

Dependence of segmental orientation on polymer conformational characteristics

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The correlation between segmental orientability and unperturbed chain dimensions has been studied. Calculations are carried out by a matrix generation technique based on a two-parameter rotational isomeric state model with interdependent bond rotation. Orientations of vectors along backbone bonds (\mathbf{u}_{\parallel}) and perpendicular to the chain contour (\mathbf{u}_{\perp}) have been considered as a function of first (σ) and second (ω) order interaction parameters along the chain. A linear relationship of the form $D_0 \cong 1.78 \times 10^{-3} \langle r^2 \rangle_0 / nl^2$ for \mathbf{u}_{\parallel} and $D_0 \cong -1.63 \times 10^{-3} \langle r^2 \rangle_0 / nl^2$ for \mathbf{u}_{\perp} is obtained between the orientability of a chain of n bonds of length l , which is expressed through the configurational factor D_0 , and the unperturbed mean-square end-to-end separation, provided that $\sigma \leq 1.8$ or $\omega \geq 0.6$.

(Keywords: polymer chains; segmental orientation; conformational characteristics)

INTRODUCTION

The state of segmental orientation in a uniaxially deformed network is generally approximated by the second Legendre polynomial P_2 , defined as

$$P_2(\alpha) = S = (3 \langle \cos^2 \alpha \rangle - 1)/2 \quad (1)$$

where S is the orientation function, also referred to as the order parameter, and α represents the angle between a segment vector embedded in the network chain and the direction of stretch. The angular brackets denote the ensemble average over all vectors of interest and over all accessible conformations of the chain. S may be related to network parameters and extension ratio by a series expansion^{1–4}, whose leading term reads

$$S = D_0(\lambda^2 - \lambda^{-1}) \quad (2)$$

where D_0 is the 'configurational factor' accounting for the specific conformational characteristics of network chains, and λ is the extension ratio. D_0 represents the orientability of the chain segments with respect to a reference direction. Positive D_0 values refer to preferential alignment along the stretch direction in uniaxial extension, while negative D_0 values indicate a tendency to orient along lateral directions. D_0 scales with n^{-1} , where n is the number of bonds in a network chain. Serial expansions for S including up to terms of order in n^{-3} are explicitly given in previous studies^{1–4}. Yet basic features of segmental orientation in networks are satisfactorily captured by the linearized expression given by equation (2).

The simplest approximation for D_0 is given by the Kuhn model⁵. In this case, the network chains are assumed to be composed of n freely jointed Kuhn

segments, and D_0 equates to $1/(5N)$, where N is the number of Kuhn segments. A more realistic expression^{2,3}, which incorporates the detailed molecular features of the polymer chain in the first-order approximation, is given by

$$D_0 = (3 \langle r^2 \cos^2 \Phi \rangle_0 / \langle r^2 \rangle_0 - 1) / 10 \quad (3)$$

where Φ is the angle between the vector \mathbf{u} , whose orientation is investigated, and the chain end-to-end vector \mathbf{r} . Angular brackets with subscript zero represent averaging over unperturbed free chains. The statistical averages appearing in equation (3) can conveniently be calculated by the matrix generation method of the rotational isomeric state (RIS) scheme². Evaluation of D_0 according to equation (3) for various \mathbf{u} vectors appended to different monomeric units in homopolymers and copolymers have demonstrated the strong dependence of the latter on the specific geometry and conformational characteristics of chain segments^{6–9}.

In this work, the moments $\langle r^2 \cos^2 \Phi \rangle_0$ and $\langle r^2 \rangle_0$ in equation (3) are evaluated by the matrix generation technique² based on the RIS model with special attention to interdependent bond rotation potentials. Contribution of first- and second-order interactions and a relationship between the orientation and the chain mean-square end-to-end length are searched. First- and second-order interactions refer to those taking place between atoms/groups separated by three and four bonds, respectively. In the following section, the application of the RIS scheme to segmental orientation is summarized. Then, results of calculations for chains with widely differing configurational characteristics are presented. Finally, the results are discussed from a general perspective and a concise expression is presented relating D_0 to $\langle r^2 \rangle_0$.

