2N})/RT]\mathrm{d}\varphi_1\cdots \mathrm{d}\varphi_{2N} \\ &= \int\cdots\int_0^{2\pi}\prod_{i=1}^{N}[w^{(1)}(\varphi_{2i-1}\varphi_{2i})w^{(2)}(\varphi_{2i}\varphi_{2i+1})]\mathrm{d}\varphi_1\cdots \mathrm{d}\varphi_{2N} \end{aligned} \quad (2)$$

where

$$w^{(p)}(\varphi_n\varphi_{n+1}) = \exp[-E^{(p)}(\varphi_n\varphi_{n+1})/RT] \quad (3)$$

p being either 1 or 2. Since $E^{(p)}(\varphi_n\varphi_{n+1})$ is a periodic function of the two variables, the same is true for $w^{(p)}(\varphi_n\varphi_{n+1})$ which therefore may be expanded into a double Fourier series (*cf.* with ref 1, eq 4)

$$\begin{aligned} w^{(p)}(\varphi_n\varphi_{n+1}) = \sum_{h=0}^{H^{(p)}}\sum_{k=0}^{K^{(p)}}(a_{hk}^{(p)} \cos h\varphi_n \cos k\varphi_{n+1} + \\ b_{hk}^{(p)} \sin h\varphi_n \sin k\varphi_{n+1} + c_{hk}^{(p)} \cos h\varphi_n \sin k\varphi_{n+1} + \\ d_{hk}^{(p)} \sin h\varphi_n \cos k\varphi_{n+1}) \end{aligned} \quad (4)$$

While in principle $H^{(p)}$ and $K^{(p)}$ should be put equal to infinity, in practice they represent the limits beyond which the coefficients are negligibly small for our purposes. The $a_{hk}^{(p)}$ and $b_{hk}^{(p)}$ coefficients are conveniently calculated by sampling the function at the nodes of a rectangular lattice with N_1 and N_2 equally spaced intervals along the two variables, under the assumption that it behaves continuously with a quasi-linear law within each lattice cell (see ref 1, eq 34, 35, and 36). Following the same logic as in ref 1, eq 2 reduces to

$$Z = (2\pi)^{2N} \text{ spur } (\mathbf{U}'\mathbf{U}'')^N = (2\pi)^{2N} \text{ spur } \mathbf{U}^N \simeq (2\pi)^{2N}\lambda^N \quad (5)$$

where $\mathbf{U}'(\bar{m}_1$ rows × $\bar{m}_2$ columns and $\mathbf{U}''(\bar{m}_2$ rows × $\bar{m}_1$ columns) are the matrices which contain respectively the Fourier coefficients of $w^{(1)}(\varphi_{2i-1}\varphi_{2i})$ and of $w^{(2)}(\varphi_{2i}\varphi_{2i+1})$ and λ is the largest eigenvalue of the square matrix $\mathbf{U} = \mathbf{U}'\mathbf{U}''$. From parallel examination of eq 2 and 4 it is not difficult to show that $\bar{m}_1$ and $\bar{m}_2$ are the lower values between $K^{(2)}$ and $H^{(1)}$ and between $K^{(1)}$ and $H^{(2)}$, respectively. For sake of simplicity, we will assume

$$\bar{m}_1 = \bar{m}_2 = \bar{m} \quad (6)$$

The structure of both $\mathbf{U}'$ and $\mathbf{U}''$ is

$$\mathbf{U}' \text{ (or } \mathbf{U}'') = \begin{pmatrix} \mathbf{U}_{cc} & \mathbf{U}_{cs} \\ \mathbf{U}_{sc} & \mathbf{U}_{ss} \end{pmatrix} \quad (7)$$

Omitting explicit reference to the p index, the general element of the submatrices in the right-hand side is (see eq 4; *cf.* with eq 6 of ref 1 for $\mathbf{U}_{cc}$ and $\mathbf{U}_{ss}$)

$$\begin{aligned} U_{cc}(h,k) &= \tfrac{1}{2}a_{h-1,k-1}(\sqrt{2})^{\delta(1,h)+\delta(1,k)} \\ U_{ss}(h,k) &= \tfrac{1}{2}b_{h,k} \\ U_{cs}(h,k) &= \tfrac{1}{2}c_{h-1,k}(\sqrt{2})^{\delta(1,h)} \\ U_{sc}(h,k) &= \tfrac{1}{2}d_{h,k-1}(\sqrt{2})^{\delta(1,k)} \end{aligned} \quad (8)$$

In eq 8 $\delta(i,j)$ stands for Kronecker δ. It should not be missed that, unlike in eq 4, in the above expressions h and k are always ≥1.

The statistical average of any function $\psi(\varphi_n)$ may be evaluated through the associated averaging matrix Ψ (see eq 14 of ref 1)

$$\Psi = \frac{1}{2\pi}\int_0^{2\pi}\Phi_n^T\dot{\psi}(\varphi_n)\Phi_n\mathrm{d}\varphi_n \quad (9)$$

where the vector Φ_n is

$$\Phi_n = (1, \sqrt{2}\cos \varphi_n, \sqrt{2} \cos 2\varphi_n, \ldots, \sqrt{2} \cos \bar{m}\varphi_n, \sqrt{2} \sin \varphi_n, \ldots, \sqrt{2} \sin \bar{m}\varphi_n) \quad (10)$$

and Φ_n^T is the corresponding transposed (*i.e.*, column) vector. The rather complicated structure of Ψ is shown in eq 17 and 18 of ref 1 in terms of the Fourier coefficients of $\psi(\varphi_n)$ expanded as a series of cos $h\varphi_n$ and sin $h\varphi_n$. Here we will show how Ψ may be derived by multiplication of simple matrices, while also obtaining the algebraic formalism corresponding to the expansion of $\psi(\varphi_n)$ as a series of exp $ih\varphi_n$.

