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Mean Square Dipole Moments in Rotational Isomeric State Chains Containing Atoms That Behave as Hard Spheres

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ABSTRACT: Response of the mean square dipole moment, $\langle \mu^2 \rangle$, to excluded volume has been evaluated for several chains via Monte Carlo methods. In the unperturbed state, configurational statistics are those specified by the usual rotational isomeric state model for linear polymethylene chains. Excluded volume is introduced by requiring chain atoms participating in long-range interactions to behave as hard spheres. Dipole moment vectors are affixed to chain bonds in various patterns. Patterns are found for which $\langle \mu^2 \rangle$ is unaffected by excluded volume. In these cases the long unperturbed chain has $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$, where $\mathbf{r}$ and μ are the end-to-end vector and dipole moment vector, respectively. However, adherence to the condition $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$ does not guarantee that the mean square dipole moment is independent of chain expansion. Patterns are found for which, even though $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$, the perturbed chain has $1 < \alpha_\mu^2 < \alpha_r^2$ or $\alpha_\mu^2 < 1 < \alpha_r^2$. Properties of these latter chains are not in harmony with previous theoretical work (Nagai, K.; Ishikawa, T. *Polym. J.* **1971,** *2,* 416. Doi, M. *Ibid.* **1972,** *3,* 252), which led to the equation $\alpha_\mu^2 - 1 = \langle \mathbf{r}\cdot\mu \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1} (\alpha_r^2 - 1)$. The combination of $\alpha_\mu^2 \neq 1$ and $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$ can be obtained when the dipole moment vector assigned to bond i has a component perpendicular to the planes of bonds i and $i - 1$. The chain giving $\alpha_\mu^2 < 1 < \alpha_r^2$ contains subchains which have a zero dipole moment when fully extended.

The mean square end-to-end distance, $\langle r^2 \rangle$, is well-known to be sensitive to excluded volume. However, the mean square dipole moment, $\langle \mu^2 \rangle$, is often found to be independent of chain expansion. An unambiguous test of insensitivity to perturbation is obtained if $\langle \mu^2 \rangle / n$ is measured as a function of the number, n, of bonds in the chain. The ratio $\langle \mu^2 \rangle / n$ has been shown to attain an asymptotic limit at large n for poly(dimethylsiloxane) in a good solvent.[1] In contrast, $\langle \mu^2 \rangle / n$ has been reported to increase with n for poly(vinyl chloride)[2] and poly(vinyl bromide).[3] The reported inconstancy of $\langle \mu^2 \rangle / n$ might arise if the fractions studied varied in stereochemical structure as well as degree of polymerization.[1,4] Essentially identical $\langle \mu^2 \rangle / n$ were obtained for two samples of poly(vinyl bromide) which differed in molecular weight by nearly a factor of 2, but had the same isotactic content.[5]

Some time ago $\langle \mu^2 \rangle$ was proposed to be insensitive to excluded volume if every repeat unit has a resultant dipole moment vector which lies in a plane bisecting the bond angle at a chain atom.[6-8] Nagai and Ishikawa[9] later employed perturbation theory to obtain the interesting relationship

$$\alpha_\mu^2 - 1 = \langle \mathbf{r}\cdot\mu \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1} (\alpha_r^2 - 1) \qquad (1)$$

The term $\langle \mathbf{r}\cdot\mu \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ is to be evaluated for an infinite chain. Nagai and Ishikawa point out that $\langle \mu^2 \rangle$ is unaffected by excluded volume when $\langle \mathbf{r}\cdot\mu \rangle_0$ is zero. They further describe symmetry conditions (symmetry planes, twofold symmetry axes, and symmetry points) which, when present in the all-trans configuration, lead to $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$. Additionally, they call attention to the prediction that chains for which $\langle \mathbf{r}\cdot\mu \rangle_0$ is nonzero will have $\alpha_\mu^2 > 1$ if $\alpha_r^2 > 1$. The situation $\alpha_\mu^2 < 1 < \alpha_r^2$ is forbidden because $\langle \mathbf{r}\cdot\mu \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ cannot be negative. Doi[10] argues that, for infinite chains, eq 1 is valid for any order of perturbation and any type of interaction, provided $\langle \mu^2 \rangle$ is not independent of n.

The current paper examines adherence to eq 1 for several model chains. While recognizing that the reader may have minimal interest in the dipole moment of polyethylene, we have nevertheless adopted a rotational isomeric state model[11,12] of this polymer for the configurational statistics of the unperturbed chain. By so doing we employ a realistic chain model which has well-known unperturbed properties. Dipole moment vectors are affixed to chain bonds in various patterns. Excluded volume is introduced by requiring chain atoms participating in long-range interactions to behave as hard spheres. As might be expected, circumstances are found where $\alpha_r^2 > 1$, $\langle \mathbf{r}\cdot\mu \rangle_0 = 0$, and $\alpha_\mu^2 = 1$. There are also chains for which $\alpha_\mu^2 = \alpha_r^2$, the factor $\langle \mathbf{r}\cdot\mu \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ being unity in such cases. However, a pattern for the dipole moment vectors is found for which $1 < \alpha_\mu^2 < \alpha_r^2$, even though $\langle \mathbf{r}\cdot\mu \rangle_0$ is zero. Furthermore, another pattern has $\alpha_\mu^2 < 1 < \alpha_r^2$, $\langle \mathbf{r}\cdot\mu \rangle_0$ being zero in this case also. While the chains were not designed to model any particular real polymer, they define some circumstances under which $\alpha_\mu^2 < 1 < \alpha_r^2$ can be expected with real chains.