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EVALUATION OF SEGMENTAL ORIENTATION BY THE RIS SCHEME

The moment $\langle r^2 \cos^2 \Phi \rangle_0$ corresponding to a vector \mathbf{u} affixed to the i th unit of a chain is evaluated by the RIS formalism^{6,10} as

$$\langle r^2 \cos^2 \Phi \rangle_0 = \mathbf{F}_1 \left(\prod_{k=2}^{i-1} \mathbf{F}'_k \right) \mathbf{F}_i \left(\prod_{k=i+1}^{n-1} \mathbf{F}'_k \right) \mathbf{F}_n Z^{-1} \quad (4)$$

where Z is the configurational partition function and \mathbf{F}_i is defined as

$$\mathbf{F}_i = (\mathbf{U}_i + \mathbf{E}_{26}) \|\mathbf{F}_i\| \quad (5)$$

Here \mathbf{E}_{26} is identity matrix of order 26. $\|\cdot\|$ denotes the direct product. $\|\mathbf{F}_i\|$ is the matrix composed of diagonal super elements of generator matrices \mathbf{F}_i of states *trans* (t), *gauche*⁻ (g^-) and *gauche*⁺ (g^+) for the backbone bond. \mathbf{F}_i is given by equation (9) of ref. 6, in which \mathbf{m}_i is replaced by \mathbf{u} . \mathbf{F}'_k is obtained by taking $\mathbf{u} = 0$ in the corresponding generator matrix. \mathbf{U}_i is the statistical weight matrix associated with the pair of bonds ($i-1, i$) and is taken to be of the form

$$\mathbf{U}_1 = \text{row}(1, 0, 0) \quad \mathbf{U}_n = \text{col}(1, 1, 1) \quad (6)$$

and

$$\mathbf{U}_2 = \mathbf{U}_{n-1} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \quad (7)$$

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad 2 < i < n-1 \quad (8)$$

where the statistical weight represented by σ refers to first-order interactions when bond i is in either of the two *gauche* states (g^\pm) and ω is the weight for the second-order interaction when bonds $i-1$ and i occupy *gauche* states of opposite signs (g^-g^+). The terminal matrices \mathbf{F}_1 and \mathbf{F}_n in equation (4) are defined as

$$\mathbf{F}_1 = \mathbf{U}_1 \|\mathbf{F}_1\| \quad \mathbf{F}_n = \mathbf{U}_n \|\mathbf{F}_n\| \quad (9)$$

where the subscripts [1 and n] represent the first row and the last column of \mathbf{F} , respectively.

Similarly, the mean-square end-to-end distance $\langle r^2 \rangle_0$ is calculated from

$$\langle r^2 \rangle_0 = Z^{-1} \mathbf{G}_1 \left(\prod_{k=2}^{n-1} \mathbf{G}_k \right) \mathbf{G}_n \quad (10)$$

where

$$\mathbf{G}_k = (\mathbf{U}_k + \mathbf{E}_{26}) \|\mathbf{G}_k\| \quad (11)$$

and $\|\mathbf{G}_k\|$ is the diagonal array of the generator matrices \mathbf{G}_k of states t, g^- and g^+ . The generator matrix \mathbf{G}_k is given in the review by Flory¹⁰.

CALCULATIONS

The model chain is composed of $n = 96$ backbone bonds with the bonds of unit length l . The angle between a given bond on the backbone, and the prolongation of the preceding bond, referred to as the supplemental bond angle, is taken as $\theta = 68^\circ$. Three rotational isomeric

states, t, g^- and g^+ , with respective torsional angles of 0° , 120° , and -120° , are accessible to the backbone bonds. The vector \mathbf{u} , whose orientation is of interest, is taken either (i) along the middle bond of the chain (\mathbf{u}_\parallel) or (ii) perpendicular to the line connecting two successive bonds lying in the plane defined by the two bonds (\mathbf{u}_\perp).