Let us first point out that all the matrix formalism discussed in ref 1 is essentially valid if the basis of the Fourier expansion changes to complex functions. This would involve, *inter alia*, changing Φ_n and Φ_n^T into complex vec-

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(7) S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

tors. For sake of convenience, we will assume the following transformation

$$\Phi_n \longrightarrow \bar{\Phi}_n = \{\exp(\bar{m}i\varphi_n),\ \exp[(\bar{m}-1)i\varphi_n],\ \ldots 1,\ \ldots,\ \exp(-\bar{m}i\varphi_n)\} \quad (11)$$

$$\Phi_n{}^T \longrightarrow (\bar{\Phi}_n{}^T)^*$$

It is easy to show that

$$\Phi_n = \bar{\Phi}_n \cdot \mathbf{Q} \qquad \Phi_n{}^T = (\mathbf{Q}^T)^* \cdot (\bar{\Phi}_n{}^T)^* \quad (12)$$

and
$\mathbf{Q} =$

$$\left(\begin{array}{ccccccc}
 & & & 1/\sqrt{2} & & & -i/\sqrt{2} \\
 & & 1/\sqrt{2}\ \cdot^{\cdot^{\cdot}} & & & -i/\sqrt{2}\ \cdot^{\cdot^{\cdot}} & \\
 & 1/\sqrt{2} & & & -i/\sqrt{2} & & \\
1 & & & & 0 & & \\
 & 1/\sqrt{2} & & & -i/\sqrt{2} & & \\
 & & 1/\sqrt{2}\ \ddots & & & -i/\sqrt{2}\ \ddots & \\
 & & & 1/\sqrt{2} & & & -i/\sqrt{2}
\end{array}\right) \quad (12')$$

all other elements of $\mathbf{Q}$ being zero. Now eq 9 becomes

$$\Psi = (\mathbf{Q}^T)^* \bar{\Psi} \mathbf{Q} \quad (13)$$

where

$$\bar{\Psi} = \frac{1}{2\pi}\int_0^{2\pi} (\bar{\Phi}_n{}^T)^* \psi(\varphi_n) \bar{\Phi}_n \mathrm{d}\varphi_n \quad (13')$$

The matrix Ψ has a simple structure if $\psi(\varphi_n)$ is expanded in terms of $\exp(ih\varphi_n)$. Let us consider the two equivalent Fourier expansions

$$\psi(\varphi_n) = \sum_{h=0}^{\bar{p}} \alpha_h \cos h\varphi_n + \sum_{h=1}^{\bar{p}} \beta_h \sin h\varphi_n = \sum_{-\bar{p}}^{+\bar{p}} A_h \exp(ih\varphi_n) \quad (14)$$

where

$$A_0 = \alpha_0$$

$$A_{\pm|h|} = \frac{1}{2}(\alpha_{|h|} \mp i\beta_{|h|}) \ (h \neq 0)$$

$$A_{-h} = A_h{}^* \text{ if } \psi(\varphi_n) = \text{real} \quad (15)$$

It is easy to see, in view of eq 13′ and 14, that the structure of $\bar{\Psi}$ is

$$\bar{\Psi} = [\bar{\Psi}(h,k)] = [A_{k-h}] \quad (16)$$

Since the order of $\bar{\Psi}$ is the same as Φ_n, *i.e.*, $2\bar{m} + 1$, the highest index of the Fourier coefficient of $\psi(\varphi_n)$ which may appear in $\bar{\Psi}$ is $2\bar{m}$. This may be seen from eq 16, putting $h = 1$ and $k = 2\bar{m} + 1$, whence $\bar{\Psi}$ $(1, 2\bar{m} + 1 = A_{2\bar{m}}$. It would be easily proven that $\bar{\Psi}$ might replace Ψ as the averaging matrix for the $\psi(\varphi_n)$ function, provided that $\mathbf{U}'$ and $\mathbf{U}''$ were replaced by

$$\bar{\mathbf{U}}'(\text{or } \bar{\mathbf{U}}'') = \mathbf{Q}\mathbf{U}'(\text{or } \mathbf{U}'')(\mathbf{Q}^T)^* \quad (17)$$

The choice of Ψ, U′ and U″ instead of Ψ, U′, and U″ corresponds to preferring the Fourier expansion of $\psi(\varphi_n)$ in terms of $\exp(ih\varphi_n)$ instead of $(\cos h\varphi_n \sin h\varphi_n)$.