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Calculations

Unperturbed Properties. Generator matrix methods[12] were used to compute average properties for unperturbed chains. The configuration partition function, Z, for a chain with a symmetric threefold rotation potential and consequential second-order interactions is written as

$$Z = \mathbf{J}^*\mathbf{U}_2...\mathbf{U}_{n-1}\mathbf{J} \tag{2}$$

where $\mathbf{J}^*$ = row (1, 0, 0), $\mathbf{J}$ = col (1, 1, 1), and the statistical weight matrix for bond i is

$$\mathrm{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix}_i \tag{3}$$

Columns and rows index states of bond i and $i - 1$, respectively, the order of indexing being trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$). Calculations reported here employ $\sigma = 0.43$ and $\omega = 0.034$, which are the weights expected for an unperturbed polymethylene chain at 300 K.[11]

Let $\mathbf{V}$ denote the vector sum of individual vectors, $\mathbf{v}_i$, affixed to each bond in the chain. The unperturbed mean square of its length is[12]

$$\langle V^2\rangle_0 = Z^{-1}\mathbf{G}_{[}\mathbf{G}_2...\mathbf{G}_{n-1}\mathbf{G}_{]} \tag{4}$$

where the $\mathbf{G}_i$ are 15 × 15 matrices in which each element of $\mathbf{U}_i$ is expanded through multiplication by

$$\mathrm{F}_\eta = \begin{bmatrix} 1 & 2\mathrm{v}^{\mathrm{T}}\mathrm{T}_\eta & v^2 \\ 0 & \mathrm{T}_\eta & \mathrm{v} \\ 0 & 0 & 1 \end{bmatrix} \tag{5}$$

Terminal matrices, denoted by $\mathbf{G}_{[}$ and $\mathbf{G}_{]}$, are a row and column, respectively, of 15 elements[12] and **0** denotes a rectangular null matrix. The transformation matrix for rotational state η, $\mathbf{T}_\eta$, is formulated by using a bond angle supplement of 68° and dihedral angles of 0, 120, and −120°, respectively, for t, g$^+$, and g$^-$.[11] The mean square unperturbed end-to-end distance is obtained when $\mathbf{v}_i$ = col (l_i, 0, 0), with l_i being the length of bond i. Similarly, the unperturbed mean square dipole moment is obtained if $\mathbf{v}_i = \mathbf{m}_i$, where $\mathbf{m}_i$ denotes the dipole moment vector for unit i. The unperturbed mean dot product of the end-to-end and dipole moment vector is obtained as[9]

$$\langle \mathbf{r}\cdot\mu\rangle_0 = (1/2)\{2\langle(\mathbf{r} + \mu)\cdot(\mathbf{r} + \mu)\rangle_0 - \langle r^2\rangle_0 - \langle\mu^2\rangle_0\} \tag{6}$$

with $\langle(\mathbf{r} + \mu)\cdot(\mathbf{r} + \mu)\rangle_0$ from eq 4 using $\mathbf{v}_i = \mathbf{l}_i + \mathbf{m}_i$.

A more compact formulation, in which $\mathbf{U}_i$ and $\mathbf{G}_i$ are of dimensions 2 × 2 and 10 × 10, respectively, can be used to compute Z and $\langle r^2\rangle_0$.[12] It can also be used for $\langle\mu^2\rangle_0$ and $\langle(\mathbf{r} + \mu)\cdot(\mathbf{r} + \mu)\rangle_0$ if the third element in $\mathbf{m}_i$ is null.

Perturbed Chains. Samples of representative chains were generated by using a priori and conditional probabilities specified by Z.[12] The first-order a priori probability that bond i is in state η is

$$p_{\eta;i} = Z^{-1}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_{i-1}\mathbf{U}_{\eta;i}'\mathbf{U}_{i+1}...\mathbf{U}_{n-1}\mathbf{J} \tag{7}$$

where $\mathbf{U}_{\eta;i}'$ differs from $\mathbf{U}_i$ in that all elements are rendered null except those in the column whose index is η. Similarly, the second-order a priori probability that bonds $i - 1$ and i are in states ξ and η, respectively, is

$$p_{\xi\eta;i} = Z^{-1}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_{i-1}\mathbf{U}_{\xi\eta;i}'\mathbf{U}_{i+1}...\mathbf{U}_{n-1}\mathbf{J} \tag{8}$$

where $\mathbf{U}_{\xi\eta;i}'$ is obtained by nulling all elements in $\mathbf{U}_i$ except $\mathbf{u}_{\xi\eta}$. The conditional probability that bond i is in state η, given that bond $i - 1$ is in state ξ, is

$$q_{\xi\eta;i} = p_{\xi\eta;i}/p_{\xi;i-1} \tag{9}$$

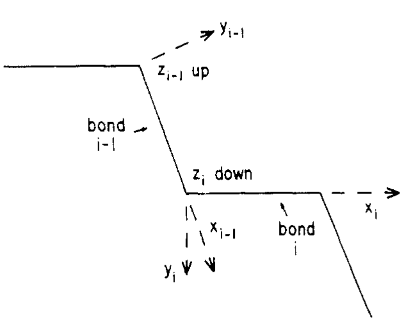

Figure 1. Local coordinate system used to express $\mathbf{m}_i$.

