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Copolymer Chain Statistics. The Pseudo-Stereochemical Equilibrium Approach within the Continuum of Rotational States. The Unperturbed Dimensions of Atactic Polypropylene

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ABSTRACT: The double Fourier expansion method (asr scheme) to calculate the configurational integral of a polymer chain with energy interactions between first-neighboring skeletal rotations is adapted to the pseudo-stereochemical equilibrium statistical treatment of linear copolymers. The unperturbed dimensions of atactic polypropylene in the range 125–175 °C are obtained, after assuming the methyl group as a spherical body with a van der Waals radius of 1.85 Å, in agreement with previous calculations. Two different statistical models of *d* and *l* unit sequences are assumed; in either case the chains upon which our calculations are based obey very closely the (first-order) Markoffian rules for unit succession. The results are in good agreement with experimental results. It is confirmed that the convergence limit is achieved by pushing the Fourier expansion up to terms of about order 10, at the temperatures under consideration.

The statistical treatments of macromolecular chains in the unperturbed state, subject to energy interactions between rotational states around neighboring chain bonds, have aroused considerable interest in recent years. They enable the calculation of several averages correlated with experimental properties of polymer solutions, such as the average square dimensions of the molecular coil in the unperturbed theta state, their higher moments, the mean-squared optical anisotropy, the stress-optical parameter $\Delta\alpha$, etc.[1]

Matrix methods based on the assumption that a suitable set of discrete rotations give a sufficiently adequate statistical description of the chain (rotational isomeric state, or ris scheme) have been proposed and successfully employed for homopolymers. Two distinct approaches may be recognized, namely the one proposed by Volkenstein,[2] Birshtein and Ptitsyn,[3] Lifson,[4] Hoeve,[5] Nagai,[6,7] and Corradini and Allegra,[8] where attention is mainly focused on infinitely long chains, and that given by Flory,[1,9] who proposes a generalized treatment for chains of any polymerization degree. Within the first approach the chain statistics are fully described by a convenient square matrix containing the statistical weights relative to the pairs of adjacent rotations on the general monomer unit by its largest eigenvalue and corresponding eigenvectors. Instead, Flory employs a larger matrix containing the statistical weights involving the terminal monomer units as well (generating matrix), obtaining all the relevant information after a suitable process of matrix self-multiplication.[9]

If the chains contain different types of comonomer units, distributed according to some statistical law (copolymer chains), the above method of statistical-mechanical description cannot be applied. In fact, the problem is now complicated to a considerable extent by the existence of two interlocking statistics, the first of which is related with the specification of the comonomer unit sequence, while the other reduces to the usual statistics in the configurational space of the rotation angles and depends in turn on the unit sequence itself. Lehman and McTague[10,11] have given an exact solution to this problem in terms of functional equations by assuming either a Bernoullian or a first-order Markoffian law for the comonomer unit distribution. In particular they have computed the temperature breadth of the helix–coil transition for DNA macromolecules characterized by different sequential statistics of the G–C and A–T base pairs.[11] Their model allows for two states on either type of units (i.e., base pairs), and it may also be applied directly, e.g., to a linear Ising ferromagnet containing two different types of spins. In the case that more than two states were to exist, it is likely that the Lehman–MacTague approach would be more and more difficult to apply, since it should involve the numerical solution of functional equations in at least $(n-1)$ variables (n = the number of states accessible to either unit).

Lifson and Allegra[12] and Allegra[13] proposed two approximate matrix approaches to the above problem, both of which are based upon the arithmetic average of the properly normalized partition functions of the different copolymer chains, instead of their geometrical average. Both methods reduce to an eigenvalue–eigenvectors formalism of the same kind as that adopted for homopolymer chains and have been successfully applied by Poland and Scheraga to investigate the helix–coil transition of DNA.[14] In particular, the second method gives better results; it is easily checked and/or improved.[13] A supermatrix built up with the correlation matrices pertaining to the different unit pairs provides all the statistical information. A proper set of multipliers, attached to the statistical weight factors of suitably chosen unit pairs (e.g., the AA and BB pairs, for an A,B copolymer), allows the selection of the statistical weights belonging to the copolymer chains which have the desired statistical structure from their most general ensemble. Physically speaking, this operation is equivalent to assuming that the general comonomer unit is formally capable of undergoing the fictitious equilibrium A $\rightleftharpoons$ B, under the constraint that the fractions of AA, AB, BA, and BB unit pairs for the whole chain are constantly equal to their expected values. It is for this reason that the method may be characterized as the *pseudo-stereochemical equilibrium approach*.[13,15] In particular, it may be proved that the configurational averages of the above fictitious chains are identical with those of an ideal copolymer system obtained under equilibrium (i.e., perfectly reversible) polymerization.[13,15] In all the cases studied hitherto, the calculated distribution of the comonomer units is very close to a first-order Markoffian sequence, in agreement with what is observed for many copolymerization processes. This is in itself a powerful argument in favor of the method's validity. Monte-Carlo techniques, inevitably involving some spreading of the results around the average, should be rendered unnecessary as long as a more compact procedure leading directly to the overall statistical averages is available.

As said at the beginning, all the above approaches are based on the ris method. This is usually applied after identification of the discrete set of rotational states with local minima of the conformational energy; if they have different breadths, an appropriate entropy factor should be attached to each of them.[16] In principle, this can be done exactly if, and only if, the minimum energy regions in the phase space of the skeletal rotations are such that in their vicinity the total energy may be expanded as a sum of terms $E(\varphi_i)$ each belonging to a single rotation. As long as irreducible contributions of the type $E(\varphi_i\varphi_{i+1})$ are present for all the adjacent pairs, the very definition of a rotational minimum for the whole chain may be very difficult if possible at all. This is the case, e.g., of the strained conformations effecting helix inversion in isotactic polypropylene, whose careful consideration is quite important in order to evaluate the molecular dimensions in unperturbed solution.[8] There is basically a single way to overcome the difficulty, i.e., to resort to the configurational integral. This, in turn, may be evaluated either through a more or less dense sampling of the rotational phase space, leading to a discrete set of skeletal rotations which may be formally treated within the ris scheme, although not being necessarily related with the lowest energy values, or through the Fourier expansion method proposed by one of the authors (*all skeletal rotations*, or asr method).[17–19] In this scheme, a formalism is developed where the Fourier coefficients of $\exp(-E(\varphi_i\varphi_{i+1})/RT)$, expanded in terms of φ_i and φ_{i+1}, play a role analogous to that of the statistical weights in the ris approach. Obviously enough, no definition of minimum energy rotations is required in this case; however, the new procedure is comparatively more time consuming than the ris method in its simplest, and most classical, applications.[20]

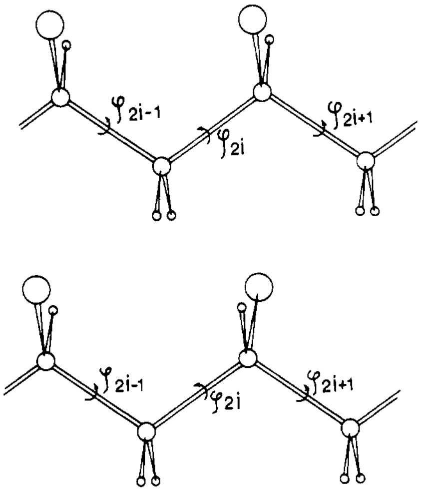

Figure 1. Sketch of isotactic (above) and syndiotactic polypropylene chains in an arbitrary zigzag planar conformation showing the numbering scheme of the torsional angles.