D_0 and $\langle r^2 \rangle_0$ are evaluated as a function of different first- and second-order interaction parameters², namely σ and ω . Calculations have been performed for the ranges $0.1 \leq \sigma \leq 5$ and $0 \leq \omega \leq 5$. Clearly, the ranges $\sigma < 1$ and $\omega < 1$ correspond to repulsive first- and second-order interactions, respectively, while $\sigma > 1$ and $\omega > 1$ refer to attractive interactions. Thus, a variety of conformational preferences is investigated by the present choice of parameters.

In Figure 1 a family of curves, each with fixed ω , is shown as a function of $\langle r^2 \rangle_0$. The first-order interaction parameter σ varies along each curve. The terminal points on the right and left of each curve correspond to $\sigma = 0.2$ and 5.0, respectively. The upper curves are obtained for \mathbf{u}_\parallel . The corresponding positive D_0 values indicate the preferential alignment of \mathbf{u}_\parallel along \mathbf{r} . The lower curves are obtained for \mathbf{u}_\perp . They indicate the tendency of those vectors to orient within a plane whose normal is \mathbf{r} . The curves for $\omega < 0.6$ exhibit both positive and negative slopes for the orientation with respect to $\langle r^2 \rangle_0$, depending on the choice of σ , which means that an increase in $\langle r^2 \rangle_0$ may lead to either a decrease or an increase in segmental orientability. The curves obtained for $\omega = 0.088$ in Figure 1, corresponding to real polyethylene (PE) chains at 140°C , are presented in more detail in Figure 2. Points corresponding to specific values of σ are indicated on the curves. In the range $0.2 \leq \sigma \leq 1.8$, D_0 for \mathbf{u}_\perp exhibits a reduction in absolute value as $\langle r^2 \rangle_0$ is decreased from 940 to 938 \AA^2 . In the range $1.8 < \sigma \leq 2.8$, an increase in chain dimensions is accompanied by a decrease in D_0 . We note that the behaviour in this region conforms with the previous calculations performed by

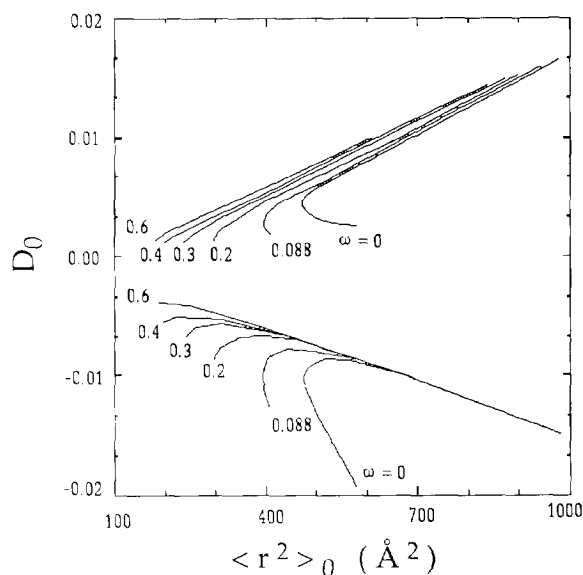


Figure 1 Dependence of configurational factor D_0 on mean-square end-to-end distance $\langle r^2 \rangle_0$. Each curve is obtained for the indicated fixed value of ω with variable σ values ($0.2 \leq \sigma \leq 5$) along the curves, with $n = 96$ and $l = 1 \text{\AA}$. The upper curves are obtained for \mathbf{u}_\parallel and the lower curves are obtained for \mathbf{u}_\perp .