Table I
Initial Slope of C_n/C_∞ vs. $1/n$

		initial slope	
C	$\mathbf{m}_i$	$\mathbf{m}_i = \mathbf{m}_{i-1}$	$\mathbf{m}_i = -\mathbf{m}_{i-1}$
C_r	not used	−6	−6
C_μ	col (1, 0, 0)	−6	−0.4
$C_{r\cdot\mu}$	col (1, 0, 0)	−6	*a*
C_μ	col (0, 1, 0)	−5	−0.6
$C_{r\cdot\mu}$	col (0, 1, 0)	−6	*a*
C_μ	col (0, 0, 1)	−0.3	1
$C_{r\cdot\mu}$	col (0, 0, 1)	*a*	*a*

[a] $C_{r\cdot\mu,n}$ is zero for large chains.

Two independent sets of unperturbed chains were grown at each n of interest using $p_{\eta;2}$ and the $q_{\xi\eta;i}$, $2 < i < n$.

Chains are perturbed by invoking long-range interactions in which interacting atoms behave as hard spheres.[13,14] Long-range interactions are defined as interactions of all chain atoms separated by at least 8 bonds. Perturbed ensembles contain only those chains for which all atoms participating in long-range interactions are separated by at least the distance r^*. The squared length of $\mathbf{V}$ was averaged over all surviving chains in each set. Results are reported as $X(x)$, where x is the range for the last digit in X if results for two independently grown representative samples are in the range $X \pm x$.

Unperturbed Chains

The characteristic ratio formulated from the mean square unperturbed end-to-end distance, denoted here as $C_{r,n}$, is $\langle r^2\rangle_0/n$ when l_i is of unit length. The asymptotic limit, 7.97, was obtained by linear extrapolation of $C_{r,n}$ vs. $1/n$ to $1/n = 0$. As expected,[11] $C_{r,n}$ is smaller than $C_{r,\infty}$. A measure of the chain length dependence is provided by the initial slope, $[\partial(C_{r,n}/C_{r,\infty})/\partial(1/n)]_{1/n\to0}$. The numerical value of the initial slope is presented in Table I.

Three types of simple chains, in which $\mathbf{m}_i$ is the same for all i, were considered. The $\mathbf{m}_i$ used were col (1, 0, 0), col (0, 1, 0), and col (0, 0, 1), with each $\mathbf{m}_i$ expressed in the coordinate system established for bond i in Figure 1.[11,12] Characteristic ratios, $C_{\mu,n}$, were formulated as $\langle\mu^2\rangle_0/n$. Of course, $C_{\mu,n} = C_{r,n}$ if $\mathbf{m}_i$ = col (1, 0, 0). The initial slope of $C_{\mu,n}/C_{\mu,\infty}$ vs. $1/n$ is nearly zero when $\mathbf{m}_i$ = col (0, 0, 1). If $\mathbf{m}_i$ = col (0, 1, 0), the initial slope of $C_{\mu,n}/C_{\mu,\infty}$ is nearly as negative as the initial slope of $C_{r,n}/C_{r,\infty}$. Three cases were also examined in which $\mathbf{m}_i$ alternates in sign, i.e., $\mathbf{m}_i = -\mathbf{m}_{i-1}$, throughout the chain. The initial slope is nearly zero if $\mathbf{m}_i$ = col (1, 0, 0) or col (0, 1, 0). It is small and positive when $\mathbf{m}_i$ = col (0, 0, 1).

One choice for $\mathbf{m}_i$, col (0, 0, 1), is not readily compatible with the form adopted for $\mathbf{U}_i$. Chains with a symmetric rotation potential would be expected to have $\mathbf{m}_i$ given by col (x, y, 0). Simultaneous use of the present form for $\mathbf{U}_i$ and a nonzero component along the third axis of $\mathbf{m}_i$ would be possible only for a chain in which dipole–dipole inter-

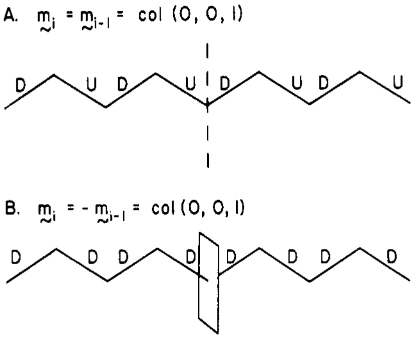

Figure 2. Twofold symmetry axis (A) and symmetry plane (B) in the all-trans configuration. Bond dipole moment vectors are oriented up (U) or down (D).

actions either make a negligible contribution to the total rotation potential or have their contribution counterbalanced by some other type of interaction. The form for $\mathbf{U}_i$ will not be modified to accommodate an asymmetry in the rotation potential because hypothetical chains will suffice to bring out the features of current interest.

Values of $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0$ are obtained via eq 6. Characteristic ratios, $C_{\mathbf{r}\cdot\mu,n}$, are defined as $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 / n$. These characteristic ratios were evaluated for the six cases defined above in the discussion of $C_{\mu,n}$. The value of $C_{\mathbf{r}\cdot\mu,n}$ is found to be zero when $\mathbf{m}_i = \text{col } (0, 0, 1)$ for all i. It is also zero for the three cases in which $\mathbf{m}_i = -\mathbf{m}_{i-1}$. Initial slopes of $C_{\mathbf{r}\cdot\mu,n}/C_{\mathbf{r}\cdot\mu,\infty}$ for the remaining two cases are collected in Table I.