In the present paper the pseudo-stereochemical equilibrium approach will be treated in terms of the full configurational integral, in order to account for the continuum of the skeletal rotation angles. The resulting theory may be viewed as a synthesis between the above copolymer approach and the asr method. It will be explicitly discussed for application to atactic polypropylene, considered as a statistical copolymer of comonomer units having opposite steric structure (i.e., *d* and *l* units), although its extension to the more general case of any copolymer chain with pairwise interdependent rotations is implicit and virtually straightforward. In a following section, the general applicability of the asr scheme to all the cases where the ris method may be adopted will be concisely pointed out.

Mathematical Formulation

Let us consider a general chain consisting of a large number N of d and l comonomer units, such as it occurs in a high molecular weight atactic polymer. If its unit sequence is $(dl \ldots ddl \ldots dd)$, e.g., and if we assume the two chain ends to be interconnected ringwise, in order to remove end effects with no consequence on the results,[4] its (classical) configurational partition function is

$$Z_N(dl \ldots dd \ldots ld) = \int_{\varphi_1} \cdots \int_{\varphi_{2N}} w_{dl}(\varphi_1\varphi_2) w_l \\ \times (\varphi_2\varphi_3) \ldots w_{dd}(\varphi_{2i-1}\varphi_{2i}) w_d \\ \times (\varphi_{2i}\varphi_{2i+1}) \ldots w_{ld}(\varphi_{2N-1}\varphi_{2N}) w_d(\varphi_{2N}\varphi_1) \prod_{k=1}^{2N} d\varphi_k \quad (1)$$

In the above equation, $w_{xy}(\varphi_{2n-1}\varphi_{2n})$ (where $x,y = d,l$) is the Boltzmann statistical weight relative to the local conformation specified by the rotation angles $\varphi_{2n-1}\varphi_{2n}$ around the two bonds connecting successive carbon atoms with x,y configurations ($x,y = d,l$) (Figure 1). As for $w_x(\varphi_{2n}\varphi_{2n+1})$, it depends on the rotations around the two bonds adjoining the same tertiary carbon. Since nonbonded interactions depending upon more than two rotation angles will not be accounted for except as an average (see following section), the energy contribution depending on $\varphi_{2n}\varphi_{2n+1}$ is independent of the type of neighboring units (see Figure 1) and so is its statistical weight.[19] The partition function of a chain capable of undergoing unrestricted equilibration between d and l units is also the sum of all the partition functions belonging to the chains having all possible structures (i.e., unit sequences) and is easily derived from eq 1:

$$Z_N = spur\left[\int_{\varphi 1}\cdots\int_{\varphi 2N}\prod_{n=1}^{N}\mathbf{W}_1(\varphi_{2n-1}\,\varphi_{2n}) \times \mathbf{W}_2(\varphi_{2n}\varphi_{2n+1})\prod_{k=1}^{2N} d\varphi_k\right] \quad (2)$$

where

$$\mathbf{W}_1(\varphi_{2n-1}\varphi_{2n}) = \begin{bmatrix} w_{dd}(\varphi_{2n-1}\varphi_{2n}) & w_{dl}(\varphi_{2n-1}\varphi_{2n}) \\ w_{ld}(\varphi_{2n-1}\varphi_{2n}) & w_{ll}(\varphi_{2n-1}\varphi_{2n}) \end{bmatrix}$$

$$\mathbf{W}_2(\varphi_{2n}\varphi_{2n+1}) = \begin{bmatrix} w_d(\varphi_{2n}\varphi_{2n+1}) & 0 \\ 0 & w_l(\varphi_{2n}\varphi_{2n+1}) \end{bmatrix} \quad (2')$$

In order to clarify the passage from eq 1 to 2, it should be remembered that the operators of integration and of summation of matrix diagonal elements (i.e., *spur*) commute between themselves. Furthermore, we have adopted the same symbol φ_k for the rotational angle around the kth bond, regardless of whether it refers to a d or l unit; in fact, distinction is not necessary because the corresponding statistical averages are performed over separate terms of the overall summation. The formal analogy between eq 2 and that giving the corresponding sum of the partition functions in the rotational isomeric state approximation (see, e.g., eq 21 of ref 13b) easily suggests that attaching two proper multipliers to w_{dd} and w_{ll} may allow the selection of the partition functions belonging to the subensemble of chains having the desired concentrations of dd and ll pairs from their most general ensemble. Let us indicate with $\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n})$ the modified matrix $\mathbf{W}_1$, i.e., (see eq 2)

$$\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n}) = \begin{bmatrix} \sigma w_{dd}(\varphi_{2n-1}\varphi_{2n}) & w_{dl}(\varphi_{2n-1}\varphi_{2n}) \\ w_{ld}(\varphi_{2n-1}\varphi_{2n}) & \tau w_{ll}(\varphi_{2n-1}\varphi_{2n}) \end{bmatrix} \quad (3)$$

and with $Z_N(\sigma,\tau)$ the corresponding expression of Z_N. The meaning of $Z_N(\sigma,\tau)$ may be illustrated as follows

$$Z_N(\sigma,\tau) = \sigma^{Nf_{dd}}\cdot\tau^{Nf_{ll}}\cdot Z_N(f_{dd},f_{ll}) \quad (4)$$

where $Z_N(f_{dd},f_{ll})$ is the partition function of a chain undergoing hypothetical equilibrium $d \rightleftharpoons l$ under the constraint that the expected frequency (i.e., probability of occurrence) of dd and ll dyads is f_{dd} and f_{ll}, respectively. The value of f_{dd}, e.g., is given by

$$f_{dd} = spur\left[\int_{\varphi 1}\cdots\int_{\varphi 2N}\prod_{n=1}^{i-1}\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n}) \times \mathbf{W}_2(\varphi_{2n}\varphi_{2n+1})\begin{bmatrix} \sigma w_{dd}(\varphi_{2i-1}\varphi_{2i}) & 0 \\ 0 & 0 \end{bmatrix}\mathbf{W}_2(\varphi_{2i}\varphi_{2i+1}) \times \left(\prod_{n=i+1}^{N}\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n})\mathbf{W}_2(\varphi_{2n}\varphi_{2n+1})\right) \times \prod_{k=1}^{2N} \mathrm{d}\varphi_k\right]\Big/ Z_N(\sigma,\tau) \quad (5)$$

A similar equation holds for f_{ll}, thus producing a system of two equations in the two unknown parameters (σ,τ), once f_{dd} and f_{ll} are given. For the above, $Z_N(f_{dd},f_{ll})$ is also the sum of all the partition functions of the chains having the same frequencies f_{dd}, f_{ll}. If all these chains have the same partition function $\overline{Z}_N(f_{dd},f_{ll})$ we have the obvious relation ($f_{dl} = f_{ld}$; $f_{dd} + f_{dl} + f_{ld} + f_{ll} = 1$)

$$Z_N(f_{dd},f_{ll}) = \frac{[N(f_{dd}+f_d)]!\,[N(f_{ld}+f_{ll})]!}{(Nf_{dd})!\,(Nf_{ll})!\,(Nf_{dl})!\,(Nf_{ld})!}\,\overline{Z}_N(f_{dd},f_{ll}) \quad (6)$$

