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Interpretation of the Mean-Square Dipole Moment of Poly(A–B) by Use of the Mean-Square End-to-End Distance for Its Didymous Partner

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ABSTRACT: For chains of the type A–B–A–B–...–A, with n bonds of length l between A and B and n bond dipole moment vectors of length m pointing from A to B, there is a didymous chain, which is defined such that $C' = D$ and $D' = C$, where $C = \langle r^2\rangle_0/nl^2$ and $D = \langle\mu^2\rangle_0/nm^2$ for the real chain and primes denote these ratios for the didymous chain. Thus the behavior of the mean-square dipole moment, $\langle\mu^2\rangle_0$, for the real chain can be deduced from the behavior of the mean-square end-to-end distance, $\langle r^2\rangle_0$, for the didymous chain. An understanding of the relationship between the real chain and its didymous partner therefore sheds insight into the relationship between C and D for the real chain. The didymous chain is described here for bonds subject to independent symmetric rotational potentials and for bonds subject to interdependent symmetric 3-fold rotation potentials. In the former case, it is sufficient to simply replace each bond angle by its supplement. In the latter case, one must also make the assignments $\psi' = \omega$ and $\omega' = \psi$, where ψ and ω are the statistical weights for the second-order interactions in g^+g^+ and g^+g^- states, respectively, in the real chain.

Introduction

A chain in which the atoms alternate between A and B, with a dipole moment vector of nonzero length colinear with each bond and pointing from A to B, is one of the simplest macromolecules with a permanent dipole moment. A fragment of this chain is depicted in Figure 1. Its unperturbed mean-square end-to-end distance and unperturbed mean-square dipole moment, denoted by $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$, respectively, are conveniently expressed by two dimensionless characteristic ratios defined as

$$C = \langle r^2\rangle_0/nl^2 \tag{1}$$

$$D = \langle\mu^2\rangle_0/nm^2 \tag{2}$$

where n is the number of bonds, l is the length of the bond vector, and m is the length of the bond dipole moment vector. Vectors of length l are connected head-to-tail, but vectors of length m are connected head-to-head and tail-to-tail, as shown in Figure 1. In the special case where the bonds are freely jointed, $C = D = 1$. In general, however, these two characteristic ratios have different values. In many models for real chains, $C > 1 > D$.

Added insight into the influence of the local structure on D can be obtained by investigation of a molecule that we call the didymous chain. In this work, primes will be appended to the properties of the didymous chain. The word "didymous" carries the connotation of "twin" in biology. We prefer the uncommon word "didymous" to the more common word "twin" because the relationships between the real chain and its didymous partner are

$$C' = D \tag{3}$$

$$D' = C \tag{4}$$

It is not their values of C, and their values of D, that are identical. Rather it is C' that behaves as D and D' that behaves as C. Definition of the relationship between a real chain and its didymous partner therefore provides additional insight into the relationship between C and D for the real chain. The relationship is trivial if the chain is freely jointed, because then $C = D = C' = D' = 1$, and the real chain is identical with the didymous chain. For more realistic models, however, the real chain is not identical with the didymous chain. The treatment here will first consider chains with bonds subject to independent symmetric rotation potentials and then chains with bonds subject to interdependent symmetric 3-fold rotational potentials.

Independent Symmetric Rotation Potential

When the internal bonds are subject to identical independent rotation potentials, the generator matrix formalism for C and D for poly(A–B) terminated with A at each end takes the blocked form[1]

$$C = n^{-1}l^{-2} \times \\ [1 \quad 0]\left\{\begin{bmatrix} 1 & 2\mathbf{l}^T\langle\mathbf{T}_A\rangle & l^2 \\ \mathbf{0} & \langle\mathbf{T}_A\rangle & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\begin{bmatrix} 1 & 2\mathbf{l}^T\langle\mathbf{T}_B\rangle & l^2 \\ \mathbf{0} & \langle\mathbf{T}_B\rangle & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}\right\}^{n/2}\begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix} \tag{5}$$

$$D = n^{-1}m^{-2} \times \\ [1 \quad 0]\left\{\begin{bmatrix} 1 & 2\mathbf{m}_A{}^T\langle\mathbf{T}_A\rangle & m^2 \\ \mathbf{0} & \langle\mathbf{T}_A\rangle & \mathbf{m}_A \\ 0 & \mathbf{0} & 1 \end{bmatrix}\begin{bmatrix} 1 & 2\mathbf{m}_B{}^T\langle\mathbf{T}_B\rangle & m^2 \\ \mathbf{0} & \langle\mathbf{T}_B\rangle & \mathbf{m}_B \\ 0 & \mathbf{0} & 1 \end{bmatrix}\right\}^{n/2}\begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix} \tag{6}$$

where $\mathbf{0}$ denotes a rectangular null block such that the initial row and last column contain five elements and the square matrices are of dimensions 5 × 5. The transpose of each bond length vector is $\mathbf{l}^T = [l \quad 0 \quad 0]$. Subscripts are appended to each bond dipole moment vector, $\mathbf{m}$, and each averaged transformation matrix, $\langle\mathbf{T}\rangle$. The bond dipole moment vectors are $\mathbf{m}_A{}^T = [m \quad 0 \quad 0]$ and $\mathbf{m}_B = -\mathbf{m}_A$. The two averaged transformation matrices will differ if $\theta_{ABA} \neq \theta_{BAB}$, where θ denotes the supplement of the bond angle specified by the subscript.