Of all the initial slopes presented in Table I, the ones largest in absolute value are those obtained with the simple chain in which $\mathbf{v}_i$ is of the form col $(x, 0, 0)$ for all i. Thus all of the averages of current interest converge to their asymptotic limits as fast as, or faster than, the characteristic ratio of the unperturbed end-to-end distance.

The ratio $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ must be one at all n if $\mathbf{m}_i = \text{col } (1, 0, 0)$. It becomes one at infinite n if $\mathbf{m}_i = \text{col } (0, 1, 0)$. With this $\mathbf{m}_i$, the ratio departs from its limiting value by about 1% when n is 50. For these two cases, α_μ^2 and α_r^2 are predicted to be identical. The prediction for $\mathbf{m}_i = \text{col } (1, 0, 0)$ must be correct for the trivial reason that $\mathbf{r}$ and $\boldsymbol{\mu}$ are identical for every chain configuration. With the remaining four cases, $\mathbf{m}_i = \text{col } (0, 0, 1)$ and the three in which $\mathbf{m}_i = -\mathbf{m}_{i-1}$, $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0$ is zero for any n of current interest. The three chains with $\mathbf{m}_i = -\mathbf{m}_{i-1}$ have the symmetry plane described by Nagai and Ishikawa.[9] The twofold symmetry axis is found in the chain with $\mathbf{m}_i = \text{col } (0, 0, 1)$ as well as the two chains with $\mathbf{m}_i = -\mathbf{m}_{i-1} = \text{col } (1, 0, 0)$ or col $(0, 1, 0)$. Examples of the symmetry plane and twofold symmetry axis are depicted in Figure 2. Equation 1 predicts the mean square dipole moment is unaffected by chain expansion when $\mathbf{m}_i = \text{col } (0, 0, 1)$ and in the three cases where $\mathbf{m}_i = -\mathbf{m}_{i-1}$.

Expansion Factors for Perturbed Chains

Expansion factors for ensembles of chains in which atoms participating in long-range interactions behave as hard spheres of diameter r^* are presented in Tables II and III. Table II contains results obotained when every bond has the same $\mathbf{m}_i$. If $\mathbf{m}_i = \text{col } (0, 1, 0)$, α_μ^2 and α_r^2 are indistinguishable at all n and r^* examined. The Monte Carlo result is in harmony with eq 1, because $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ is one at large n when $\mathbf{m}_i = \text{col } (0, 1, 0)$.

Table II
Expansion Factors for Chains with the Same $\mathbf{m}_i$ for All i

n	r^*/l	α_r^2	α_μ^2 for indicated $\mathbf{m}_i$	
			col (0, 1, 0)	col (0, 0, 1)
100	2.4	1.198 (2)	1.198 (2)	0.912 (3)
	2.7	1.224 (1)	1.224 (1)	0.898 (6)
	3.0	1.264 (2)	1.264 (1)	0.880 (12)
200	2.4	1.324 (6)	1.318 (2)	0.896 (5)
	2.7	1.372 (9)	1.372 (10)	0.884 (9)
	3.0	1.451 (8)	1.452 (11)	0.860 (9)
300	2.4	1.405 (7)	1.407 (7)	0.870 (4)
	2.7	1.454 (17)	1.456 (16)	0.857 (5)
	3.0	1.488 (6)	1.488 (11)	0.846 (14)
400	2.4	1.505 (1)		0.868 (7)
	2.7	1.548 (3)		0.838 (2)
	3.0	1.630 (21)		0.822 (2)

Table III
Expansion Factors When $\mathbf{m}_i = -\mathbf{m}_{i-1}$

n	r^*/l	α_r^2	α_μ^2 for indicated $\mathbf{m}_i$		
			col (1, 0, 0)	col (0, 1, 0)	col (0, 0, 1)
100	2.4	1.198 (2)	1.010 (2)	1.010 (2)	1.030 (2)
	2.7	1.224 (1)	1.011 (2)	1.010 (2)	1.031 (2)
	3.0	1.264 (2)	1.020 (1)	1.020 (1)	1.040 (4)
200	2.4	1.324 (6)	1.010 (14)	1.013 (13)	1.066 (14)
	2.7	1.372 (9)	1.013 (14)	1.015 (14)	1.072 (13)
	3.0	1.451 (8)	1.017 (34)	1.018 (35)	1.089 (30)
300	2.4	1.405 (7)	0.996 (2)	0.994 (1)	1.076 (9)
	2.7	1.454 (17)	1.006 (16)	1.004 (13)	1.102 (17)
	3.0	1.488 (6)	0.974 (50)	0.974 (52)	1.102 (23)
400	2.4	1.505 (1)			1.054 (11)
	2.7	1.548 (3)			1.059 (16)
	3.0	1.630 (21)			1.140 (75)

A markedly different result is obtained with $\mathbf{m}_i = \text{col } (0, 0, 1)$. Here $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0$ is zero, which would require $\alpha_\mu^2 = 1$ at all α_r^2 if expansion factors were to follow the behavior predicted by eq 1. Instead Monte Carlo results show $\langle \mu^2 \rangle$ is affected by the perturbation. Furthermore, the perturbation produces $\alpha_\mu^2 < 1$ for expanded chains. The combination $\alpha_\mu^2 < 1$ and $\alpha_r^2 > 1$ is completely incompatible with eq 1 because $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0^2 (\langle r^2 \rangle_0 \langle \mu^2 \rangle_0)^{-1}$ cannot be negative.