Under the above assumption, the chain undergoing stereochemical equilibrium is characterized by a first-order Markoffian distribution of monomer units, because these are the statistics corresponding to an ensemble of equiprobable chains having all possible structures with fixed pair frequencies. In such a case we must have, e.g.,

$$f_{ddl} = f_{dd}\cdot p_{dl} = f_{dd}\cdot f_{dl}/(f_{dd}+f_{dl}) \quad (7)$$

where p_{dl} is the conditional probability that an l unit follows a d unit, irrespective of its predecessor. All the $f_{xyz\ldots}$ (x, y, $z = d$, l) frequencies may be calculated from equations similar to 5, so that the above condition can be readily verified. To the extent that it were not verified, the pseudo-equilibrated chain would not be first-order Markoffian, because some particular chain structures give a larger contribution to $Z_N(f_{dd},f_{ll})$ than others. The partition function of these dominant chains is still obtainable from $Z_N(f_{dd},f_{ll})$ as in eq 6, except for the introduction of a more complicated factorial term.[15] If we *want* to select the partition function of the first-order Markoffian chains, we might resort to the technique of constraining the triples ddd, ddl, ... (instead of the pairs) at the Markoffian values, thus getting a better approximation at the expense of using more expanded matrices and introducing more multipliers.[13] If any of the statistical weights w_{dd}, w_{dl}, w_{ld}, w_{ll}, w_d, w_l is expanded into a cosine–sine double Fourier series up to terms of order $\bar{m}$,[17–19] it may be expressed as a matrix product of the type, e.g.,

$$w_{dd}(\varphi_{2n-1}\varphi_{2n}) = \mathbf{\Phi}(\varphi_{2n-1})\cdot\mathbf{U}_{dd}\cdot\mathbf{\Phi}^{\mathrm{T}}(\varphi_{2n}) \quad (8)$$

with

$$\mathbf{\Phi}(\varphi_k) = [1, \sqrt{2}\cos(\varphi_k), \sqrt{2}\cos(2\varphi_k), \ldots, \sqrt{2}\cos(\bar{m}\varphi_k), \sqrt{2}\sin(\varphi_k), \ldots, \sqrt{2}\sin(\bar{m}\varphi_k)]$$

while $\mathbf{\Phi}^{\mathrm{T}}(\varphi_k)$ is the transposed vector and $\mathbf{U}_{dd}$ contains the Fourier coefficients (we send the reader to ref 17–19 for further details). Expressions analogous to eq 8 hold for w_{dl}, w_{ld} .... With the use of the above formalism, it is easy to verify that $\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n})$ and $\mathbf{W}_2(\varphi_{2n}\varphi_{2n+1})$ reduce to (cf. eq 2 and 3)

$$\mathbf{W}_1{}^{(\sigma,\tau)}(\varphi_{2n-1}\varphi_{2n}) = \left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\otimes\mathbf{\Phi}(\varphi_{2n-1})\right) \times \begin{bmatrix} \sigma\mathbf{U}_{dd} & \mathbf{U}_{dl} \\ \mathbf{U}_{ld} & \tau\mathbf{U}_{ll} \end{bmatrix}\cdot\left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\otimes\mathbf{\Phi}^{\mathrm{T}}(\varphi_{2n})\right)$$

$$\times\,\mathbf{W}_2(\varphi_{2n}\varphi_{2n+1}) = \left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\otimes\mathbf{\Phi}(\varphi_{2n})\right) \times \begin{bmatrix} \mathbf{U}_d & 0 \\ 0 & \mathbf{U}_1 \end{bmatrix}\left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\otimes\mathbf{\Phi}^{\mathrm{T}}(\varphi_{2n+1})\right) \quad (9)$$

where ⊗ is the symbol of the direct product. Before introducing the above formalism into the expressions of $Z_N(\sigma,\tau)$ (cf. eq 2 except for the absence of σ and τ inside $\mathbf{W}_1$) and f_{dd} (eq 5), let us consider the following identity

$$\int_0^{2\pi}(\mathbf{E}_2\otimes\mathbf{\Phi}^{\mathrm{T}}(\varphi_k))\cdot(\mathbf{E}_2\otimes\mathbf{\Phi}(\varphi_k))\,\mathrm{d}\varphi_k = \int_0^{2\pi}\mathbf{E}_2 \otimes(\mathbf{\Phi}^{\mathrm{T}}(\varphi_k)\,\mathbf{\Phi}(\varphi_k))\,\mathrm{d}\varphi_k = 2\pi\mathbf{E}_{2\bar{m}+1}\otimes\mathbf{E}_2 \doteq 2\pi\mathbf{E}_{4\bar{m}+2} \quad (10)$$

where $\mathbf{E}_t$ stands for the identity matrix of order t. In eq 10 we have made obvious use of the orthonormality of the functions composing $\mathbf{\Phi}(\varphi_k)$ (cf. eq 8). After the above, substituting eq 9 into 2, $Z_N(\sigma,\tau)$ becomes (N large)

$$Z_N(\sigma,\tau) = (2\pi)^{2N} spur\left(\begin{bmatrix} \sigma\mathbf{U}_{dd} & \mathbf{U}_{dl} \\ \mathbf{U}_{ld} & \tau\mathbf{U}_{ll} \end{bmatrix} \times \begin{bmatrix} \mathbf{U}_d & \mathbf{0} \\ \mathbf{0} & \mathbf{U}_l \end{bmatrix}\right)^N \simeq (2\pi)^{2N}\cdot\lambda^N \quad (11)$$

where λ is the largest eigenvalue of the matrix

$$\mathbf{U}(\sigma,\tau) = \mathbf{U}_1(\sigma,\tau)\cdot\mathbf{U}_2 = \begin{bmatrix} \sigma\mathbf{U}_{dd} & \mathbf{U}_{dl} \\ \mathbf{U}_{ld} & \tau\mathbf{U}_{ll} \end{bmatrix}\cdot\begin{bmatrix} \mathbf{U}_d & \mathbf{0} \\ \mathbf{0} & \mathbf{U}_l \end{bmatrix} \quad (12)$$

The last approximate equality in eq 11 becomes rigorous in the limit $N \rightarrow \infty$. If $\mathbf{a}^*$ and $\mathbf{a}$ are the row and column eigenvectors of $\mathbf{U}(\sigma,\tau)$ corresponding to λ, using eq 8–12 and following standard procedures in matrix algebra,[3] we have from eq 5:

$$f_{dd} = spur\left(\mathbf{U}^{i-1}(\sigma,\tau) \times \begin{bmatrix} \sigma\mathbf{U}_{dd} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \cdot \mathbf{U}_2 \cdot \mathbf{U}^{N-i}(\sigma,\tau)\right) \Big/ spur\ \mathbf{U}^N(\sigma,\tau) = \mathbf{a}^* \begin{bmatrix} \sigma\mathbf{U}_{dd} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \times \begin{bmatrix} \mathbf{U}_d & \mathbf{0} \\ \mathbf{0} & \mathbf{U}_l \end{bmatrix} \mathbf{a}/\lambda \quad (13)$$