The average of any $\psi(\varphi_n)$ function, as well as of any product $\psi_1(\varphi_n)\psi_2(\varphi_{n+1})\psi_3(\varphi_{n+2}) \cdots$, is evaluated following the same general criteria which lead to eq 19 of ref 1. However, in the present case distinction must be done between n even and odd. Let us first define $\mathbf{a}^*$ and $\mathbf{a}$ as the left- and right-handed eigenvectors of the largest eigenvalue λ relative to $\mathbf{U} = \mathbf{U}'\mathbf{U}''$. If ψ_i is the averaging matrix corresponding to $\psi_i(\varphi_n)$ (see eq 9), the statistical averages are

$$\begin{tikzcd}
 & & \mathbf{a}^*\mathbf{U}'\Psi_1\mathbf{U}''\mathbf{a}/\lambda \\
\langle\psi_1(\varphi_n)\rangle = \arrow[urr, "n \text{ even}"] \arrow[drr, "n \text{ odd}"'] & & \\
 & & \mathbf{a}^*\Psi_1\mathbf{a} \\
 & & \mathbf{a}^*\mathbf{U}'\Psi_1\mathbf{U}''\Psi_2\mathbf{a}/\lambda \\
\langle\psi_1(\varphi_n)\psi_2(\varphi_{n+1})\rangle = \arrow[urr, "n \text{ even}"] \arrow[drr, "n \text{ odd}"'] & & \\
 & & \mathbf{a}^*\Psi_1\mathbf{U}'\Psi_2\mathbf{U}''\mathbf{a}/\lambda
\end{tikzcd} \quad (18)$$

etc...

If $\psi(\varphi_n)$ are rotation matrices, then the above formalism still holds provided that the matrices U's and $\mathbf{Q}$ are replaced by their direct product with the unit matrix of order 3 (*i.e.*, $\mathbf{E}_3$), and that the α and β coefficients appearing in $\psi(\varphi_n)$ (see eq 14) become[1]

$$\psi(\varphi_n) \longrightarrow \mathbf{T}(\varphi_n) = \mathbf{T}_0 + \mathbf{T}_c \cos\varphi_n + \mathbf{T}_s \sin\varphi_n$$

$$\alpha_0 \longrightarrow \mathbf{T}_0 = \begin{pmatrix} -\cos\theta & -\sin\theta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\alpha_1 \longrightarrow \mathbf{T}_c = \begin{pmatrix} 0 & 0 & 0 \\ \sin\theta & -\cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (19)$$

$$\beta_1 \longrightarrow \mathbf{T}_s = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ \sin\theta & -\cos\theta & 0 \end{pmatrix}$$

In eq 19 θ is the angle between the nth and the $(n + 1)$-th skeletal bonds, and each bond is oriented along the x axis of the corresponding intrinsic frame. All other Fourier coefficients of $\psi(\varphi_n)$ must be regarded as zero matrices of order 3.

We shall indicate with Ψ_{T0} and Ψ_{T1} the matrices corresponding to the $\mathbf{T}(\varphi_n)$ functions for even and odd skeletal bonds, the respective bond angles corresponding to the B and A chain atoms (see the scheme at the beginning of this section). Furthermore, we shall connote with $\mathbf{a}_3{}^*$, $\mathbf{a}_3$, $\mathbf{U}_3{}'$, $\mathbf{U}_3{}''$ the direct products of $\mathbf{a}^*$, $\mathbf{a}$, $\mathbf{U}'$ and $\mathbf{U}''$ with the unit matrix of order 3.

The mean-square end-to-end distance of any polymer chain with $2N$ bonds of equal length l, may be expressed as shown in eq 20,[7]

$$\langle r^2\rangle = \left\langle\left(\sum_{n=1}^{2N}\vec{l}_n\right)\left(\sum_{n=1}^{2N}\vec{l}_n\right)\right\rangle = l^2(100)\left\{2N + 2\sum_{n=1}^{2N-1}\langle\mathbf{T}\varphi_n\rangle + 2\sum_{n=1}^{2N-2}\langle\mathbf{T}\varphi_n\mathbf{T}\varphi_{n+1}\rangle + 2\sum_{n=1}^{2N-3}\langle\mathbf{T}\varphi_n\mathbf{T}\varphi_{n+1}\mathbf{T}\varphi_{n+2}\rangle + \ldots\right\}\begin{pmatrix}1\\0\\0\end{pmatrix} \quad (20)$$

where $\vec{l}_n$ is the vector associated with the general bond. If the chain is very long (*i.e.*, $N \rightarrow \infty$) so that all the monomer units are equivalent, distinguishing between even and odd bonds we have from eq 20

$$\langle r^2\rangle/2Nl_\infty^2 = (100)\{[1 + \langle \mathbf{T}\varphi_{2n}\rangle + \langle \mathbf{T}\varphi_{2n}\mathbf{T}\varphi_{2n+1}\rangle + \langle \mathbf{T}\varphi_{2n}\mathbf{T}\varphi_{2n+1}\mathbf{T}\varphi_{2n+2}\rangle + \cdots] + [\langle \mathbf{T}\varphi_{2n+1}\rangle + \langle \mathbf{T}\varphi_{2n+1}\mathbf{T}\varphi_{2n+2}\rangle + \cdots]\}\begin{pmatrix}1\\0\\0\end{pmatrix} \quad (21)$$

