# Configurational-conformational statistics of atactic polypropylene

**Giovanni Carlo Alfonso***
*Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, 16132 Genova, Italy*

**and Deyue Yan and Zhiping Zhou**
*Department of Applied Chemistry, Shanghai Jiao Tong University, 1954 Hua Shan Road, Shanghai 200030, People's Republic of China*
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The configurational-conformational characteristics of polypropylene are discussed by considering every polymer chain as constituted by the periodic repetition of a sequence of monomeric units in a given configuration. Sample calculations are presented for the special case in which *meso* and *racemic* dyads are distributed according to Bernoullian statistics. Numerical results show that the characteristic ratio of atactic polypropylene reaches an asymptotic value of 5.34 when the size of the periodic sequence corresponds to six monomeric units. The temperature coefficient is calculated to be $-1.34 \times 10^{-3}\,\mathrm{K}^{-1}$, in good agreement with experimental data reported in literature. The characteristic ratio of the mean-square radius of gyration, $\langle R_g^2 \rangle / nl^2$, obtained from our calculations for the atactic polymer is 0.86. The effect of the fraction of *meso* dyads in Bernoullian polypropylene chains on the conformational and configurational entropy is also evaluated.

**(Keywords: conformational statistics; polypropylene; polymer chains)**

## INTRODUCTION

The stereochemical constitution of polypropylene chains has a strong influence on the dimensions of the molecular coils in the unperturbed state and their temperature coefficients, as well as on several properties of polymer solutions.

The configurational-conformational statistics of polypropylene has been treated in several theoretical studies based on the rotational isomeric state scheme. Two main methods have been proposed for the calculation of the chain averages: the Monte Carlo method[1] and the 'all skeletal rotations' method coupled with the pseudostereochemical equilibrium treatment of copolymer chains[2,3].

In the Monte Carlo approach the non-stereoregular sequence of dyads of an atactic polypropylene chain is assumed to obey either Bernoullian or first-order Markovian statistics with a probability of *meso* dyad, $P_m$, and a conditional probability of a *racemic* dyad following a *meso* one, $P_{m/r}$. The representative chains are generated by computer simulation and the result of the configurational-conformational statistics is obtained by averaging over several computer-generated chains. To obtain satisfactory results, long computing time is necessary due to the very large number of monomeric units in a single chain and to the variety of possible configurations. The studies that have been carried out so far using this approach were confined to the consideration of small sets of relatively short chains, with less than 200 units[1,4–11].

The pseudostereochemical equilibrium method introduces a unified correlation matrix for various configurational sequences along the chain and assumes that both rotational isomeric states and configurations accessible to the monomeric units undergo a fictitious dynamic equilibrium.

Allegra[2] proved that the average of the pseudostereochemical equilibrium model is identical with the average of a conveniently chosen subset of chains with fixed configuration, whose configuration sequences approach the first-order Markovian distribution.

The configurational characteristics of polypropylene samples can be experimentally studied using infrared spectroscopy and high-resolution nuclear magnetic resonance (n.m.r.) that allow one to evaluate the occurrence probability of various sequences of dyads and that aid the understanding of configurational sequences[12–14]. A vast literature on the experimental and theoretical aspects of the stereoconfiguration of vinyl polymers is already available[15–34]. In this paper we develop a new theoretical approach in which matrix algebra is directly combined with the occurrence probability of configurational sequences. This enables us to evaluate the mean-square end-to-end distance and its temperature coefficient and the mean-square radius of gyration for atactic polypropylene as a function of the fraction of *meso* dyads. The results of these calculations are in good agreement with the experimental data reported in the literature[35–39].

## THEORETICAL MODEL

According to the stereochemical terminology of organic chemistry, an atactic vinyl polymer chain can be

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* To whom correspondence should be addressed

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described by a sequence of *meso* and *racemic* dyads of random length, for instance:

... *mmmrrrrrrmmrmmmmrrrmrrmrr* ...

A sketch of such a chain is shown in *Figure 1* where $l$ and $l'$ are the lengths of the skeletal and side bonds, respectively, and $\vartheta$ and $\vartheta'$ are the supplements of bond angles between two skeletal bonds and between skeletal and side bonds, respectively.