The average product of any number of functions depending on consecutive rotation angles $\langle F_1(\varphi_k)F_2(\varphi_{k+1})F_3(\varphi_{k+2}) \ldots \rangle$ may now be reduced to a process of the same type as that described for $+\!\text{A–B}\!+_n$ homopolymer chains within the asr scheme.[17,18] As a particular example, let us suppose that we deal with a single function $F(\varphi)$, which is also assumed to be the same whether a d or an l monomer unit is being considered. By analogy with eqs 5 and 13 the statistical average of $F(\varphi)$, considering even bonds first, is

$$\langle F(\varphi_{2i})\rangle = \mathbf{a}^*\mathbf{U}_1(\sigma,\tau) \cdot \mathbf{F}^{(2)}\mathbf{U}_2\mathbf{a}/\lambda \quad (14)$$

where

$$\mathbf{F}^{(2)} = \mathbf{E}_2 \otimes \frac{1}{2\pi}\int_0^{2\pi} \mathbf{\Phi}^{\mathrm{T}}(\varphi)F(\varphi)\mathbf{\Phi}(\varphi)\,\mathrm{d}\varphi = \mathbf{E}_2 \otimes \mathbf{F} \quad (15)$$

is a matrix of order $2(2\bar{m} + 1)$ containing two identical matrices F or order $2\bar{m} + 1$ as diagonal blocks, and $\mathbf{U}_1(\sigma,\tau)$ and $\mathbf{U}_2$ are defined in eq 12. The elements of $\mathbf{F}$ are simple linear combinations of the Fourier coefficients of $F(\varphi)$.[17,18] With a procedure analogous to that leading to eq 14, we also obtain

$$\langle F(\varphi_{2n-1})\rangle = \mathbf{a}^*\mathbf{F}^{(2)}\mathbf{a}$$

$$\langle F(\varphi_{2n-1})F(\varphi_{2n})\rangle = \mathbf{a}^*\mathbf{F}^{(2)}\mathbf{U}_1(\sigma,\tau)\mathbf{F}^{(2)}\mathbf{U}_2\mathbf{a}/\lambda$$

$$\langle F(\varphi_{2n})F(\varphi_{2n+1})\rangle = \mathbf{a}^*\mathbf{U}_1(\sigma,\tau)F^{(2)}\mathbf{U}_2\mathbf{F}^{(2)}\mathbf{a}/\lambda \quad (16)$$

etc. For the particular case where the function to be averaged is the matrix performing the rotation of the Cartesian orthogonal coordinate system associated with each chain bond into that of the successive bond, we have

$$\mathbf{T}(\varphi,\theta) = \begin{bmatrix} -\cos\theta & -\sin\theta & 0 \\ \sin\theta\cos\varphi & -\cos\theta\cos\varphi & -\sin\varphi \\ \sin\theta\sin\varphi & -\cos\theta\sin\varphi & \cos\varphi \end{bmatrix} = \mathbf{T}_0(\theta) + \mathbf{T}_1(\theta)\cos\varphi + \mathbf{T}_2(\theta)\sin\varphi \quad (17)$$

Assuming for simplicity the bond angle θ to be constant and identical for all chain bonds, the successive average products are given by eq 14–16 except for the substitution $F(\varphi) \rightarrow \mathbf{T}(\varphi,\theta) = \mathbf{T}(\varphi)$ and for changing all other matrices into their direct products with $\mathbf{E}_3$ (e.g., $\mathbf{\Phi}(\varphi) \rightarrow \mathbf{\Phi}(\varphi) \otimes \mathbf{E}_3 = \mathbf{\Phi}_3(\varphi)$, $\mathbf{a} \rightarrow \mathbf{a} \otimes \mathbf{E}_3 = \mathbf{a}_3, \ldots$). Let us define the two matrices

$$\Psi_{\mathrm{T}}^{(2)} = \mathbf{E}_2 \otimes \Psi_{\mathrm{T}} = \mathbf{E}_2 \otimes \frac{1}{2\pi}\int_0^{2\pi} \mathbf{\Phi}_3{}^{\mathrm{T}}(\varphi)\mathbf{T}(\varphi)\mathbf{\Phi}_3(\varphi)\,\mathrm{d}\varphi$$

$$\mathbf{Z} = (\mathbf{U}_1(\sigma,\tau) \otimes \mathbf{E}_3) \cdot \Psi_{\mathrm{T}}^{(2)} \cdot (\mathbf{U}_2 \otimes \mathbf{E}_3)/\lambda \quad (18)$$

We may now procede in analogy with eq 20–23 of ref 18, obtaining the mean-square (unperturbed) end-to-end distance of the chain $\langle r^2\rangle_0$ as (l = length of C–C chain bond)

$$C_\infty = \langle r^2\rangle_0/2Nl^2 = [1\ \ 0\ \ 0]\mathbf{a}^*{}_3 \times (\mathbf{E} + \Psi_{\mathrm{T}}^{(2)})(\mathbf{E} - \mathbf{Z}\Psi_{\mathrm{T}}^{(2)})^{-1}(\mathbf{E} + \mathbf{Z})\mathbf{a}_3 \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad (19)$$

where C_∞ is known as the characteristic ratio[8] and $\mathbf{E}$ is the identity matrix of order $6(2\bar{m} + 1)$.

Table I

Geometrical Parameters of the Polymer Chain and Parameters for the Nonbonded Interactions

($V_{ij} = A_{ij}/r^{12} - B_{ij}/r^6$)[a]

(1) Geometrical Parameters

Bond lengths, Å	Bond angles, deg
C–C = 1.54	C–C–C = 112
C–H = 1.09	$\left.\begin{matrix}\text{CH}_3\text{–C–H} \\ \text{H–C–H}\end{matrix}\right\} = 109.5$
	$\left.\begin{matrix}\text{CH}_3\text{–C–C} \\ \text{H–C–C}\end{matrix}\right\} = 108.8$

(2) Nonbonded Interactions Parameters[b]

	A_{ij}	B_{ij}
H···H	4.71×10^3	49
H···C	3.97×10^4	134
C···C	2.94×10^5	381
H···CH_3	1.48×10^5	367
C···CH_3	1.02×10^6	1024
CH_3···CH_3	3.53×10^6	2750

[a] r_{ij} in Å; V_{ij} in kcal/mol. [b] The van der Waals radii of C, H, and CH_3 are 1.70, 1.20, and 1.85 Å, respectively.