In the hypothesis of first-neighbor interactions, the above averages may be calculated by making use of eq 18. If we introduce the following symbols

$$\mathbf{Z} = \mathbf{U}_3'\Psi_{T_0}\mathbf{U}_3''/\lambda$$

$$\mathbf{E} = \text{unit matrix of order } 3(2\overline{m} + 1) \quad (22)$$

eq 21 becomes eq 23. It is worth being pointed out that eq

$$C_\infty = \langle r^2\rangle_0/2Nl_\infty^2 = (100)\mathbf{a}_3^*\{[\mathbf{E} + \mathbf{Z} + \mathbf{Z}\Psi_{T_1} + (\mathbf{Z}\Psi_{T_1})\mathbf{Z} + (\mathbf{Z}\Psi_{T_1})^2 + \cdots] + [\Psi_{T_1} + \Psi_{T_1}\mathbf{Z} + \Psi_{T_1}(\mathbf{Z}\Psi_{T_1}) + \Psi_{T_1}(\mathbf{Z}\Psi_{T_1})\mathbf{Z} + \cdots]\}\mathbf{a}_3\begin{pmatrix}1\\0\\0\end{pmatrix} = (100)\mathbf{a}_3^*(\mathbf{E} + \Psi_{T_1})(\mathbf{E} - \mathbf{Z}\Psi_{T_1})^{-1}(\mathbf{E} + \mathbf{Z})\mathbf{a}_3\begin{pmatrix}1\\0\\0\end{pmatrix} \quad (23)$$

23 may also be interpreted as the expression of C_∞ in the ris scheme if the meaning of symbols is changed. Namely, in this case, $\mathbf{U}'$ and $\mathbf{U}''$ are the matrices containing the correlation factors between neighboring rotational states (instead of the Fourier expansion coefficients) and Ψ_{T0} and Ψ_{T1} contain the rotation matrices of their respective states along the main diagonal. In particular, it might be shown that the expression obtained by Hoeve for the ris scheme (eq 16 of ref 8) is reducible to eq 23 of this paper after the substitutions

$$\begin{aligned} \mathbf{X}^* &\longrightarrow \mathbf{a}_3^* \\ \mathbf{X} &\longrightarrow \mathbf{a}_3 \\ \mathbf{D}' &\longrightarrow \Psi_{T_0} \\ \mathbf{D}'' &\longrightarrow \Psi_{T_1} \\ \mathbf{W}' &\longrightarrow \mathbf{U}' \\ \mathbf{W}'' &\longrightarrow \mathbf{U}'' \end{aligned} \quad (24)$$

Conformational Energy of the POM Chain. The conformational energy belonging to each of the two distinct pairs of neighboring rotations ($\varphi_{2i-1}\varphi_{2i}$) and ($\varphi_{2i}\varphi_{2i+1}$) (see Figure 1) has been evaluated according to

$$E(\varphi_n\varphi_{n+1}) = \tfrac{1}{2}U_0(1 + \cos 3\varphi_n) + \sum_{i<j}\sum V_{ij}(r_{ij}) \quad (25)$$

Here U_0 is the potential barrier inherent to the threefold rotation around the CH_2-O bonds, which the same value (1 kcal/mol) as obtained for CH_3OH has been given,[9] while V_{ij} is the non-bonded interaction energy between the atoms i and j, r_{ij} being their distance. The sum is extended to all the pairs of atoms whose distance is defined by the skeletal rotations φ_n and φ_{n+1}, all bond lengths and angles being kept fixed ($\varphi_{C\text{-}O} = 1.43$ Å; $\varphi_{C\text{-}H} = 1.08$ Å; all bond angles tetrahedral). In order to avoid counting any interaction twice, the V_{ij} terms belonging to atoms separated by three bonds have been taken into account only in one energy map $E(\varphi_n\varphi_{n+1})$, where φ_n is the dihedral angle defined by the three bonds (see eq 25). The interaction energy between methylene groups separated by four skeletal bonds has been calculated giving an arbitrary trans (180°) conformation to the first and fourth bonds of the sequence. This has been done in order to account, although in an approximate way, for the important interactions between the hydrogen atoms, whose relative distance cannot be rigorously specified by two rotation angles only (*cf.* Figure 1).

The V_{ij} energy contribution results from two components, namely the van der Waals (vdW) and the Coulombic (C) interaction energies. Let us consider them separately.

Since uncertainty in the choice of the vdW interaction parameters is always a major source of error in conformational analysis, we have considered two distinct sets of functions (see Table I). Set I consists of the parameters suggested by one of us for the C · · · C, C · · · H, and H · · · H interactions in a conformational study of poly(isobutylene),[10] and by Giglio[11] for O · · · O, while the parameters of the O · · · H and O · · · C interactions are derived as the geometrical average of the respective homonuclear functions. Set II consists entirely of the parameters suggested by Giglio in a study of the crystalline packing of some organic molecules.[11] The second set corresponds to "harder" potentials, *i.e.*, their slope is larger at short distances. Table I also shows the van der Waals radii of the atoms for both sets, defined as one-half of the equilibrium distance of the corresponding homonuclear interactions.