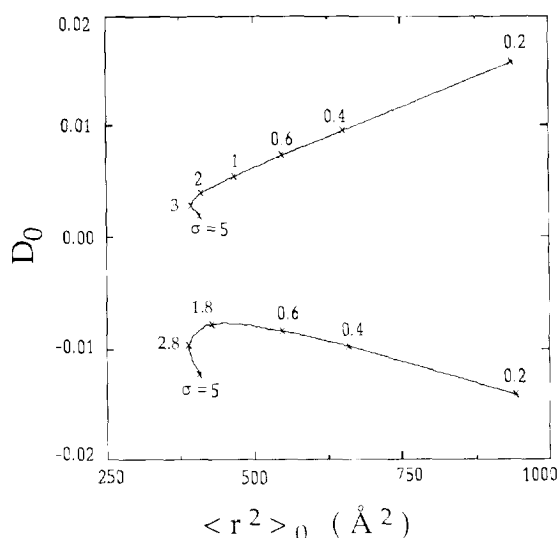


Figure 2 Dependence of D_0 for \mathbf{u} (upper curves) and \mathbf{u}_\perp (lower curves) on $\langle r^2 \rangle_0$ for $\omega = 0.088$, $n = 96$ and $l = 1 \text{ \AA}$. σ values are indicated along the curves ($0.2 \leq \sigma \leq 5$)

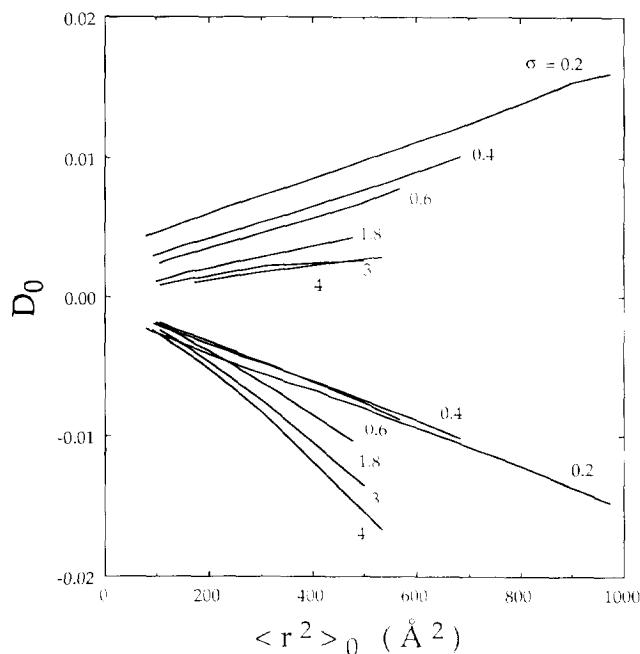


Figure 3 Dependence of D_0 for \mathbf{u} (upper curves) and \mathbf{u}_\perp (lower curves) on $\langle r^2 \rangle_0$. The curves are obtained for identical fixed values of σ , with varying ω ($0 \leq \omega \leq 5$) values (decreasing from left to right) along the curves, using $n = 96$ and $l = 1 \text{ \AA}$

Bahar and Mattice¹¹ for real PE chains, subject to excluded volume effect. If we proceed further along the curve for $\omega = 0.088$, again we reach a region (for $\sigma > 2.8$) where D_0 increases with chain dimensions. Concerning the dependence of D_0 on chain dimensions for \mathbf{u}_\perp , two distinct behaviours are observed with an increase in chain dimensions: (i) an increase in D_0 in the range $\sigma < 3$ and (ii) a decrease in D_0 for $\sigma > 3$.

To explore the influence of second-order interactions, curves in Figure 3 are drawn obtained for fixed σ (as indicated) but varying ω values. In all cases, a positive correlation is observed between orientation and mean-square separation, i.e. the orientability of the chain

segments is enhanced with increasing $\langle r^2 \rangle_0$. Thus, for a given σ , the decrease in chain dimensions induced by favourable second-order interactions always leads to a decrease in the orientability of the chain, i.e. a decrease in the absolute value of D_0 . In general, favourable first-order interactions accompanied by highly repulsive second-order interactions lead to a succession of helical segments comprising a sequence of *gauche* bonds of the same sign. Poly(oxymethylene) (POM), for example, has a strong preference for *gauche* states together with highly unfavourable interactions in $\bar{g}^- \bar{g}^-$ states, and consequently exhibits segments of left-handed or right-handed helices¹². Its average dimensions increase with the probability of *gauche* states. Helical conformation implies stronger orientation for \mathbf{u}_\perp and weaker orientation for \mathbf{u}_\parallel , because of the defined positions of these two vectors on the chain backbone. Comparison of D_0 values in Figure 3 for \mathbf{u}_\parallel and \mathbf{u}_\perp obtained for large σ and low ω values corroborates this behaviour.