Application to Atactic Polypropylene

(a) Conformational Energy Maps. The calculations were carried out in close analogy with those reported in a previous paper on the unperturbed dimensions of isotactic polypropylene, also obtained within the asr scheme.[19] The methyl group is treated as a spherical body, thereby making the specification of its rotation angle around the C–CH_3 bond unnecessary. Justification of this assumption proceeds from the several degrees of freedom, arising both from the rotation itself and from the bending of the valence angles, inherent to the methyl group, which make it much "softer" than ordinary atoms; we believe the error involved in this approximation to be no larger than those arising from other assumptions. Bond lengths and angles are kept fixed at their probable values (see Table I). The chain energy is expressed as a sum of components $E(\varphi_n\varphi_{n+1})$, which implies that interactions between nonbonded atoms separated by more than four bonds cannot be accounted for except as an average. Each energy component may be expressed as

$$E(\varphi_n\varphi_{n+1}) = \frac{1}{2}U_0(1 + \cos 3\varphi_n) + \sum_{i<j}\sum V_{ij}(r_{ij}) \quad (20)$$

where U_0 is the inherent threefold barrier to the rotation around C–C bonds, and V_{ij} is the nonbonded interaction potential between atoms or groups labeled as i and j, as a function of their distance r_{ij}. In order to avoid counting twice any interaction we calculated $E(\varphi_n\varphi_{n+1})$ so that it contains contributions due either to φ_n only or to both φ_n and φ_{n+1}. As a consequence, in the above summation the atom or group pairs whose distance depends only upon φ_{n+1} are excluded. We have chosen $U_0 = 3$ kcal/mol, as in ethane.[19] In view of the assumption of fixed bond lengths and angles, the distance between atoms separated by less than three bonds cannot change, so that their contribution is not included in (20). In order to attribute a given interaction V_{ij} to a single energy term $E(\varphi_n\varphi_{n+1})$, the distance r_{ij} must be specified either by φ_n only or by both φ_n and φ_{n+1}, the atoms being separated by three or four bonds in either case. The nonbonded interaction potentials employed by us are of the type $V_{ij} = A_{ij}/r_{ij}{}^{12} - B_{ij}/r_{ij}{}^6$, and the parameters are identical with those proposed by Scott and Scheraga,[21] except for the additional interactions

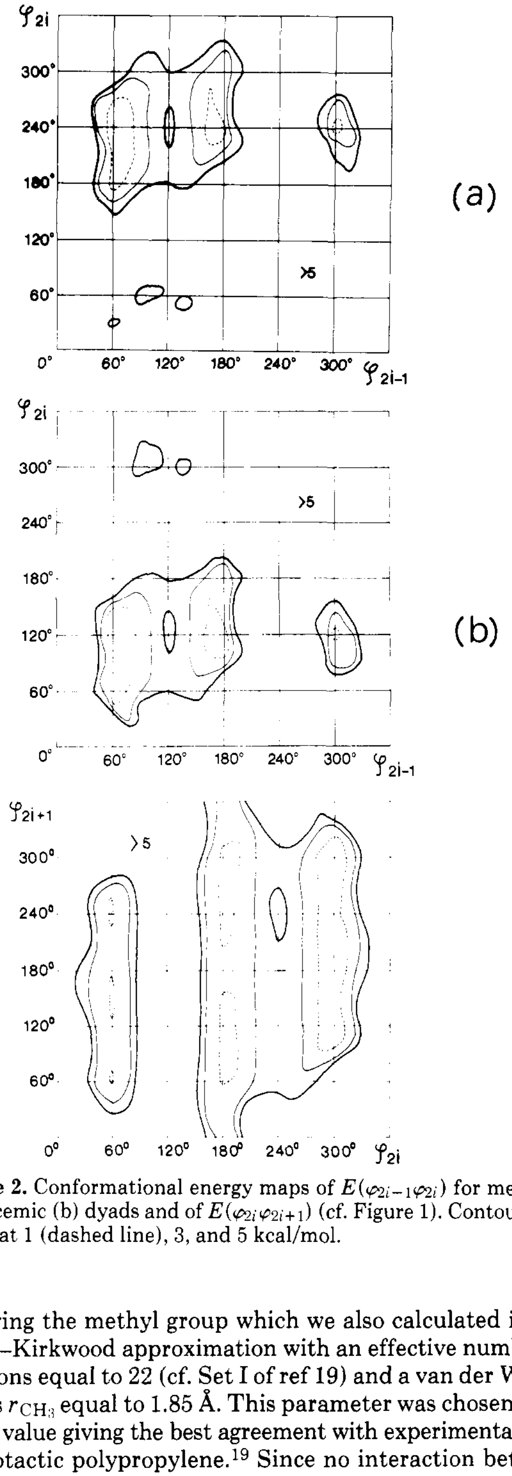

Figure 2. Conformational energy maps of $E(\varphi_{2i-1}\varphi_{2i})$ for meso (a) and racemic (b) dyads and of $E(\varphi_{2i}\varphi_{2i+1})$ (cf. Figure 1). Contours are drawn at 1 (dashed line), 3, and 5 kcal/mol.

involving the methyl group which we also calculated in the Slater–Kirkwood approximation with an effective number of electrons equal to 22 (cf. Set I of ref 19) and a van der Waals' radius r_{CH_3} equal to 1.85 Å. This parameter was chosen close to the value giving the best agreement with experimental data for isotactic polypropylene.[19] Since no interaction between atoms separated by more than four bonds may be specified by two rotation angles only, the V_{ij} term belonging to chain atoms four bonds apart (i.e., two methylenic carbons in the odd–even and two tertiary carbons in the even–odd plots, see Figure 1) has been chosen to correspond to methyl groups, in order to account approximately for the steric effect associated with the surrounding hydrogen atoms. The odd–even maps corresponding to both the iso- and the syndiotactic dyads (chosen as *dd* and *dl* pairs, respectively) and the even–odd map (identical for both placements but referred to as a *d* unit) have been calculated for all the points of a regular square network drawn at intervals of 5° along each rotation angle. Table I gives all the relevant parameters, and Figure 2 shows the three nonequivalent conformational energy maps $E(\varphi_n\varphi_{n+1})$. The two $E(\varphi_{2i-1}\varphi_{2i})$ maps (i.e., E_{dd} and E_{dl}) are nearly symmetrical after the transformation φ_{2i}(syndio) = φ_{2i}(iso) − 120°, as must be expected considering that the two dyads are mutally interchanged upon substitution of a chain methylene for a side methyl group and vice versa; the symmetry is incomplete as long as the two groups are not perfectly equivalent in terms of the nonbonded interactions. The E_{ll}, E_{ld}, and E_l maps may be easily obtained from those reported in Figure 2 which refer to the optically opposite configurations by simply changing the signs of the rotation angles.

(b) Statistical Stereochemical Models. Strong evidence is now available that the stereochemical defects present in predominantly isotactic polypropylene chains are mainly of the type . . . *ddddlddd* . . . (or vice versa),[22] which seems to imply that each chain grows on a single catalytic center with a definite optical sign.[23] This is not true for substantially syndio- or atactic chains, for which no simple statistical model can be derived from experimental data.[24]

Accordingly, we have considered two limiting statistical models, in analogy with what was already done by one of us in a simplified treatment based on a three-state ris scheme.[25] The first of them is purely random, which means that *d* and *l* units are equally probable for any single chain, so that the stereochemical defects for predominantly isotactic chains are of the type . . . *dddllll* . . . or vice versa. In mathematical terms, the model is obtained by taking $\sigma = \tau$ (see, e.g., eq. 11), in view of the equivalence between the **U** matrices having the *d* and *l* indices interchanged. The random model should be a substantially satisfactory representation for chains which contain a small fraction of isotactic dyads. The second is an alternating model, in the sense that *l* units are only allowed if flanked by *d* units. This corresponds to taking $\tau = 0$ in eq 8, which implies forbidding *ll* pairs. The alternating model should be a satisfactory representation for predominantly isotactic chains.