To the effect of evaluating the coulombic interactions, the amount of electric charge localized on the chain atoms is coupled with the value ϵ of the local dielectric constant through the relation

$$V_{ij}^{(C)} = 332\delta_i\delta_j/(\epsilon r_{ij}) \text{ kcal/mole} \quad (26)$$

where δ_i is the charge (in electrons) on the ith atom. From eq 26 it is apparent that the effective charge parameters are $\delta_i/(\epsilon)^{1/2}$. As for the electric charges, we have attributed equal values with opposite sign to the carbon ($-\delta$ electrons) and oxygen ($+\ \delta$) atoms, formally assuming the charge to be concentrated in the atomic centers.[12] The approximate values of δ may be derived by the dipole moments of the poly(oxymethylene) dimethyl ethers $CH_3(OCH_2)_{n-1}OCH_3$ with n = 1, 2, and 3.[13] From the experimental data an average value $\mu_O = 1.2$ D is obtained for the dipole moment associated to each C-O bond; the corresponding value is 0.35 electron (from $\mu_O = \tfrac{1}{2}\delta l_{C\text{-}O}$, which takes into account that each atom is shared by two bonds). Owing to the fact that the experimental determinations of the unperturbed dimensions have been carried out in polar solvents,[14,15] we have performed calculations with $\delta/(\epsilon)^{1/2}$ comprised in the range 0-0.25. As an example, taking the relatively small value[16] $\epsilon = 4$—characteris-

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Table I
Parameters for the Non-bonded Interactions ($V_{ab} = A_{ab} \exp(-C_{ab} r_{ab})/r^n{}_{ab} - B_{ab}/r^6{}_{ab})^a$

	Set I					Set II				
X	VdW Radius (Å)	A_{ab}	B_{ab}	C_{ab}	n	VdW Radius (Å)	A_{ab}	B_{ab}	C_{ab}	n
C····C	1.70	2.94×10^5	381	0	12	1.75	3.01×10^5	327	0	12
H····H	1.20	4.71×10^3	49	0	12	1.50	6.6×10^3	49	4.08	0
O····O	1.75	2.59×10^5	359	0	12	1.75	2.59×10^5	359	0	12
C····H		3.97×10^4	134	0	12		4.48×10^4	125	2.04	6
C····O		2.76×10^5	370	0	12		2.79×10^5	342	0	12
H····O		3.49×10^4	133	0	12		4.20×10^4	133	2.04	6

^{a} r_{ab} in Å; V_{ab} in kcal/mol.

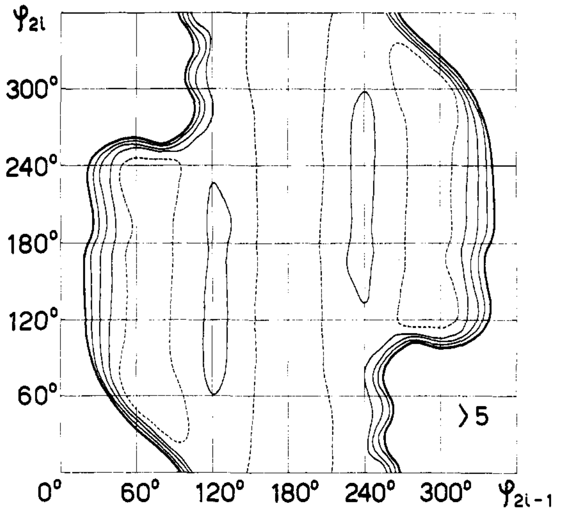

Figure 2. $E(\varphi_{2i-1}\varphi_{2i})$ plot (see Figure 1). Energy levels are drawn at 1 (dashed line), 2, 3, ..., 5 kcal per mol.

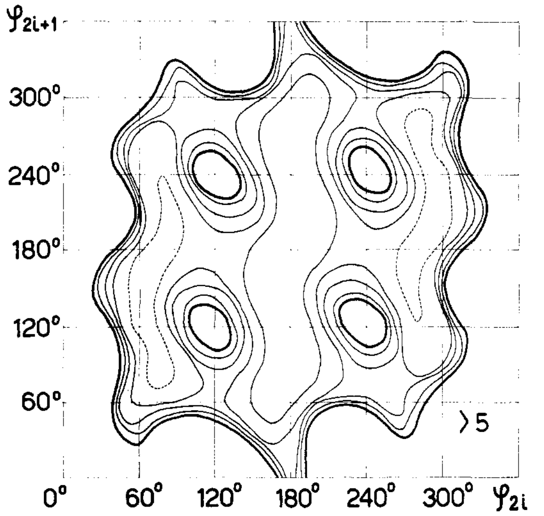

Figure 3. $E(\varphi_{2i}\varphi_{2i+1})$ plot (see Figure 1). Energy levels are drawn at 1 (dashed line), 2, 3, ..., 5 kcal per mol.

tic of such poorly polar liquids as bromoform and ε-bromotoluene—the upper limit corresponds to a charge of 0.5 electron, *i.e.*, well above the value deduced from the dipole moments.

As an example, Figure 2 shows the energy maps $E^{(1)}(\varphi_{2i-1}\varphi_{2i})$ and $E^{(2)}(\varphi_{2i}\varphi_{2i+1})$ obtained with set I and $\delta/(\epsilon)^{1/2} = 0.125$. The trans (T) is preferred over the gauche (G) conformation by about 0.4 kcal/mol. This figure has been derived from the energy function characteristic of the helical conformations with equivalent monomer units (*i.e.*, with $\cdots \varphi_{2i-1} = \varphi_{2i+1} = \cdots = \varphi_{\mathrm{I}}$ and $\cdots \varphi_{2i} = \varphi_{2i+2} = \cdots = \varphi_{\mathrm{II}}$)

$$E_{\mathrm{h}}(\varphi_{\mathrm{I}}\varphi_{\mathrm{II}}) = E^{(1)}(\varphi_{\mathrm{I}}\varphi_{\mathrm{II}}) + E^{(2)}(\varphi_{\mathrm{II}}\varphi_{\mathrm{I}}) \qquad (27)$$