DISCUSSION AND CONCLUSION

The calculations of the previous section show that D_0 is strongly affected by the conformational properties of the polymer chain and, in general, is not a monotonic function of the energy parameters σ and ω . In Figure 1, as discussed above, there is either a positive or negative correlation between $\langle r^2 \rangle_0$ and D_0 , depending on the choice of parameters σ and ω . If, on the other hand, attention is confined to the part of the curves obtained for $\sigma \leq 1.8$ with any fixed ω , D_0 and $\langle r^2 \rangle_0$ obey an approximately linear relationship. Likewise, for $\omega \geq 0.6$, the same relationship is valid, irrespective of the magnitude of σ .

Based on this information it is possible to obtain an approximate linear relationship between D_0 and $\langle r^2 \rangle_0$ for \mathbf{u} and \mathbf{u}_\perp provided that the first- and second-order interaction parameters lie within the ranges (i) $\sigma \leq 1.8$ or (ii) $\omega \geq 0.6$. The calculations performed with these parameters may be extended to chains of different size and bond lengths, n and l , by proper rescaling of the proportionality constants, using the fact that $\langle r^2 \rangle_0$ scales with nl^2 for sufficiently long ($n \geq 60$) chains. The resulting configurational factors for segmental orientation are displayed in Figure 4 as a function of $\langle r^2 \rangle_0/nl^2$. The small circles represent the result from calculations. The lines are drawn by least-squares fit through the points. It is interesting to observe that a unique relationship is predicted between the characteristic ratio $\langle r^2 \rangle_0/nl^2$ and the segmental orientation in the uniaxially deformed state as

$$D_0 \cong 1.78 \times 10^{-3} \langle r^2 \rangle_0 / nl^2 \quad \text{for } \mathbf{u}_\parallel \quad (12)$$

$$D_0 \cong -1.63 \times 10^{-3} \langle r^2 \rangle_0 / nl^2 \quad \text{for } \mathbf{u}_\perp \quad (13)$$

Equations (12) and (13) are applicable to all polymer chains whose first- and second-order interaction parameters are within the ranges $\sigma \leq 1.8$ and $\omega \geq 0.6$. Some example polymers are PE^{2,11}, poly(oxymethylene) (POE)², poly(dimethylsiloxane) (PDMS)^{2,13}. In particular, we note that the segmental orientation in model networks of PDMS under uniaxial deformation has been recently measured by Fourier transform infra-red spectroscopy¹⁴, for various chain lengths. For $n = 100$ for example, the

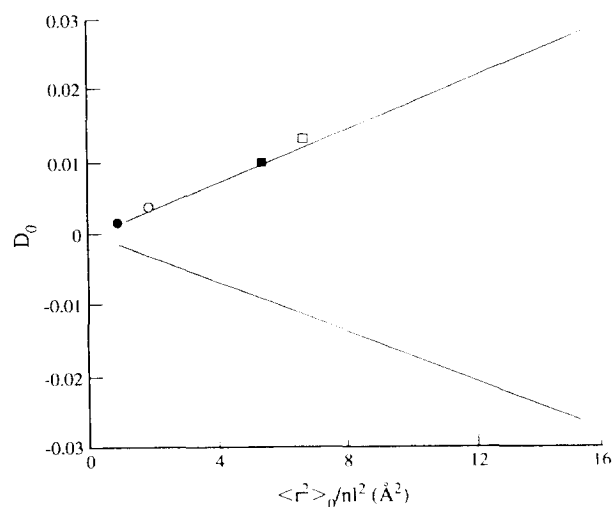


Figure 4 Dependence of D_0 on $\langle r^2 \rangle_0 / nl^2$. The points are obtained for the cases of $\sigma < 1.8$ or $\omega \geq 0.6$. Filled and empty circles represent D_0 values for freely jointed and freely rotating chains, respectively. A polyethylene chain with fixed bond angles and independent bond rotational potential is represented by the filled square. The empty square corresponds to the case of polyethylene

value $D_0 \approx 0.085$ is found from the interpolation of experimental data. Using the parameters $\sigma = 0.6$ and the approximation $\omega = 0.08$ at 20 C of Flory *et al.*¹⁵ for PDMS, Figure 3 yields an estimate of ~ 0.075 , which compares favourably with experimental data.