(c) Characteristic Ratio. Results and Comparison with Experiment. Each of the six **U** matrices (i.e., $\mathbf{U}_{dd}$, $\mathbf{U}_{dl}$, $\mathbf{U}_{ld}$, $\mathbf{U}_{ll}$, $\mathbf{U}_d$, and $\mathbf{U}_l$, see eq 12) has the structure

$$\mathbf{U} = \begin{bmatrix} \mathbf{U}_{cc} & \mathbf{U}_{cs} \\ \mathbf{U}_{sc} & \mathbf{U}_{ss} \end{bmatrix} \qquad (21)$$

where $\mathbf{U}_{cs}$, e.g., is built up with the coefficients of the cos $(m\varphi_i)$ sin $(n\varphi_{i+1})$ terms belonging to the Fourier expansion of $w(\varphi_i\varphi_{i+1})$ (cf. eq 8). It is convenient to label rows and columns of each of the four submatrices according to the *m* and *n* indices of the Fourier terms; consequently, if the largest index is $\bar{m}$, the rows of $\mathbf{U}_{cc}$ and $\mathbf{U}_{cs}$ range from 0 to $\bar{m}$, unlike those of $\mathbf{U}_{sc}$ and $\mathbf{U}_{ss}$ which are indexed 1 to $\bar{m}$. The symmetrical rules for the columns are easily derived by considering that both $\mathbf{U}_{cc}$ and $\mathbf{U}_{ss}$ are square matrices. The general element *a* of the $\mathbf{U}_{cc}$ matrix, e.g., is obtained from the appropriate energy map through

$$a_{pq} = \frac{4}{2^{\delta 0,p+\delta 0,q}} \frac{1}{N^2} G(p,N)G(q,N) \times \sum_{h,k=1}^{N}\sum w\left(2\pi\frac{h}{N}, 2\pi\frac{k}{N}\right) \times \cos\left(2\pi p\frac{h}{N}\right)\cos\left(2\pi q\frac{k}{N}\right) \qquad (22)$$

where $\delta_{i,j}$ is the Kronecker delta,

$$w(\varphi_n\varphi_{n+1}) = \exp(-E(\varphi_n\varphi_{n+1})/kT)$$

$$G(p,N) = \sin^2(p\pi/N)/(p\pi/N)^2 \quad (G(0,N) = 1) \qquad (23)$$

and in our case *N*, i.e., the number of intervals along either angle, is 72, corresponding to 5° steps. The *G* factors arise from the requirement that the statistical weight behaves as a continuous function within each square of the network.[17]

Four distinct Fourier developments of all the $w(\varphi_n\varphi_{n+1})$ maps were carried out, up to (cos $\bar{m}\varphi_k$, sin $\bar{m}\varphi_k$) terms with $\bar{m}$ equal to 8, 9, 10, 11 for the two temperature values of 127

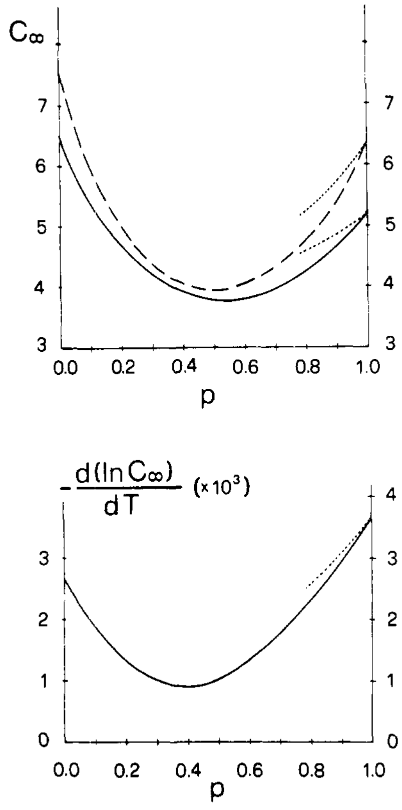

Figure 3. Plot of $C_\infty = \langle r^2\rangle_0/2Nl^2$ and of its average temperature derivative in the range 127–177 °C for the random and for the alternating model of monomer unit sequences (see text); in the second case the partial range $0.8 < p < 1.0$ is covered, where p is the fraction of meso dyads. The C_∞ values are given for 127 °C (above) and for 177 °C (below).

and 177 °C (i.e., 400 and 450 K). Chains with different percentages of meso (i.e., *dd* or *ll*) dyads were generated by taking arbitrary values either for $\sigma = \tau$ (for the random model) or for σ alone with $\tau = 0$ (for the alternating model), then obtaining the fraction of *dd* dyads f_{dd} from eq 13. Then the characteristic ratio was evaluated in each case from eq 19, the results being reported in Figure 3, which also shows the average value of the temperature coefficient d(ln C_∞)/dt in the temperature range taken into consideration. In comparison with the results previously obtained by one of us within the ris scheme,[25] the new values are substantially smaller everywhere, in spite of the relatively small difference between the energy maps adopted. No doubt this is related to some sacrifice of chain flexibility involved in the adoption of our old three-state scheme. By far the largest disagreement between the old and the new results concerns the case of the isotactic chains, which now appear to be less expanded in unperturbed solution than those of the syndiotactic polymer, contrary to the old calculations; this is a further proof of the difficulty of accounting for the critical helix-reversal conformations of isotactic polypropylene within the ris scheme.[8,26] Our results are in reasonable agreement with several experimental data, at least for the extreme cases of the iso-[27,28] and syndiotactic[29] chains; the results for the atactic chains (i.e., $p \sim 0.5$, see Figure 3) are somewhat smaller than the experimental values although the disagreement may be attributed, at least in part, to an incomplete randomness in the samples of the atactic polymer. However, it is worth stressing that some experimental data, where the iso- and atactic polymers are investigated using the same theta solvents, consistently show that the unperturbed dimensions of atactic polypropylene as well as of atactic poly-*n*-butene-1 and of poly-*n*-pentene-1 are invariably smaller than those of the isotactic polymers (and the same is true of their temperature coefficients, in agreement with Figure 3) in the temperature range considered by us.[30,31] Considering the different temperature ranges at which the experiments were performed, the results obtained by other authors (see, in particular, ref 16, Table VIII) do not appear to contradict this statement.

Our C_∞ results show some discrepancies from those obtained by Suter and Flory,[16] which may be attributed partly to differences in the conformational energy maps and partly to the fact that the quoted authors employ the ris scheme, contrary to us. In particular, the lowest C_∞ values correspond to the atactic and to the isotactic polymer for our calculations and for Suter and Flory's respectively. As for the larger results for the syndiotactic case obtained by these authors, they are probably due to the lower energy of the TT compared to the GG sequences appearing in their energy maps. The plots of d ln C_∞/dT are in qualitative agreement except that our results are somewhat larger in absolute value; the experimental data obtained by Moraglio and co-workers compare rather satisfactorily with those reported in our Figure 3.