For a polypropylene chain composed of $x$ monomeric units, or $n=2x-1$ bonds, there are $2^{x-1}$ distinguishable configurations. The mean-square end-to-end distance $\langle r^2\rangle$ of chains with the $i$th configuration is given, as will be discussed in detail in the next section, by

$$\langle r^2\rangle_i=\left[J^*\left(\prod_{k=1}^{x-1}U_k^{(2)}\right)J\right]^{-1}(J^*\otimes J_{\mathrm{p}})\|g_1\| \times\left(\prod_{k=1}^{x-1}g_k^{(2)}\right)\|g_n\|(J\otimes J_{\mathrm{Q}}) \qquad (1)$$

where the dyad matrices of the $k$th bond dyad are:

$$U_k^{(2)}=\begin{cases}U_{\mathrm{m}}^{(2)} & \text{for } meso \text{ dyads}\\ U_{\mathrm{r}}^{(2)} & \text{for } racemic \text{ dyads}\end{cases} \qquad (2)$$

$$g_k^{(2)}=\begin{cases}g_{\mathrm{m}}^{(2)} & \text{for } meso \text{ dyads}\\ g_{\mathrm{r}}^{(2)} & \text{for } racemic \text{ dyads}\end{cases} \qquad (3)$$

and $J^*$, $J$, $J_{\mathrm{p}}$ and $J_{\mathrm{Q}}$ are defined in equations (16) and (17).

The mean-square end-to-end distance of an ensemble of chains with different configurations is

$$\langle r^2\rangle=\sum_{i=1}^{2^{x-1}}Q_i\langle r^2\rangle_i \qquad (4)$$

where $Q_i$ is the occurrence probability of the $i$th configuration of the chain.

This expression accounts for the total contribution of all $x$-ads of the chain under consideration. However, owing to the large number of possible configurations for a long chain polymer, it is difficult to arrive at the result directly from equation (4). Frisch *et al.*[23] have developed the concept of configurational sequences, dyads, triads, tetrads etc., to characterize the microstructure of vinyl polymer chains. According to this approach, it is conceivable that a macromolecular chain, $x$ monomeric units long and with a given configuration, could be considered as one of the $x$-ads, i.e. the full sequence of $x$-1 dyads. To simplify the calculations, the Monte Carlo method selects some of the longest configurational sequences as the representative chains. The criterion of selection used here is different: sequences of monomeric units are chosen that repeat along the chain; then, by appropriately averaging over all representative chains, the mean-square end-to-end distance is derived. Evidently, it is convenient to assume that the representative chains have configurations dictated by a succession of periodic microstructures. In this view, the repeating motif is a type of short sequence. For example, in a chain consisting of regular alternations of one *meso* and two *racemic* dyads:

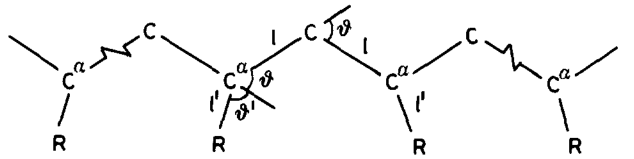

**Figure 1** Representation of the structure of a polypropylene chain ($R=-CH_3$)

... *mrrmrrmrrmrr* ...

the repeating sequence is the tetrad *mrr*, defined as a period of magnitude 3.

Under general periodic conditions, equations (1) and (4) can be written as:

$$\langle r^2\rangle_i=\left[J^*\left(\prod_{k=1}^{p}U_k^{(2)}\right)^{(x-1)/p}J\right]^{-1}(J^*\otimes J_{\mathrm{p}})\|g_1\| \times\left(\prod_{k=1}^{p}g_k^{(2)}\right)^{(x-1)/p}\|g_n\|(J\otimes J_{\mathrm{Q}}) \qquad (5)$$

and

$$\langle r^2\rangle=\sum_{i=1}^{2^p}P_i\langle r^2\rangle_i \qquad (6)$$

where $p$ is the number of dyads in a repeating motif. $P_i$ represents the occurrence probability of the $i$th sequence of the $(p+1)$-ads. In this scheme $P_i$ also denotes the occurrence probability of the $i$th representative chain in the subensemble of representative chains. Since chains are much longer than sequences, it can safely be assumed that $(x-1)/p$ is an integer.