The difficulty with α_μ^2 when $\mathbf{m}_i = \text{col } (0, 0, 1)$ is not easily avoided by suggesting behavior compatible with eq 1 might be recovered at much larger n. For the range of n covered in Table II, α_μ^2 decreases continuously with n. The Monte Carlo results therefore provide no basis for assuming α_μ^2 might approach unit as n becomes infinite. The prediction embodied in eq 1 is realized for chains with as few as 100 bonds when $\mathbf{m}_i = \text{col } (0, 1, 0)$. Results collected in Table I show $C_{\mu,n}$ and $C_{\mathbf{r}\cdot\mu,n}$ approach their asymptotic limits much faster when $\mathbf{m}_i = \text{col } (0, 0, 1)$ than they do when $\mathbf{m}_i = \text{col } (0, 1, 0)$. The behavior of the unperturbed chain therefore does not suggest a significantly larger number of bonds would be required to reach limiting behavior when $\mathbf{m}_i = \text{col } (0, 0, 1)$ than is required when $\mathbf{m}_i = \text{col } (0, 1, 0)$.

Table III collects α_μ^2 for chains in which $\mathbf{m}_i = -\mathbf{m}_{i-1}$. According to eq 1, $\langle \mu^2 \rangle$ should be unaffected by the perturbation because $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0$ is zero for the three types of chains considered. This prediction is realized at $n = 300$ for the two cases where $\mathbf{m}_i = -\mathbf{m}_{i-1}$ is either col $(1, 0, 0)$ or col $(0, 1, 0)$. Different behavior is seen when $\mathbf{m}_i = -\mathbf{m}_{i-1} = \text{col } (0, 0, 1)$. For this chain, $1 < \alpha_\mu^2 < \alpha_r^2$. Equation 1 is in harmony with the Monte Carlo results if the third element in $\mathbf{m}_i$ is null. Disagreement between eq 1 and Monte Carlo results is seen if the last element in $\mathbf{m}_i$ is nonzero.

Distribution Functions

Figure 3 depicts end-to-end distance distribution functions computed from 15 000 representative chains con-

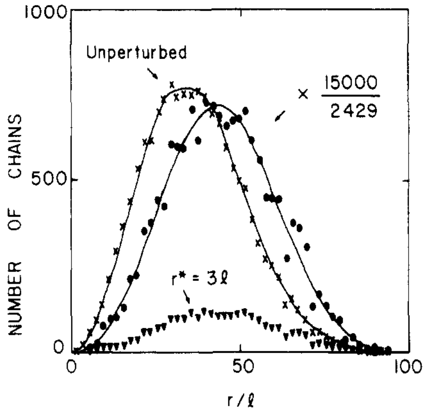

Figure 3. End-to-end distances for chains of 200 bonds when unperturbed (×) and perturbed using $r^* = 3l$ (triangles). Unperturbed and perturbed distribution functions are based on 15000 and 2429, respectively, representative chains. Chains are collected in groups of breadth $2l$. Solid circles depict points obtained when the triangles are multiplied by 15000/2429.

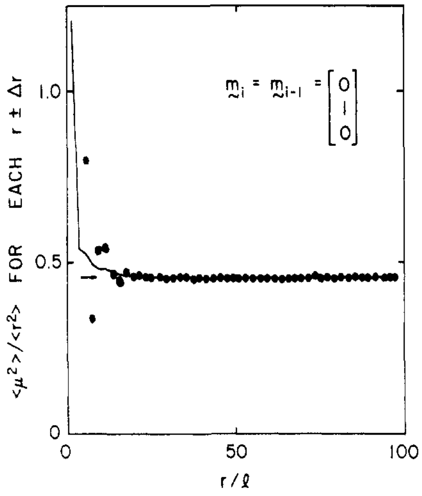

Figure 4. Ratio of the mean square dipole moment, evaluated by using $\mathbf{m}_i$ = col (0, 1, 0), to the mean square end-to-end distance for chains of 200 bonds. Averaging takes place over chains in the interval $r/l \pm l$. The solid line depicts the distribution obtained with 15000 unperturbed chains, while filled circles depict the distribution for 2429 perturbed chains ($r^* = 3l$). The horizontal arrow denotes $\langle\mu^2\rangle_0/\langle r^2\rangle_0$ for the entire ensemble.

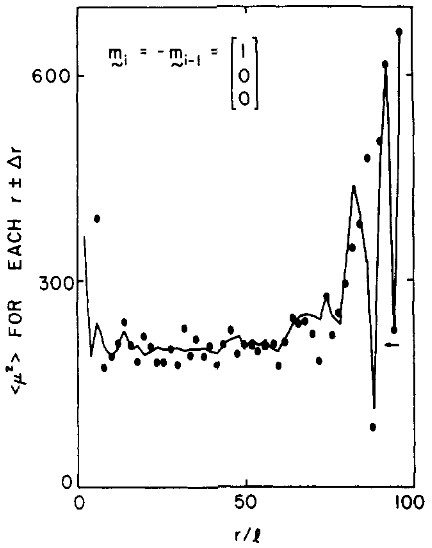

Figure 5. Distribution for $\langle\mu^2\rangle$ for chains of 200 bonds, using $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (1, 0, 0). Averaging takes place over chains in the interval $r/l \pm l$. The solid line depicts the distribution obtained with 15000 unperturbed chains, and filled circles depict the distribution for 2429 perturbed chains ($r^* = 3l$). The horizontal arrow denotes $\langle\mu^2\rangle_0$ for the entire ensemble.