Table II
Test of Convergence for $\bar{Z}_N^{1/N}$ and C_∞ at T = 400 K

	Isotactic		Syndiotactic		Atactic	
$\bar{m}$	C_∞	$\bar{Z}_N^{1/N}$	C_∞	$\bar{Z}_N^{1/N}$	C_∞	$\bar{Z}_N^{1/N}$
8	6.65	1.052			3.94	1.084
9	6.55	1.077	7.79	1.110	3.96	1.097
10	6.33	1.088	7.52	1.121	3.96	1.107
11	6.28	1.092	7.44	1.124	3.92	1.111

Table II shows the results obtained for the random statistical model for different degrees $\bar{m}$ of the Fourier expansion, indicating that at $\bar{m}$ = 11 a satisfactory convergence is obtained both for the partition function and for the characteristic ratio. From eq 4 and 6, the partition function $\bar{Z}_N(f_{dd},f_{ll})$ is obtained after dividing $Z_N(\sigma,\tau)$ (see eq 11) by the factor

$$\exp\{N[f_d \ln f_d + f_l \ln f_l - f_{dd} \ln (f_{dd}/\sigma) - f_{ll} \ln (f_{ll}/\tau) - f_{dl} \ln f_{dl} - f_{ld} \ln f_{ld}]\}$$

which is the exponential form of the combinatorial factor in eq 6. As already pointed out, this factor is exact only in the case of a monomer unit distribution strictly obeying the first-order Markoffian law. That this is indeed true for both stereochemical models is shown in Table III, where $p_{(x)yz}$ (x, y, z = d, l) are the conditional probabilities that z follows y when y is preceded by x, and they must be independent of x in the Markoffian case. (Each $p_{(x)yz}$ was obtained as f_{xyz}/f_{xy}, the frequencies being obtained by equations analogous to 13; see also ref 13b, eq 30.) The percentage disagreement between the two values corresponding to $x = d$, l for the same y and z is always well below 1%; therefore the Markoffian law is extremely well reproduced.

The $\bar{Z}_N^{1/N}$ values reported in Table II for the isotactic polymer do not agree with those reported in the previous paper on the asr method applied to the same polymer (cf. ref 19, Table III, $\lambda = \bar{Z}_N^{1/N}$) because of a different choice for the zero energy in the conformational maps. The zero energy is chosen in the same way for the meso- and for the racemic dyads, so that the free energy of chains having different unit sequences is given on the same scale. In particular, putting $\sigma = \tau = 1$ in eq 11 we obtain the partition function for a chain undergoing unrestricted stereochemical equilibration at the temperature under consideration.[32] Our results show some deviation from the experimental results on the equilibration of propylene olygomers,[33] since we obtain about 49% of meso dyads in the whole temperature range from −100 to 200 °C, while the experimental figures are 46 and 48%, respectively.

Table III
Test of Markoffian Sequence for both the Random and the Alternating Model at 400 and 450 K[a]

	Random model		Alternating model	
% isotactic	$p_{(d)dd}$	$p_{(l)dd}$	$p_{(d)dd}$	$p_{(p)dd}$
	(1) T = 400 K			
91.0			0.953	0.953
89.6	0.896	0.897		
79.4			0.885	0.886
74.4	0.743	0.746		
49.3	0.492	0.494		
24.5	0.244	0.246		
9.8	0.098	0.098		
	(2) T = 450 K			
91.1			0.953	0.953
89.7	0.897	0.896		
75.0			0.857	0.858
74.5	0.744	0.746		
49.4	0.493	0.495		
24.6	0.246	0.246		
9.8	0.098	0.098		

[a] These results have been obtained with $\bar{m}$ = 10. For the significance of $p_{(x)yz}$ see the text.

However, it is not difficult to show that very modest changes in the nonbonded interaction potentials may lead to variations of the above order of magnitude. The order of magnitude of the free energy change, required to match calculations with experimental results, may be roughly evaluated as follows. Let Δe and Δs be the *average* extra-energy and entropy of a meso compared with a racemic dyad. In terms of the stereochemical equilibrium, statistical weights equal to $\exp(-[\Delta e - T\Delta s]/RT)$ and 1 may be respectively attributed to these two dyads. The experimental data may be fitted by taking Δe = 0.04 kcal/mol and $\Delta s = -0.09$ cal/(K mol). Since our calculations give $\Delta e \simeq 0$, $\Delta s = -0.06$ cal/(K mol), it is apparent that the disagreement is small indeed if compared with the approximations involved.

Our calculations were carried out on the UNIVAC 1108 computer of the Polytechnic of Milan. Once the three energy maps were obtained (~7 min), each C_∞ value involved about 2 min, including the evaluation of the Fourier coefficients.

General Equivalence between the ris and the asr Methods

In the present paper we have shown that the asr method may be extended to the copolymer case. More generally we want to show that the evaluation of any configurational average in the ris scheme for a chain with first-neighbor interactions has a strictly analogous asr counterpart. Let us consider a chain with $(n + 1)$ skeletal bonds $w^{(h)}(\varphi_h\varphi_{h+1})$ being the statistical weight belonging to the general pair of rotations on the h, $h + 1$ bond pair. Within the ris method the rotations are confined to a discrete set, so that the notation $w^{(h)}(i_hi_{h+1})$ is more convenient, i_h being the index number of the general rotation allowed around the hth bond. Following well-known results, the chain partition function will be expressed as

$$Z = \sum_{\{i_h\}} w^{(1)}(i_1i_2)w^{(2)}(i_2i_3)\ldots w^{(n)}(i_ni_{n+1})$$

$$= [11\ldots 1] \prod_{h=1}^{n} \mathbf{W}^{(h)} \begin{bmatrix}1\\1\\\vdots\\1\end{bmatrix} \qquad (24)$$

where $\mathbf{W}^{(h)}$ contains the statistical weights $w^{(h)}(i_hi_{h+1})$ and i_h, i_{h+1} are the row and column indices, respectively. The statistical average of a function $F(i_h)$ of the hth rotation may be expressed in terms of the diagonal matrix

$$\mathbf{F} = \begin{bmatrix} F_1 & & \\ & F_2 & \\ & & \ddots \end{bmatrix}$$

where F_k stands for $F(i_h = k)$; we get

$$\langle F\rangle = [1\ 1\ \ldots\ 1] \left(\prod_{l=1}^{h-1} \mathbf{W}^{(l)}\right) \mathbf{F} \left(\prod_{l=h}^{n} \mathbf{W}^{(l)}\right) \begin{bmatrix}1\\1\\\vdots\\1\end{bmatrix} \Bigg/ Z \qquad (25)$$

Adopting the asr scheme, the configurational integral may be easily transformed as follows

$$Z' = \int_{\varphi_1}\ldots\int_{\varphi_n} w^{(1)}(\varphi_1\varphi_2)w^{(2)}(\varphi_2\varphi_3)\ldots w^{(n)}(\varphi_n\varphi_{n+1})$$

$$\times \prod \mathrm{d}\varphi_h = \int_0^{2\pi} \mathbf{\Phi}(\varphi_1)\,\mathrm{d}\varphi_1 \prod_{h=1}^{n-1}\left[\mathbf{U}^{(h)} \int_0^{2\pi} \mathbf{\Phi}^{\mathrm{T}}(\varphi_{h+1})\right.$$

$$\left.\times\, \mathbf{\Phi}(\varphi_{h+1})\,\mathrm{d}\varphi_{h+1}\right] \cdot \mathbf{U}^{(n)} \int_0^{2\pi} \mathbf{\Phi}^{\mathrm{T}}(\varphi_{n+1})\,\mathrm{d}\varphi_{n+1}$$

$$= (2\pi)^{n+1}[1\ 0\ldots 0] \prod_{h=1}^{n} \mathbf{U}^{(h)} \begin{bmatrix}1\\0\\\vdots\\0\end{bmatrix} \qquad (26)$$

where $\mathbf{U}^{(h)}$ contains the Fourier coefficients of the expansion of $w^{(h)}(\varphi_h\varphi_{h+1})$. The analogy between eq 24 and 26 is obvious.