The occurrence probability $P_i$ is related to the statistical model of the polymerization reaction. The probability functions for pentad sequences with Bernoullian and first-order Markovian statistics are given in *Table 1*[32–34] where the occurrence probabilities of *meso* and *racemic* dyads are denoted by $P_{\mathrm{m}}=\alpha$ and $P_{\mathrm{r}}=1-\alpha$, respectively. The conditional probabilities that a given dyad is followed by an homologous or heterologous one are given by:

$$P_{\mathrm{m/r}}=\beta;\quad P_{\mathrm{m/m}}=1-\beta;\quad P_{\mathrm{r/r}}=1-\frac{\alpha\beta}{1-\alpha};\quad P_{\mathrm{r/m}}=\frac{\alpha\beta}{1-\alpha}$$

N.m.r. provides information on the occurrence probability of short sequences (usually involving up to six bonds) and enables one to evaluate $\alpha$ or $\alpha$ and $\beta$ for

**Table 1** Probability functions for Bernoullian and first-order Markovian statistics

| Probability function | Bernoullian statistics | First-order Markovian statistics |
|---|---|---|
| *Pmmmm* | $\alpha^4$ | $P_{\mathrm{m}}P_{\mathrm{m/m}}^3=\alpha(1-\beta)^3$ |
| *Pmmmr* | $\alpha^3(1-\alpha)$ | $P_{\mathrm{m}}P_{\mathrm{m/m}}^2P_{\mathrm{m/r}}=\alpha\beta(1-\beta)^2$ |
| *Prmmm* | $\alpha^3(1-\alpha)$ | $P_{\mathrm{r}}P_{\mathrm{r/m}}P_{\mathrm{m/m}}^2=\alpha\beta(1-\beta)^2$ |
| *Pmrmm* | $\alpha^3(1-\alpha)$ | $P_{\mathrm{m}}P_{\mathrm{m/r}}P_{\mathrm{r/m}}P_{\mathrm{m/m}}=(\alpha\beta)^2(1-\beta)/(1-\alpha)$ |
| *Pmmrm* | $\alpha^3(1-\alpha)$ | $P_{\mathrm{m}}P_{\mathrm{m/m}}P_{\mathrm{m/r}}P_{\mathrm{m/m}}=(\alpha\beta)^2(1-\beta)/(1-\alpha)$ |
| *Pmmrr* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{m}}P_{\mathrm{m/m}}P_{\mathrm{m/r}}P_{\mathrm{r/r}}=\alpha\beta(1-\beta)(1-\alpha\beta/(1-\alpha))$ |
| *Prrmm* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{r}}P_{\mathrm{r/r}}P_{\mathrm{r/m}}P_{\mathrm{m/m}}=\alpha\beta(1-\beta)(1-\alpha\beta/(1-\alpha))$ |
| *Prmmr* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{r}}P_{\mathrm{r/m}}P_{\mathrm{m/m}}P_{\mathrm{m/r}}=\alpha\beta^2(1-\beta)$ |
| *Pmrrm* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{m}}P_{\mathrm{m/r}}P_{\mathrm{r/r}}P_{\mathrm{r/m}}=(\alpha\beta)^2(1-\alpha\beta/(1-\alpha))/(1-\alpha)$ |
| *Pmrmr* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{m}}P_{\mathrm{m/r}}^2P_{\mathrm{r/m}}=\alpha^2\beta^3/(1-\alpha)$ |
| *Prmrm* | $\alpha^2(1-\alpha)^2$ | $P_{\mathrm{r}}P_{\mathrm{r/m}}^2P_{\mathrm{m/r}}=\alpha^2\beta^3/(1-\alpha)$ |
| *Prrrm* | $\alpha(1-\alpha)^3$ | $P_{\mathrm{r}}P_{\mathrm{r/r}}^2P_{\mathrm{r/m}}=\alpha\beta(1-\alpha\beta/(1-\alpha))^2$ |
| *Pmrrr* | $\alpha(1-\alpha)^3$ | $P_{\mathrm{m}}P_{\mathrm{m/r}}P_{\mathrm{r/r}}^2=\alpha\beta(1-\alpha\beta/(1-\alpha))^2$ |
| *Prmrr* | $\alpha(1-\alpha)^3$ | $P_{\mathrm{r}}P_{\mathrm{r/m}}P_{\mathrm{r/r}}P_{\mathrm{m/r}}=\alpha\beta^2(1-\alpha\beta/(1-\alpha))$ |
| *Prrmr* | $\alpha(1-\alpha)^3$ | $P_{\mathrm{r}}P_{\mathrm{r/r}}P_{\mathrm{r/m}}P_{\mathrm{m/r}}=\alpha\beta^2(1-\alpha\beta/(1-\alpha))$ |
| *Prrrr* | $(1-\alpha)^4$ | $P_{\mathrm{r}}P_{\mathrm{r/r}}^3=(1-\alpha)(1-\alpha\beta/(1-\alpha))^3$ |

Bernoullian or Markovian statistics, respectively. If n.m.r. could give access to information on occurrence of longer sequences (more than six) our procedure would be directly applicable, with no need of any *a priori* statistical model for the growing chain.