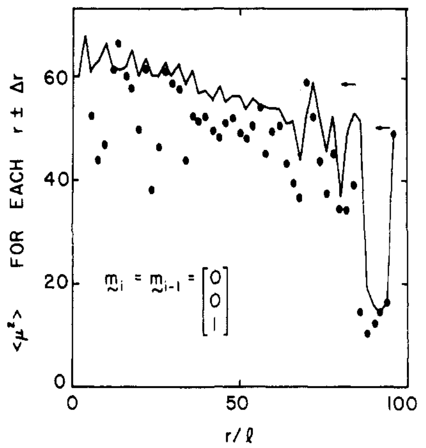

Figure 6. Distribution for $\langle\mu^2\rangle$ for chains of 200 bonds, using $\mathbf{m}_i$ = col (0, 0, 1). Averaging takes place over chains in the interval $r/l \pm l$. The solid line depicts the distribution obtained with 15000 unperturbed chains, and filled circles depict the distribution for 2429 perturbed chains ($r^* = 3l$). Upper and lower horizontal arrows denote $\langle\mu^2\rangle_0$ and $\langle\mu^2\rangle$, respectively, averaging taking place over all chains in the appropriate sample.

taining 200 bonds. Chains are assigned to groups of width $2l$. The distribution function for the unperturbed chain exhibits a maximum near $r/l = 35$. No chains have r/l greater than 96. Only 2429 chains survive when $r^* = 3l$. As shown in Table II, α_r^2 is then 1.45. The distribution function for the surviving chains is depicted by triangles in Figure 3. When normalized to the same value, distribution functions for perturbed and unperturbed chains cross when r/l is near 40. Chains with shorter end-to-end distances become less prevalent when excluded volume interactions are introduced.

Figures 4–7 depict distribution functions for the mean square dipole moment for chains described in Figure 3. Different bond dipole moment vectors are employed in each figure. The bond dipole moment vector is col (0, 1, 0) in Figure 4. Only at very small end-to-end distances does $\langle\mu^2\rangle_0/\langle r^2\rangle_0$ differ significantly from the ensemble average. Such compact chains make only a small contribution to the configuration partition function. Figure 4 shows $\langle\mu^2\rangle_0/\langle r^2\rangle_0$ is unaffected upon going from the unconstrained chain to chains in which r is fixed (but the chain is otherwise unperturbed) provided the end-to-end distance chosen is larger than $15r/l$. The distribution for the 2429 surviving perturbed chains from Figure 3 is distinguishable from the unperturbed distribution only for rare compact chain configurations. Excluded volume interactions do not modify $\langle\mu^2\rangle/r^2$ if r/l is fixed at a value larger than 15. Expanded chains therefore have $\alpha_\mu^2 = \alpha_r^2$ when $\mathbf{m}_i$ = col (0, 1, 0). This result is in harmony with eq 1, because $\langle \mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2(\langle r^2\rangle_0\langle\mu^2\rangle_0)^{-1} = 1$ for large chains.

Figure 5 depicts distributions for $\langle\mu^2\rangle$ when $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (1, 0, 0). Figure 3 shows the major contribution to the unperturbed configuration partition function is made by chains with end-to-end distances lying between $10r/l$ and $60r/l$. For chains with r lying in this range, $\langle\mu^2\rangle_0$ in Figure 5 shows no trend with changes in dimensions. Scatter becomes much more severe in the wings, where only a small number of chains are available for averaging. Perturbation of the chains using $r^* = 3l$ also increases the scatter because the number of chains in the sample has been reduced by a factor of 6. However, there is no suggestion that perturbation has altered $\langle\mu^2\rangle$ for chains of specified r. Consequently chain expansion does not affect

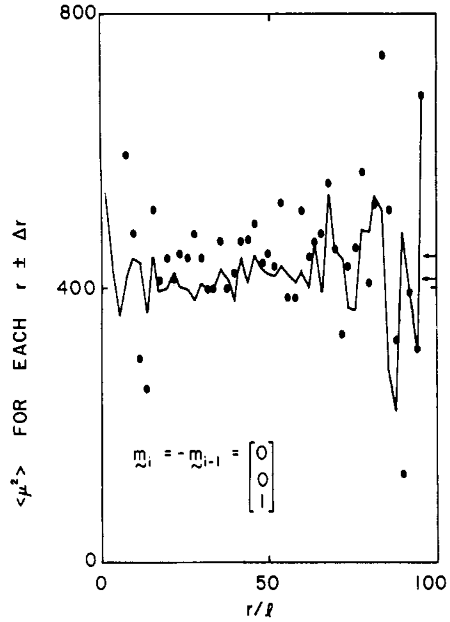

Figure 7. Distribution for $\langle \mu^2 \rangle$ for chains of 200 bonds, using $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (0, 0, 1). Averaging takes place over chains in the interval $r/l \pm l$. The solid line depicts the distribution obtained with 15 000 unperturbed chains, and filled circles depict the distribution for 2429 perturbed chains ($r^* = 3l$). Upper and lower horizontal arrows denote $\langle \mu^2 \rangle$ and $\langle \mu^2 \rangle_0$, respectively, averaging taking place over all chains in the appropriate sample.