by taking the difference $E_{\mathrm{h}}(\mathrm{GG}) - E_{\mathrm{h}}(\mathrm{GT}) \simeq E_{\mathrm{h}}(\mathrm{GT}) - E_{\mathrm{h}}(\mathrm{TT})$. In order to account for the actual position of the energy minima (Figure 3), the gauche states have been identified with the rotations ±75°. The lowest energy conformation corresponds therefore to the trans planar chain. Taking $\delta/(\epsilon)^{1/2} = 0.25$, the increased coulombic attraction between C and O atoms separated by three bonds makes the ($\cdots \mathrm{G}^{\pm}\mathrm{G}^{\pm}\mathrm{G}^{\pm}\mathrm{G}^{\pm}\cdots$) sequence (a uniform helix) more stable than the trans sequence by about 0.25 kcal/mol per chain bond. The former sequence is very close to the conformation established for the polymer in the more stable (hexagonal) crystalline form (Figure 3), where $\varphi_{\mathrm{I}} = \varphi_{\mathrm{II}} = \pm 77.5°$.[17] The conformation in the alternative orthorhombic form ($\varphi_{\mathrm{I}} = \varphi_{\mathrm{II}} = \pm 63°$[18]) lies above the minimum by about 0.4 kcal/mol only, per each chain bond. Closely analogous results are derived from the energy map obtained with the interaction parameters of set II (see Table I) and the same values of $\delta/(\epsilon)^{1/2}$. As it should be expected, lower values of $\delta/(\epsilon)^{1/2}$ lead to progressive stabilization of the trans with respect to the gauche conformation, until for $\delta/(\epsilon)^{1/2} = 0$ the (gauche-trans) energy difference rises to 0.6 and 0.8 kcal per mol for the parameters of set I and set II, respectively. Since in the crystalline state only gauche skeletal rotations are found, it might be inferred that $\delta/(\epsilon)^{1/2}$ must be larger than 0.15–0.20 electron inside the crystals, if attention is confined to the intramolecular energy. However, a detailed analysis of several reasonable ways of packing among the chains carried out by Cesari and Perego shows that the ···GGGG··· conformation is definitely more suitable to fill the space than ···TTTT···,[19] which puts some doubt on the value of this argument.

A stronger indication in favor of the greater stability of the gauche conformation in POM chains comes from the analysis of the dipole moments of dimethoxymethane ($\mathrm{CH_3OCH_2OCH_3}$) in the gaseous state carried out by Uchida *et al.*[13] From measurements performed at temperatures comprised in the range 25–200° they find a (trans-gauche) energy difference of 1.7 kcal/mol. We were puzzled by the question whether such a high value could be explained in terms of our scheme of non-bonded interactions between atoms carrying effective charges in agreement with the observed molecular dipole moments. The bond dipole moment which fits at best the experimental

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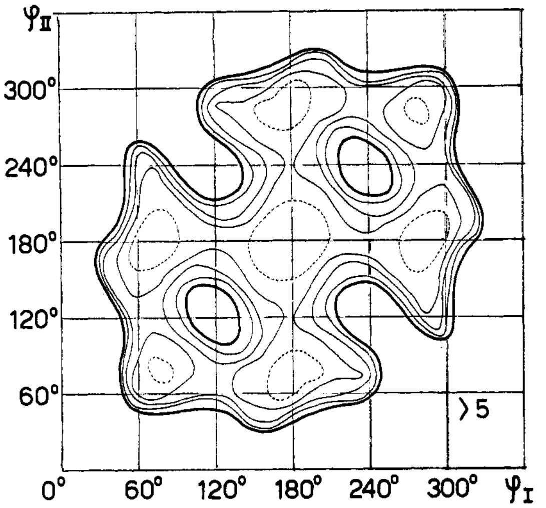

Figure 4. $E_h(\varphi_I\varphi_{II})$ plot for the helical chain. Energy levels are drawn at 1 (dashed line), 2,3, ..., 5 kcal per mol.

Table II
Characteristic Ratios (C_∞) of POM with Different Electronic Charge (Expressed as $\delta/(\epsilon)^{1/2}$) Calculated with the asr and ris Schemes for both Sets of Non-bonded Interaction Parameters (See Text)

	Set I			Set II	
$\delta/(\epsilon)^{1/2}$	0°	100°	200°	100°	200°
		ars Scheme			
0	9.72	8.19	7.39	9.19	8.11
0.125	8.89	7.95	7.36		
0.250	7.67	7.51	7.30	8.05	7.82
		ris Scheme			
0	10.09	8.60	7.78	8.96	7.82
0.125	9.11	8.31	7.77		
0.250	8.11	7.96	7.80	7.90	7.73

Table III
Test of Convergence for λ and C_∞ on the Basis of the Parameters of Set I with $\delta/(\epsilon)^{1/2}$ = 0.25 electron