Clearly, when equations (5) and (6) replace equations (1) and (4), the larger the repeating period taken, the more accurate the results will be. The difference will vanish if $p$ equals $x-1$.

## CALCULATION PROCEDURE

We have adopted the three-state model that successfully describes the characteristic ratio $(\langle r^2\rangle/nl^2)_\infty$ of polypropylene and its temperature coefficient for the infinite isotactic chain.

According to the fundamental papers of Flory *et al.*[4,11], the internal rotation characteristic of vinyl polymers can be expressed in terms of the three statistical weight matrices:

$$U'=\begin{pmatrix}\eta & 1 & \tau\\ \eta & \omega & \tau\\ \eta & 1 & \tau\omega\end{pmatrix} \tag{7}$$

for the first of the two bonds connecting two consecutive asymmetric carbon atoms, and

$$U''_{\mathrm{m}}=\begin{pmatrix}\eta\omega'' & 1 & \tau\omega'\\ \eta & \omega & \tau\omega'\\ \eta\omega' & \omega' & \tau\omega\omega''\end{pmatrix} \tag{8}$$

$$U''_{\mathrm{r}}=\begin{pmatrix}\eta & \omega' & \tau\omega''\\ \eta\omega' & 1 & \tau\omega\\ \eta\omega'' & \omega & \tau\omega'^2\end{pmatrix} \tag{9}$$

for the second bond of the *meso* and *racemic* bond dyad, respectively.

The considered rotation angles are

$$\begin{aligned}\phi_{\mathrm{t}}&=\Delta\phi\\ \phi_{\mathrm{g}}&=120^\circ-\Delta\phi\\ \phi_{\bar{\mathrm{g}}}&=240^\circ\\ \Delta\phi&=5^\circ\end{aligned} \tag{10}$$

and a set of accepted values at 130°C of the parameters in the statistical weight matrices is[5]

$$\begin{aligned}\eta&=0.9\\ \omega&=0.0932\\ \omega'=\omega''&=0.0565\\ \tau&=0.6\end{aligned} \tag{11}$$

The mean-square end-to-end distance of chains with periodicity in the sequence of monomeric units were already given by equations (5) and (6) for a specific chain configuration. In these equations

$$U^{(2)}_{\mathrm{m}}=U'U''_{\mathrm{m}} \tag{12}$$

$$U^{(2)}_{\mathrm{r}}=U'U''_{\mathrm{r}} \tag{13}$$

$$g^{(2)}_{\mathrm{m}}=[(U'\otimes E_5)\|g^*\|][(U''_{\mathrm{m}}\otimes E_5)\|g^*\|] \tag{14}$$

$$g^{(2)}_{\mathrm{r}}=[(U'\otimes E_5)\|g\|][(U''_{\mathrm{r}}\otimes E_5)\|g^*\|] \tag{15}$$

$$J^*=(1\ 0\ 0);\qquad J=(1\ 1\ 1)^{\mathrm{T}} \tag{16}$$

$$J_{\mathrm{p}}=(1\ 0\ 0\ 0\ 0);\qquad J_{\mathrm{Q}}=(0\ 0\ 0\ 0\ 1)^T \tag{17}$$

and the bond matrix, $g$, is

$$g=\begin{pmatrix}1 & 2l^{\mathrm{T}}T & l^2\\ 0 & T & l\\ 0 & 0 & 1\end{pmatrix} \tag{18}$$

$$g^*=g(T^*,l) \tag{19}$$

where $E_5$ is the unit matrix of order $5\times 5$ while $T$ and $T^*$ are the transformation matrices associated to the reference frames of two successive Cartesian coordinate systems attached to the bonds[4,11]:

$$T=\begin{pmatrix}\cos\theta & \sin\theta & 0\\ \sin\theta\cos\phi & -\cos\theta\cos\phi & \sin\phi\\ \sin\theta\sin\phi & -\cos\theta\sin\phi & -\cos\phi\end{pmatrix} \tag{20}$$

$$T^*=\begin{pmatrix}\cos\theta & \sin\theta & 0\\ \sin\theta\cos\phi & -\cos\theta\cos\phi & -\sin\phi\\ \sin\theta\sin\phi & -\cos\theta\sin\phi & \cos\phi\end{pmatrix} \tag{21}$$