$\langle \mu^2 \rangle$. This result is in harmony with eq 1, because $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0$ is zero. Similar results (not shown) are obtained for the distribution when $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (0, 1, 0).

Figure 6 depicts distribution functions for $\langle \mu^2 \rangle$ when $\mathbf{m}_i$ = col (0, 0, 1). Now $\langle \mu^2 \rangle_0$ exhibits a definite downward trend as the end-to-end distance rises above $15r/l$. Perturbation of chains at constant r brings about a further decrease in the mean square dipole moment. The decline in $\langle \mu^2 \rangle_0$ with r and the effect of excluded volume at constant r both contribute to $\alpha_\mu^2 < 1$ for expanded chains. The relative importance of the two effects was assessed by computing an ensemble average for $\langle \mu^2 \rangle$ using the perturbed end-to-end distance distribution function from Figure 3 in conjunction with the unperturbed $\langle \mu^2 \rangle$ distribution in Figure 6. This trial calculation yields the value expected for $\langle \mu^2 \rangle$ if the probability of a chain being rejected upon introduction of excluded volume is a function of its end-to-end distance but independent of its dipole moment. The result of this calculation is $\alpha_\mu^2 = 0.97$. When the calculation is performed with the perturbed dipole moments (filled circles in Figure 6), α_μ^2 drops to 0.86. Therefore the major cause of $\alpha_\mu^2 < 1$ is that configurations with small μ^2 are better able to survive when excluded volume is introduced into chains of specified r. In terms of Figure 6, greater importance is to be placed on the circles tending to fall below the solid line at specified r than on the trends seen with changes in r. The fully extended configuration has the twofold symmetry axis depicted in Figure 2A, and generator matrix calculations verify $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 = 0$. Nevertheless, $\alpha_\mu^2 < 1 < \alpha_r^2$ when the chain expands. Behavior of this chain is completely incompatible with eq 1.

Figure 7 depicts the distribution for $\langle \mu^2 \rangle$ when $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (0, 0, 1). There is now a definite tendency for the filled circles to lie above the solid line. In contrast to the results seen in Figure 6, configurations with large μ^2 are now better able to survive when excluded volume is introduced into chains of specified r. For this reason, $\alpha_\mu^2 > 1$ for expanded chains. The fully extended configuration has the symmetry plane depicted in Figure 2B, and generator matrix calculations verify $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 = 0$. Nevertheless, $1 < \alpha_\mu^2 < \alpha_r^2$ when the chain expands. This result is not in agreement with eq 1.

Table IV
Selected Expansion Factors When $\mathbf{m}_i$ Has Multiple Nonzero Components

			α_μ^2 at indicated r^*/l		
$\mathbf{m}_i$	$\mathbf{m}_{i-1}$	n	2.4	2.7	3.0
col (1, 1, 0)	col (−1, −1, 0)	100	1.006 (2)	1.008 (1)	1.016 (2)
		200	1.008 (16)	1.010 (16)	1.012 (22)
col (1, 1, 1)	col (−1, −1, −1)	100	1.028 (1)	1.028 (0)	1.038 (1)
		200	1.055 (3)	1.062 (5)	1.082 (8)
col (1, 1, 1)	col (−1, −1, 1)	100	0.956 (11)	0.949 (12)	0.944 (14)
		200	0.948 (2)	0.937 (5)	0.912 (13)

Implications for Real Polymers

A qualitative explanation for the behavior of the chain with $\mathbf{m}_i$ = col (0, 0, 1) is obtained with the aid of Figure 2A. A fully extended subchain has a squared dipole moment of m^2 or zero, depending on whether the number of bonds is odd or even. Consequently $\langle \mu^2 \rangle_0$ is expected to be small for highly extended chains, as seen in Figure 6. If the presence of fully extended subchains enhances the probability that a configuration will survive the introduction of excluded volume into chains of specified r, then $\langle \mu^2 \rangle$ should be smaller than $\langle \mu^2 \rangle_0$ at that r. This effect is also seen in Figure 6. It is of greater importance than the trends seen upon changes in r. These qualitative considerations suffice to rationalize $\alpha_\mu^2 < 1 < \alpha_r^2$, eq 1 notwithstanding.

Table IV presents α_μ^2 for selected chains in which two or three components of $\mathbf{m}_i$ are nonzero. Qualitative behavior is that expected from the results presented in Tables II and III. If $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (1, 1, 0) α_μ^2 is indistinguishable from one when the chain contains 200 bonds. Addition of an alternating z component, $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (1, 1, 1), causes $1 < \alpha_\mu^2 < \alpha_r^2$, with the α_μ^2 being not quite as large as in the chain having $\mathbf{m}_i = -\mathbf{m}_{i-1}$ = col (0, 0, 1) (Table III). If the z components are all of the same sign, i.e., if $\mathbf{m}_i$ = col (1, 1, 1) and $\mathbf{m}_{i-1}$ = col (−1, −1, 1), the result is $\alpha_\mu^2 < 1 < \alpha_r^2$. The α_μ^2 are somewhat closer to one than was the case when $\mathbf{m}_i = \mathbf{m}_{i-1}$ = col (0, 0, 1) (Table II).