	0°		100°		200°	
$\bar{m}$	$\lambda \times 10^5$	C_∞	$\lambda \times 10^5$	C_∞	$\lambda \times 10^5$	C_∞
6	898	7.76	2832	7.51	5871	7.28
9	900	7.66	2836	7.51	5878	7.30
12	898	7.67	2834	7.51	5976	7.30

data is μ_0 = 1.31 D,[13] which corresponds to effective charges of −0.19, −0.38, and +0.38 electron on the methyl and methylene groups and on the oxygen atom, respectively. Assuming the lowest possible value for ϵ (ϵ = 1), which enhances at most the coulombic contribution, the average calculated (trans-gauche) energy difference is 1.3 kcal/mol for both set I and set II, within 0.1 kcal/mol. Although the choice of the unit value for the local dielectric constant is somehow arbitrary, the qualitative agreement between the calculated and experimental figure is remarkable. For sake of comparison, the same energy difference for POM, calculated with $\delta/(\epsilon)^{1/2}$ = 0.38 (*i.e.*, adopting the same bond dipole moment as for dimethoxymethane), is 1.4 and 1.2 kcal per mol for sets I and II, respectively, *i.e.*, practically identical with the values obtained for the model molecule. However, some care is required to interpret this apparent coincidence, since it is due to the cancellation of two opposite effects. In fact, while in the polymer the effective charges are larger on the average than in dimethoxymethane, which leads to an increase in the (trans-gauche) energy difference, the O···O repulsions between atoms separated by four bonds give a virtually identical effect with opposite sign.

In conclusion, the possible values of $\delta/(\epsilon)^{1/2}$ for the polymer in polar solvents should not exceed the range 0–0.25, if δ is taken as 0.35 electron (from the average values of poly(oxymethylene) dimethyl ethers[13]) and ϵ is assumed to be larger than 4 (the value corresponding to bromoform and to *o*-bromotoluene). For the polymer in the pure (crystalline or molten) state, a reasonable choice seems to be ~5, *i.e.*, as for dimethyl ether, which leads to a plausible value of $\delta/(\epsilon)^{1/2}$ around 0.15.

Unperturbed Mean-Square End-to-End Distance. Table II gives some C_∞ values at different temperatures in the range 0–200° calculated according to the asr scheme for both sets of non-bonded interactions parameters (see Table I) and for different values of $\delta/(\epsilon)^{1/2}$. Although the pattern of the results for set II is less complete than for set I, due to the need of saving computing time, it is apparent that their general trend is the same, set II values being slightly larger (by about 6–10%). Equation 23 has been employed, the highest index $\bar{m}$ considered in the Fourier expansions of the statistical weights being 8. Incidentally, owing to the symmetry of the chain, any pair of neighboring rotation angles ($\varphi_n\varphi_{n+1}$) is equivalent to the same pair with the signs reversed (*i.e.*, $-\varphi_n-\varphi_{n+1}$) with the consequence that $\mathbf{U}_{cs}$ and $\mathbf{U}_{sc}$ (see eq 7) are zero matrices, as it was the case with polyethylene.[1] With reference to the case of set I and $\delta/(\epsilon)^{1/2}$ = 0.25, Table III shows the results of both λ (see eq 5) and C_∞ for $\bar{m}$ = 6, 9, and 12, showing that complete convergence of the results is virtually reached at $\bar{m}$ = 6. The corresponding value for polyethylene was 10,[1] the difference being due to the higher energy barrier between the minima of polyethylene (>3 kcal/mol) with respect to POM (~1.8 kcal/mol, including the non-bonded interactions). Table II also shows the results of C_∞ obtained within the rotational isomeric state (ris) scheme (eq 23 with the substitutions shown in eq 24). No matter how the parameters are changed, the energy minima are always located in a good approximation at φ = ±75° ($G^\pm$) and 180° (T), which have been chosen as our rotational isomers, the statistical weights being evaluated from the corresponding $E(\varphi_n\varphi_{n+1})$ values. As it was the case with polyethylene,[1] the agreement between the results of C_∞ obtained with either (asr or ris) method is remarkable. As it may be seen, at lower temperatures C_∞ decreases rather appreciably with increasing $\delta/(\epsilon)^{1/2}$, but it is interesting that at about 200° the result is virtually independent of $\delta/(\epsilon)^{1/2}$($C_\infty \simeq$ 7.3 for set I and $\simeq$7.9 for set II).

There is a satisfactory agreement between the results reported in Table II and those obtained in a previous study by Flory and Mark.[6] These authors carried out calculations for two distinct values of the gauche rotational state, *i.e.*, ±60 and ±80° (±120 and ±100° in their notation, based on the assumption $T \equiv 0°$): obviously, comparison with our results must involve their second choice, since we have assumed $G \equiv \pm 75°$. With reference to Figure 2 of the quoted paper,[6] we see that the C_∞ values belonging to the (primed) curves corresponding to $G \equiv \pm 80°$ are comprised in the range 7.5–11 if ln σ (in the abscissa of the figure) is in the range (−1 to +1). This confines the (gauche-trans) energy difference to being not larger than *RT*, in absolute value, which is essentially the case with our calculations. In fact, the range spanned by our C_∞ values is quite similar. More appropriately, our results compare rather well with the B′ curve of the figure under discussion, which was calculated in the assumption that the $G^\pm G^\mp$ sequences across an oxygen atom are slightly

Table IV
Intramolecular Contribution to the Heat of Melting ($\Delta H_M{}^{\text{intra}}$ kcal/mole, See Text), Calculated with Both Sets of the Non-bonded Interaction Parameters (T_M = 190°)

	Set I		Set II	
	asr Scheme	ris Scheme	ars Scheme	ris Scheme
0	0.38	0.50	0.51	0.38
0.125	0.26	0.36		
0.250	0.21	0.29	0.07	0.11

unfavored with respect to the $G^{\pm}G^{\mp}$'s, as it is in our case. In particular, the limiting value of C_∞ predicted by the B′ curve at high temperature (~7.3) is in agreement with that found by us. It must be pointed out, however, that we do not assume that any gauche conformation has the same energy whether it is preceded by a trans or by a similar gauche conformation, as Flory and Mark do.[6]

Finally, the negative value of the temperature coefficient of C_∞ resulting from Flory-Mark plots[6] is also confirmed by our calculations.