$\|g\|$ is obtained by placing the $g$ matrices for the various rotational states of skeletal bonds in a diagonal array:

$$\|g\|=\begin{bmatrix}g^{(\mathrm{t})} & & 0\\ & g^{(\mathrm{g})} & \\ 0 & & g^{(\bar{\mathrm{g}})}\end{bmatrix} \tag{22}$$

$g_1$ and $g_n$ are bond matrices of the first and the last bonds along the chain, respectively, with $\phi_1=\phi_n=0$, and $U_1$ and $U_n$ are unit matrices of order $3\times 3$.

*Figure 2* shows the dependence of the characteristic ratio of the mean-square end-to-end distance on period length, $p$, for atactic polypropylene ($P_{\mathrm{m}}=0.5$). It appears that the characteristic ratio calculated from equation (6) is a wave-like curve in the region of short sequences of the periodic microstructure; however, a substantial independence of this conformational characteristic from the period length is achieved already when $p\geqslant 6$. In fair agreement with the results of the Monte Carlo model[4], the characteristic ratio of the mean-square end-to-end distance of the atactic polypropylene chain converges to

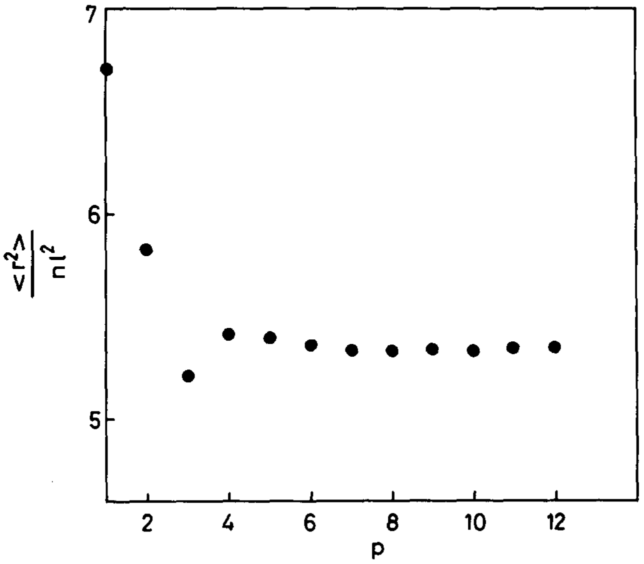

**Figure 2** Dependence of the calculated characteristic ratio of the mean-square end-to-end distance for atactic polypropylene on the number of monomeric dyads in the repeating period

5.34. Here and in the following figures, the results are shown for chains composed of 800 bonds with the set of parameters given in equation (11).

The dependence of the characteristic ratio on the occurrence probability of *meso* dyads, $P_m$, is reported in *Figure 3*. For this calculation we have considered chains with eight monomeric dyads in the repeating period, for which the deviation from the asymptotic limit is negligible. Biskup and Cantow[5] obtained similar results using the Monte Carlo computation method. Through a different approach, our results also substantiate those of Allegra and Brückner[3]: the atactic polymer coil has the most compact chain conformation and the isotactic chains are less expanded than those of the syndiotactic polymer. The present results appear to agree better with some experimental data since the dependence of the characteristic ratio on the fraction of *meso* dyads is less pronounced than that given in reference 3.

The temperature coefficient of the mean-square end-to-end distance, calculated from

$$K = \sum_{i=1}^{2^p} P_i \, \mathrm{d} \ln \langle r^2 \rangle_i / \mathrm{d}T \qquad (23)$$

is reported in *Figure 4*. The value of $K$ obtained here for atactic polypropylene, $-1.34 \times 10^{-3}\,\mathrm{K}^{-1}$, is intermediate to those of Biskup and Cantow[5] and of Allegra and Brückner[3]: $-1.8 \times 10^{-3}$ and $-1.0 \times 10^{-3}\,\mathrm{K}^{-1}$, respectively. It compares quite satisfactorily with the experimental results of Danusso *et al.*[36–38] and Moraglio *et al.*[39].