From equations (12) and (13), we note that the ratio of D_0 for \mathbf{u}_\parallel to that of \mathbf{u}_\perp is ~ -1.09 . In the planar form of the chain, each \mathbf{u}_\perp vector is perpendicular to the chain axis and each \mathbf{u}_\parallel vector makes an angle of 34° with the chain axis. Substituting these values in equation (3) for fixed value of $\langle r^2 \rangle_0$ leads to the ratio of ~ -1.06 for $D_0(\mathbf{u}_\parallel)/D_0(\mathbf{u}_\perp)$. This indicates that the relationship between D_0 and $\langle r^2 \rangle_0$ remains valid up to the limit of the fully extended planar zigzag form.

The quantity $\langle r^2 \cos^2 \Phi \rangle_0$ in equation (3) may be approximated for \mathbf{u}_\perp by the first two terms of a Taylor series expansion² as

$$\langle r^2 \cos^2 \Phi \rangle_0 = \langle r^2 \rangle_0 / 3 + (2/5) \langle r^4 \rangle_0 / nl^2 l^2 \quad (14)$$

Substituting equation (14) in equation (3) and rearranging leads to the approximation

$$D_0 = \left[\frac{3}{25nl^2 l^2} \frac{\langle r^4 \rangle_0}{\langle r^2 \rangle_0} \right] \langle r^2 \rangle_0 \quad (15)$$

Previous calculations of the ratio $\langle r^4 \rangle_0 / \langle r^2 \rangle_0$ appearing in the brackets in equation (15) for various chain models² have shown that for sufficiently long chains this term depends weakly on chain conformational properties and on chain length. In this case, equation (15) may be used for

expressing D_0 of \mathbf{u}_\parallel as an approximately linear function of $\langle r^2 \rangle_0$. For freely jointed chains², $\langle r^2 \rangle_0 = nl^2$ and $\langle r^4 \rangle_0 = (5/3)n^2 l^4$ and equation (15) yields $D_0 = 1/(5n)$. This corresponds to the Kuhn model of segmental orientation and is represented by the filled circle in Figure 4. For a freely rotating chain consisting of n tetrahedrally bonded bonds, $\langle r^2 \rangle_0 = nl^2[(1 + \cos \theta)/(1 - \cos \theta)] \cong 2nl^2$ and $\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2 \cong 1.575$ (ref. 2). If we insert those values in equation (15) for the chain of 100 bonds of unit length each, D_0 equates to ~ 0.004 with corresponding $\langle r^2 \rangle_0 / nl^2$ equating to 1.92 as shown by the large empty circle in Figure 4. For a typical tetrahedral chain subject to independent bond rotations having $\langle r^2 \rangle_0 \cong 6.1nl^2$, the ratio $\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2$ is calculated² as 1.55. Substituting these values in equation (15) leads to $D_0 \cong 0.010$, shown by the filled square in Figure 4. For a polyethylene chain with 100 bonds, $\langle r^2 \rangle_0 / nl^2 \cong 6.87$ and $\langle r^4 \rangle_0 / \langle r^2 \rangle_0^2 \cong 1.52$ (ref. 2). Substituting these values into equation (15) gives D_0 as ~ 0.013 shown by the empty square in Figure 4.

Thus, the present results give us an insight about the orientability of polymer segments under uniaxial deformation, provided that the conformational characteristics of the polymer, expressed by the statistical parameters σ and ω , are known. For sufficiently long chains, the unique relationships expressed by equations (12) and (13) are obtained between segmental orientation and chain dimensions.

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