The experimentally determined values of C_∞ are 7.5 ± 0.8, at 90° in phenol solution[14] ($\epsilon \simeq 10$ for phenol), and 10.5 ± 1.5 at 25° in a mixed solvent hexafluoroacetone-water[15] (estimated $\epsilon \simeq 20$). These figures are comprised within the range of our results. The second value is especially interesting inasmuch as it shows that the joint effect of a lower temperature and a higher dielectric constant (*i.e.*, a lower $\delta/(\epsilon)^{1/2}$) leads to a higher characteristic ratio, as predicted by our calculations. The lower value agrees within error limits with all our asr results of C_∞ at 100° except for the case of set II, $\delta/(\epsilon)^{1/2} = 0$.

Average Conformational Energy of POM Chains. Under the assumption that the macromolecule contains a large number N of monomer units, in the asr scheme, the conformational free energy of the unperturbed chain is given by

$$A^{\text{conf}} = -RT \ln Z = -NRT \ln (4\pi^2\lambda) \qquad (28)$$

where the connection between Z and λ is given by eq 5. From the well-known equation

$$E = -T^2[\partial(A/T)/\partial T]_V \qquad (29)$$

remembering eq 28 and considering that the chain conformation is virtually independent of the volume of the solution, we obtain

$$E^{\text{conf}}/N = RT^2 \mathrm{d} \ln \lambda/\mathrm{d}T \qquad (30)$$

for the average conformational energy per monomer unit.[1] In spite of the starting assumption that the chains be in the unperturbed state, eq 30 should be reasonably valid under less restrictive conditions, such as, *e.g.*, in a good solvent. In fact, departure from the unperturbed conditions involves the existence of long-range interactions, which are not likely to modify substantially the spectrum of conformations accessible to limited sequences of monomer units, although possibly leading to serious perturbations in the *size* of the polymer coil. As a consequence, unless relatively strong and specific polymer-solvent interactions arise, we should also expect that the useful thermodynamic functions not directly related to the overall chain dimensions, such as the intramolecular energy, should not change appreciably. These conclusions apply particularly well to the molten state, where the interchain packing requirements and the excluded volume effects should represent relatively minor factors affecting the local chain conformation. Consequently, eq 30 may yield the intramolecular contribution to the heat of melting if (i) we take $T = T_M$ (melting temperature) = 190° (average value from ref 20 and 21); (ii) the energy scale is so adjusted that the conformational energy of the minimum corresponding to the crystalline state is given a zero value; (iii) an average potential energy of $\frac{1}{2}RT_M$ per each skeletal bond is subtracted form E^{conf} under the simplifying assumption that the torsional vibrations within the crystallites at the melting point are both independent from each other and purely harmonic in nature. The results of $\Delta H_M{}^{\text{intra}} = (E^{\text{conf}} - RT_M)/N$, calculated for both sets of parameters, are reported in Table IV. In the same table the results obtained from the ris method, where no correction for the crystalline vibrations is needed, are also given. As it may be observed, there is a good agreement between the figures evaluated with either method; the agreement within the two sets is also reasonable. Taking $\delta/(\epsilon)^{1/2} = 0.15$, the average value of $\Delta H_M{}^{\text{intra}}$ is 0.25 kcal/mol. Since the most recent experimental values of ΔH_M are between 1.59[20] and 1.76[21] kcal per mol, we may conclude that for POM the intramolecular contribution to the heat of melting is around 15% of the total value. This fraction is remarkably smaller than in the case of polyethylene[22] where, at $T_M \simeq 140°$, the calculated value of $\Delta H_M{}^{\text{intra}}$ referred to a $\text{-CH}_2\text{-CH}_2\text{-}$ monomer unit is about 0.7 kcal/mol (0.66 and 0.76 kcal per mol from the ris and from the asr schemes, respectively, the latter value being corrected for the vibrational potential energy around skeletal bonds, as above[1]) *vs.* an experimental value $\Delta H_M = 1.9$ kcal/mol,[21] which means that the intramolecular contribution is about 35–40% the total amount.

Concluding Remarks. Perhaps the most interesting conclusion, somehow unexpected by us at the beginning, is that the ris scheme still gives essentially correct results both for C_∞ and for the intramolecular conformational energy content—after correction for the torsional vibrations, assumed to be of a harmonic type—although the energy barriers between rotational minima are of the order of 2 kcal/mol only. The agreement between the C_∞ values obtained from the ris and the asr schemes for PE—where the lower rotational barriers are about 3 kcal/mol—had already been recognized in a previous paper.[1] In this case, too, the discrepancy between the values of the average conformational energy obtained from either method is also satisfactorily accounted for with the assumption of harmonic, independent oscillations around skeletal bonds.

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