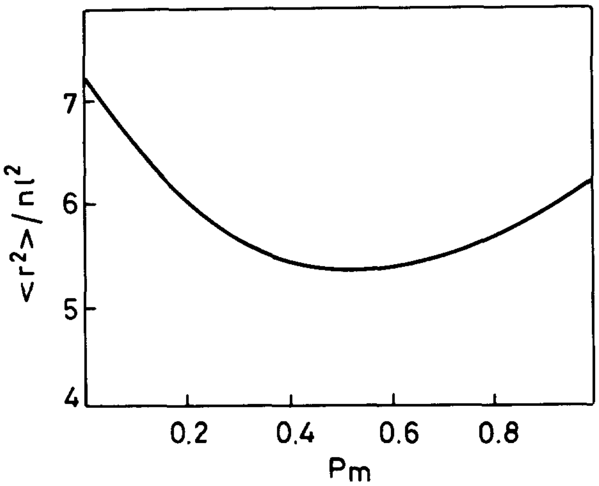

**Figure 3** Characteristic ratio of the mean-square end-to-end distance for polypropylene with Bernoullian statistics as a function of the occurrence probability of *meso* dyads

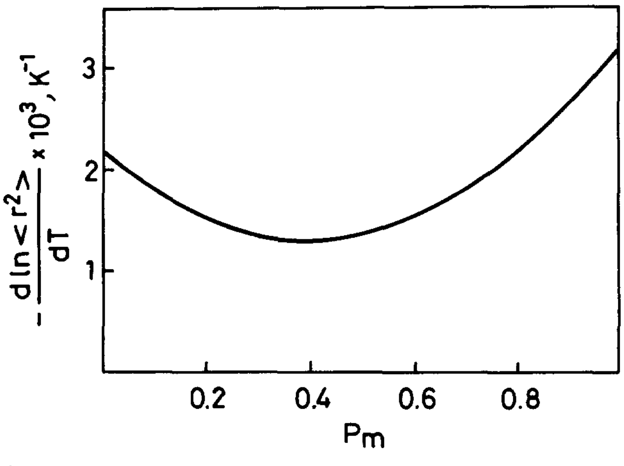

**Figure 4** Temperature coefficient of the characteristic ratio of the mean-square end-to-end distance as a function of occurrence probability of *meso* dyads

The mean-square radius of gyration of polypropylene has received less theoretical interest than the conformational characteristics discussed above. Following our approach and taking into account the effect of the $CH_3$ side groups, it can be shown, after tedious elaboration, that the mean-square radius of gyration of polypropylene chains with the $i$th configuration is given by:

$$\begin{aligned} \langle R_g^2 \rangle_i = 1/M^2 \left[ J^* \left( \prod_{k=1}^{p} U_k^{(2)} \right)_i^{(x-1)/p} J \right]^{-1} \\ \times (J^* \otimes J_{p'}) \Bigg[ \|G_1\| \left( \prod_{k=1}^{p} G_k^{(2)} \right)_i^{(x-1)/p} \|G_n\| \\ + m_b m' \|H_1\| \left( \prod_{k=1}^{p} H_k^{(2)} \right)_i^{(x-1)/p} \|H_n\| \\ + m_a m' \|V_1\| \left( \prod_{k=1}^{p} V_k^{(2)} \right)_i^{(x-1)/p} \|V_n\| \\ + m_b m' \|B_1\| \left( \prod_{k=1}^{p} B_k^{(2)} \right)_i^{(x-1)/p} \|B_n\| \\ + m_a m' \|D_1\| \left( \prod_{k=1}^{p} D_k^{(2)} \right)_i^{(x-1)/p} \|D_n\| \\ + m^{12} \|W_1\| \left( \prod_{k=1}^{p} W_k^{(2)} \right)_i^{(x-1)/p} \|W_n\| \Bigg] (J \otimes J_{Q'}) \end{aligned} \qquad (24)$$

where $M$ is the molecular weight of the chain and $m_a$, $m_b$ and $m'$ denote the masses of CH, $CH_2$ and $CH_3$, respectively. Then, by averaging over all representative chains and taking into account the occurrence probability of the various sequences, the mean-square radius of gyration of an ensemble of chains is obtained:

$$\langle R_g^2 \rangle = \sum_{i=1}^{2^p} P_i \langle R_g^2 \rangle_i \qquad (25)$$