Only one of the model chains considered here has $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 \neq 0$. The behavior of α_μ^2 for that model chain is in harmony with eq 1. A much different situation is encountered with chains for which $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 = 0$. Some such chains do indeed have $\alpha_\mu^2 = 1 < \alpha_r^2$, but others show the behavior $1 < \alpha_\mu^2 < \alpha_r^2$, and for still others the expansion factors are $\alpha_\mu^2 < 1 < \alpha_r^2$! Clearly, eq 1 does not hold in general when $\langle \mathbf{r} \cdot \boldsymbol{\mu} \rangle_0 = 0$. Observations that $\langle \mu^2 \rangle$ is solvent dependent have often been attributed to a solvent effect on the unperturbed dimensions. This interpretation may bear reexamination if the chain has a nonzero z component for $\mathbf{m}_i$ or if there are subchains which can attain a dipole moment of zero upon extension.

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Dielectric Relaxation of Oxide Polymers in Dilute Solution[†]

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ABSTRACT: Dielectric relaxation measurements were made on dilute solutions of poly(propylene oxides) in benzene over a wide frequency range from 10 MHz to 10 GHz using time-domain reflectometry. Two relaxation processes were found. The lower frequency process, depending strongly on the molecular weight, is explained completely by the normal mode theory of Rouse and Zimm. Another process, independent of molecular weight, is caused by an elementary process in the backbone motion. The magnitude of the relaxation time is explained satisfactorily by Kramers' rate constant theory at the low-friction limit, if the elementary process is assumed to be a rotational transition of a chain bond. The relaxation process observed in poly(ethylene oxide) in benzene is also explained by Kramers' theory. The effect of chemical structure of oxide polymers on the higher frequency relaxation process is discussed.

I. Introduction

Three kinds of dielectric relaxation processes have been found in solutions of flexible polar polymers. If a polymer has dipole components parallel to its chain contour, a rotational diffusion of the polymer molecule gives rise to a relaxation process depending on molecular weight in a relatively low frequency region.[1] The relaxation time is explained quite satisfactorily by the nomal mode theory of Rouse and Zimm.[2,3] The theory predicts relaxation time as

$$\tau_{\text{rot}} = A_1 M[\eta]\eta_0/RT \tag{1}$$

where M is the molecular weight, $[\eta]$ the intrinsic viscosity, η_0 the solvent viscosity, R the gas constant, and T the absolute temperature. The factor A_1 takes a value of 1.21 for the free-draining case and 0.85 for the nondraining case. Poly(ϵ-caprolactone) (PCL) and poly(olefin sulfones) in solution exhibit this relaxation process.[4–6]

Generally, polar polymers have dipole components perpendicular to the chain contour and show a relaxation process independent of molecular weight which is observed in a relatively high frequency region.[1,7–9] Chain motions associated with conformational transitions in the chain backbone give rise to this relaxation. Recent study of methyl methacrylate–methyl acrylate copolymers in dilute solution has indicated that the elementary process in the chain motion is essentially a bond rotation which occurs independently between isomeric transition states.[10]

Poly(p-chlorostyrene) is a typical polymer having a dipole component of this type. The relaxation peak was found at about 30 MHz in solution.[7–9] The relaxation time is expressed experimentally by[7]

$$\tau_{\text{back}} = A_2\eta_0 \exp(\Delta H_{\text{A}}/RT) \tag{2}$$

This expression is explained quite satisfactorily by Kramers' rate constant theory at the high-friction limit.[11,12] The value of ΔH_{A} represents the potential barrier height for bond rotation. If correlated motions are assumed to exist among several neighboring bonds, the magnitude of the factor A_2 is explained by Kramers' theory.[7]

If the relaxation peak is found at a frequency lower than 100 MHz, the same argument can hold well for other polar polymers such as vinyl polymers[7,8] and poly(alkyl methacrylates)[13] in dilute solution.

Recently, a relaxation caused by internal rotations of side groups has been found in poly(methyl vinyl ketone) in benzene.[15] Rotation of acetyl side groups gives a relaxation peak at 1 GHz. Relaxation of this kind in the solid state is observed in a number of polymers. This result indicates that relaxation caused by side-group rotation exists even in a dilute polymer solution.

If a polymer contains oxygen atoms in the chain backbone, as in the polyethers, a dielectric relaxation peak occurs at a very high frequency. Poly(ethylene oxide) (PEO) exhibits a peak at about 10 GHz in benzene,[16] and PCL has one at 2 GHz in dioxane.[4,17] Poly(styrene oxide) (PSO) shows a peak at 450 MHz in benzene, which is about 5 times higher than that of polystyrene.[18]

Most likely, the backbone motions in these polymers also cause the relaxation observed. Therefore, it is thought to be quite important in interpreting chain dynamics to examine whether Kramers' rate constant at the high-friction limit can or cannot be applied to the relaxation times of these polymers as well as of vinyl polymers and to determine why the relaxation time is very small in comparison with other polar polymers.

In this work poly(propylene oxides) with different molecular weights were used as the polymer having oxygen atoms in the chain backbone, and dielectric relaxation

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[†] This paper is dedicated, with great pleasure and appreciation, to Professor Walter H. Stockmayer on the occasion of his 70th birthday celebration.

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