As for the average of $F(\varphi_h)$, in the asr scheme, its calculation follows lines analogous to those leading to eq 14–16, the result being

$$\langle F(\varphi_h)\rangle = [1\ 0\ldots 0] \prod_{l=1}^{h-1} \mathbf{U}^{(l)}\mathbf{F}'$$

$$\times \prod_{l=h}^{n} \mathbf{U}^{(l)} \begin{bmatrix}1\\0\\\vdots\\0\end{bmatrix} \Bigg/ [1\ 0\ldots 0] \prod_{h=1}^{n} \mathbf{U}^{(h)} \begin{bmatrix}1\\0\\\vdots\\0\end{bmatrix} \qquad (27)$$

where $\mathbf{F}'$ is given by $(1/2\pi)\int_0^{2\pi} \mathbf{\Phi}^{\mathrm{T}}(\varphi)F(\varphi)\mathbf{\Phi}(\varphi)\,\mathrm{d}\varphi$. The full equivalence between eq 25 and 27 is readily established with the substitutions $[1\ 1\ldots 1] \rightarrow [1\ 0\ 0\ldots 0]$ (or their transposed vectors), $\mathbf{F} \rightarrow \mathbf{F}'$, $\mathbf{W}^{(h)} \rightarrow \mathbf{U}^{(h)}$. In conclusion, the two methods are completely equivalent in the formal sense, matrices and vectors need only be redefined. In particular, with minor readjustments the present scheme should be readily adapted to Flory's matrix self-multiplication technique.[1,9]

As a final remark, a particular average is perhaps worth being discussed separately, namely the probability that a given rotation $\bar{i}_h$ takes place on the hth bond (in ris language), or that σ_h is comprised within $\varphi_h - \Delta$ and $\varphi_h + \Delta$ (in asr language). In the former case, the probability is obtained from eq 25 after substitution of $\mathbf{F}$ with $\mathbf{P}$ which is zero everywhere except for the $(\bar{i}_h, \bar{i}_h)$ element which is unity.[5] In the latter case, the corresponding $\mathbf{P}'$ matrix is

$$\mathbf{P}' = \frac{1}{2\pi}\int_0^{2\pi} \mathbf{\Phi}^{\mathrm{T}}(\varphi)P(\bar{\varphi}_h,\Delta)\mathbf{\Phi}(\varphi)\,\mathrm{d}\varphi \qquad (28)$$

where $P(\bar{\varphi}_h,\Delta)$ is unity in the interval $(\bar{\varphi}_h - \Delta, \bar{\varphi}_h + \Delta)$ and zero elsewhere. The simple algebra involved in the above integral leads to the following rules to construct the $\mathbf{P}'$ matrix: (i) perform the dyadic product $\mathbf{\Phi}^{\mathrm{T}}(\bar{\varphi}_h) \cdot \mathbf{\Phi}(\bar{\varphi}_h)$ and linearize all the elements in the resulting square matrix (e.g., $\cos\bar{\varphi}_h \cos 3\bar{\varphi}_h = \frac{1}{2}\cos 4\bar{\varphi}_h + \frac{1}{2}\cos 2\bar{\varphi}_h$); (ii) multiply each term $\cos n\bar{\varphi}_h$ or $\sin n\bar{\varphi}_h$ by $S(n\Delta) = \sin(n\Delta)/(n\Delta)$, taking $S(0) = 1$; call

$\mathcal{P}'(\bar{\varphi}_h,\Delta)$ the resulting matrix; (iii) $\mathbf{P}'$ is given by $\Delta/\pi \cdot \mathcal{P}'(\bar{\varphi}_h,\Delta)$. Since $S(n\pi)$ $(n \neq 0)$ is zero, if $\Delta = \pi$, $\mathbf{P}'$ reduces to the identity matrix, as it must be.

Concluding Remarks

The asr method may be easily adapted to the pseudo-stereochemical-equilibrium treatment of infinite copolymer chains. Results of the unperturbed dimensions obtained for atactic polypropylene show a substantial agreement with experimental data. They also show that the chain ensemble to which our calculations refer is very closely described by a Markoffian sequence of *d* and *l* units. As seen in previous calculations, a satisfactory convergence is obtained in the calculations if the Fourier expansion of the statistical weights is pushed up to terms of order about 10.

The authors would be glad to provide the whole set of the Fortran computing programs to anybody interested. They presently can perform the calculations reported in the present paper for any polymer, or copolymer, having $\text{-}\!\!\left(\text{A–B}\right)\!\!\text{-}$ monomer units, provided its conformational energy may be given as a sum of terms each depending on two consecutive skeletal rotations.

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Dielectric and Dynamic Mechanical Relaxations in 3,3,3-Trifluoro-2-trifluoromethylpropene (Hexafluoroisobutylene)/1,1-Difluoroethylene Alternating Copolymers

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ABSTRACT: The α and β dielectric relaxations for an alternating copolymer of poly(vinylidene fluoride/3,3,3-trifluoro-2-trifluoromethylpropene) have been studied. It is proposed that these relaxations are the glass transition and a local mode motion of the polymer chain, respectively. The relatively high value of T_g (~405 K at 120 Hz) is discussed in terms of chain stiffness due to steric interactions and electronic repulsion. On the basis of the T_g relaxation in the copolymer, it is postulated that poly(3,3,3-trifluoromethylpropene) would probably possess an exceptionally high T_g. The β relaxation (205 K at 120 Hz) is assigned to a low amplitude motion of the main chain.

Fluoro- and perfluoropolymers have important industrial applications in that they exhibit high dielectric breakdown strength, are excellent insulators, and exhibit very low surface tension characteristics.[1,2] These materials exhibit the characteristic properties of many polymer systems in that they can be semicrystalline or amorphous and many of their dynamic properties (T_g and sub-T_g relaxations) can be related to their proton substituted counterparts.[3] Additionally, some of the crystalline polymorphs of these fluoropolymers exhibit piezo- and pyroelectric properties.[4,5]

Polytetrafluoroethylene (PTFE) has been widely adopted for industrial use. Unfortunately, thermal processing of PTFE is made difficult by its high viscosity (10^{11} P at 750 K). Recently, a fluoropolymer has been introduced which exhibits many of the desired properties of PTFE and, additionally, is melt processable. This polymer is an alternating semicrys-