In equation (24), the symbols have the following meanings:

$$J_{p'} = (1\ 0\ 0\ 0\ 0\ 0\ 0); \qquad J_{Q'} = (0\ 0\ 0\ 0\ 0\ 0\ 1)^T \qquad (26)$$

$$\xi_k^{(2)} = \begin{cases} \xi_m^{(2)} & \text{for } \textit{meso} \text{ dyads} \\ \xi_r^{(2)} & \text{for } \textit{racemic} \text{ dyads} \end{cases} \qquad (27)$$

where $\xi = U, G, H, V, B, D$ or $W$

$$\xi_m^{(2)} = [(U' \otimes E_7) \|\xi'_m\|][(U''_m \otimes E_7) \|\xi''_m\|] \qquad (28)$$

$$\xi_r^{(2)} = [(U' \otimes E_7) \|\xi'_r\|][(U''_r \otimes E_7) \|\xi''_r\|] \qquad (29)$$

where $\xi = G, H, V, B, D$ or $W$

$$G'_m = \begin{pmatrix} 1 & m_a J_p g^* & m_a m_b J_p g^* J_Q \\ 0 & g^* & m_b g^* J_Q \\ 0 & 0 & 1 \end{pmatrix} = G(m_a, m_b, g^*) \qquad (30)$$

$$G''_m = G''_r = G(m_b, m_a, g^*) \qquad (31)$$

$$G'_r = G(m_a, m_b, g) \qquad (32)$$

$$H'_m = \begin{pmatrix} 1 & & 0 \\ & g^* & \\ 0 & & 1 \end{pmatrix} = H(g^*) \qquad (33)$$

$$H'_{\mathrm{r}}=H(g) \tag{34}$$

$$H''_{\mathrm{m}}=\begin{pmatrix}1 & J_{\mathrm{p}}g^* & J_{\mathrm{p}}g_\beta g_\gamma J_{\mathrm{Q}}\\ 0 & g^* & g_\beta g_\gamma J_{\mathrm{Q}}\\ 0 & 0 & 1\end{pmatrix}=H''_{\mathrm{r}} \tag{35}$$

$$V'_{\mathrm{m}}=B''_{\mathrm{m}}=B''_{\mathrm{r}}=D''_{\mathrm{m}}=D''_{\mathrm{r}}=W'_{\mathrm{m}}=H'_{\mathrm{m}} \tag{36}$$

$$V'_{\mathrm{r}}=W'_{\mathrm{r}}=H'_{\mathrm{r}} \tag{37}$$

$$V''_{\mathrm{m}}=V''_{\mathrm{r}}=\begin{pmatrix}1 & J_{\mathrm{p}} & l'^2\\ 0 & g^* & g_\beta g_\gamma J_{\mathrm{Q}}\\ 0 & 0 & 1\end{pmatrix} \tag{38}$$

$$B'_{\mathrm{m}}=\begin{pmatrix}1 & J_{\mathrm{p}}g_\alpha g^* & J_{\mathrm{p}}g_\alpha g^* J_{\mathrm{Q}}\\ 0 & g^* & g^* J_{\mathrm{Q}}\\ 0 & 0 & 1\end{pmatrix}=B(g^*) \tag{39}$$

$$B'_{\mathrm{r}}=B(g) \tag{40}$$

$$D'_{\mathrm{m}}=\begin{pmatrix}1 & J_{\mathrm{p}}g_\alpha g^* & 0\\ 0 & g^* & J_{\mathrm{Q}}\\ 0 & 0 & 1\end{pmatrix}=D(g^*) \tag{41}$$

$$D'_{\mathrm{r}}=D(g) \tag{42}$$

$$W''_{\mathrm{m}}=W''_{\mathrm{r}}=\begin{pmatrix}1 & J_{\mathrm{p}}g_\alpha & 0\\ 0 & g^* & g_\beta g_\gamma J_{\mathrm{Q}}\\ 0 & 0 & 1\end{pmatrix} \tag{43}$$

where

$$g_\beta=g(T_\beta, l) \tag{44}$$

$$T_\beta=T^*(\theta', \phi-\varphi) \tag{45}$$

$$g_\alpha=g(T_\alpha, l') \tag{46}$$

$$T_\alpha=-T_\beta^{-1}T^* \tag{47}$$

$$g_\gamma=g(T_\gamma, l') \tag{48}$$

and $\varphi$ is given by

$$\cos\varphi=-\frac{\cos\theta'(1+\cos\theta)}{\sin\theta\sin\theta'} \tag{49}$$

Since only the last three columns of $g_\gamma$ are required, $T_\gamma$ need not be defined. $E_7$ is the unit matrix of order 7 × 7.

$\|\xi\|$ is defined similarly to equation (22), $\xi_1$ and $\xi_n$($\xi=H$, $V$, $B$, $D$, $G$ or $W$) are terminal matrices of $\xi$, i.e. the matrices associated with the first and the last bonds of the chain, respectively.

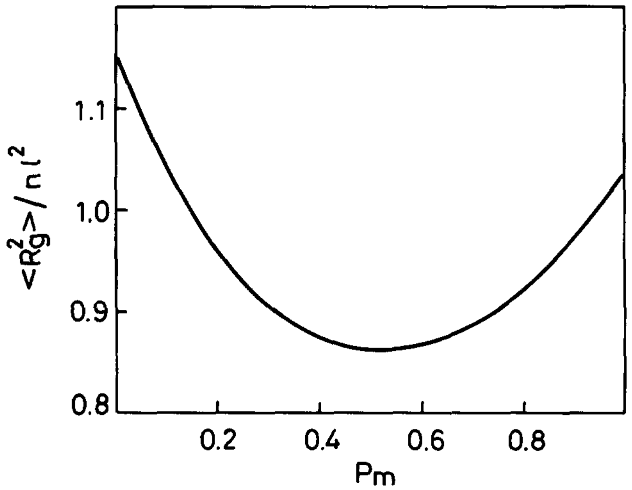

**Figure 5** Characteristic ratio of the mean-square radius of gyration for polypropylene chains with different percentages of *meso* dyads

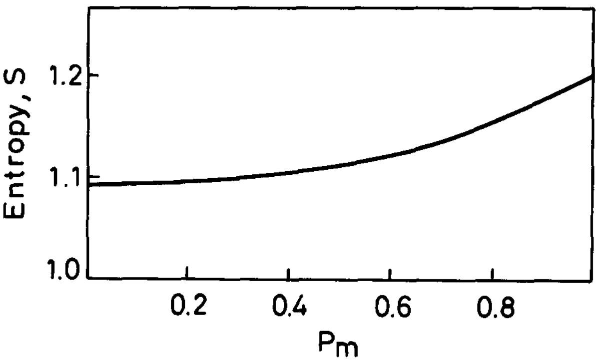

**Figure 6** Entropy of polypropylene chains (in cal K$^{-1}$ mol$^{-1}$ of backbone bonds) as a function of the occurrence probability of *meso* dyads

*Figure 5* shows the relation of the characteristic ratio of the mean-square radius of gyration, $\langle R_g^2\rangle/nl^2$, with the probability of *meso* dyads, $P_{\mathrm{m}}$. The more compact coil is anticipated for the atactic polymer, the syndiotactic one being the most expanded.

Calculation of the molecular weight dependence of the radius of gyration for all possible chain configurations from equations (24) and (25) requires long computing time. We have limited ourselves to the special case of the isotactic polymer ($P_{\mathrm{m}}=1$) and have obtained:

$$\langle R_g^2\rangle^{1/2}=0.34M^{1/2} \tag{50}$$

This theoretical result is in fair agreement with the data obtained by Ballard *et al.*[40] from small-angle neutron scattering experiments.

From the partition function of the $i$th representative chain:

$$Z_i=J^*\left(\prod_{k=1}^{p}U_k^{(2)}\right)^{(x-1)/p}J \tag{51}$$

the entropy of the system can be calculated by considering the contribution of all representative chains as:

$$S=\sum_{i=1}^{2^p}P_iR(\ln Z_i+(T/Z_i)\mathrm{d}Z_i/\mathrm{d}T) \tag{52}$$

The results of our approach are given in *Figure 6*, where the conformational entropy per mole of backbone bonds is plotted as a function of $P_{\mathrm{m}}$. Rather surprisingly, it appears that $S$ is a smoothly increasing function of the content of *meso* dyads in the chain. As a consequence, our model suggests that the isotactic chains are slightly more flexible than the syndiotactic and atactic ones.

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