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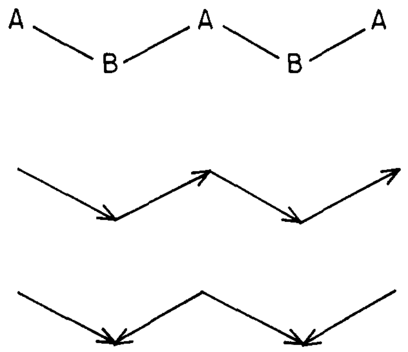

Figure 1. Segment of a chain in which the atoms of type A alternate with atoms of type B, followed by the representations of the same segment using bond vectors, $\mathbf{l}_i$, that are connected head-to-tail and bond dipole moment vectors, $\mathbf{m}_i$, that are connected head-to-head and tail-to-tail.

For independent, symmetric rotation potentials, the form of the average transformation matrix is

$$\langle \mathbf{T}_A \rangle = \begin{bmatrix} \alpha_A & \beta_A & 0 \\ -\beta_A\eta & \alpha_A\eta & 0 \\ 0 & 0 & \eta \end{bmatrix} \tag{7}$$

where α_A and β_A denote, respectively, $\cos\theta_{ABA}$ and $\sin\theta_{ABA}$ and η is $\langle\cos\phi\rangle$. The dihedral angle, ϕ, is zero for a cis placement and increases upon a clockwise rotation. Substitution of α_B and β_B, which are $\cos\theta_{BAB}$ and $\sin\theta_{BAB}$, gives $\langle\mathbf{T}_B\rangle$. The same η is used in both matrices because independent rotation about the central bond in B–A–B–A is identical with rotation about the central bond in A–B–A–B. The symmetry of the rotation potential causes $\langle\sin\phi\rangle$ to be zero.

Upon use of unit length for $\mathbf{l}$, $\mathbf{m}_A$, and $\mathbf{m}_B$, the product of the two square matrices in eq 5 is

$$(\mathbf{G}_A\mathbf{G}_B)_c = \begin{bmatrix} 1 & 2(\alpha_A\alpha_A + \alpha_B - \beta_A\beta_B\eta) & 2(\alpha_A\beta_B + \beta_B + \alpha_B\beta_A\eta) & 0 & 2(1+\alpha_A) \\ 0 & \alpha_A\alpha_B - \beta_A\beta_B\eta & \alpha_A\beta_B + \alpha_B\beta_A\eta & 0 & 1+\alpha_A \\ 0 & -(\alpha_B\beta_A + \alpha_A\beta_B\eta)\eta & (\alpha_A\alpha_B\eta - \beta_A\beta_B)\eta & 0 & -\beta_A\eta \\ 0 & 0 & 0 & \eta^2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{8}$$

and the product of the two square matrices in eq 6 is

$$(\mathbf{G}_A\mathbf{G}_B)_D = \begin{bmatrix} 1 & 2(\alpha_A\alpha_B - \alpha_B - \beta_A\beta_B\eta) & 2(\alpha_A\beta_B - \beta_B + \alpha_B\beta_A\eta) & 0 & 2(1-\alpha_A) \\ 0 & \alpha_A\alpha_B - \beta_A\beta_B\eta & \alpha_A\beta_B + \alpha_B\beta_A\eta & 0 & 1-\alpha_A \\ 0 & -(\alpha_B\beta_A + \alpha_A\beta_B\eta)\eta & (\alpha_A\alpha_B\eta - \beta_A\beta_B)\eta & 0 & \beta_A\eta \\ 0 & 0 & 0 & \eta^2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{9}$$

The terminal row and column vectors in eq 5 and 6 extract the last element in the first row of the $n/2$ power of the matrices in eq 8 and 9, respectively. This element is $2(1 + \alpha_A)$ in eq 8 and $2(1 - \alpha_A)$ in eq 9, and therefore C is different from D at $n = 2$ if θ_{ABA} is different from $\pi/2$. The differences in four other elements in eq 7 and 8, specifically the second and third elements in the first row and the second and third elements in the last column, ensure that C will remain different from D at larger n as well, barring a fortuitous compensation. The third elements in the last columns of eq 8 and 9 differ only in sign, but the 1,2 elements, 1,3 elements, and 2,5 elements differ in absolute value.

The Didymous Chain. We now consider the matrices that are the counterparts of eq 8 and 9 for the didymous chain. In the present case, the didymous chain is generated from the real chain by simply replacing each bond angle by its supplement. These substitutions only require $\alpha_A' = -\alpha_A$ and $\alpha_B' = -\alpha_B$, where the prime denotes the values for the didymous chain. Consequently $(\mathbf{G}_A\mathbf{G}_B)_{C'}$ and $(\mathbf{G}_A\mathbf{G}_B)_{D'}$ can be written in terms of the properties of the real chain as

$$(\mathbf{G}_A\mathbf{B}_B)_{C'} = \begin{bmatrix} 1 & 2(\alpha_A\alpha_B - \alpha_B - \beta_A\beta_B\eta) & -2(\alpha_A\beta_B - \beta_B + \alpha_B\beta_A\eta) & 0 & 2(1-\alpha_A) \\ 0 & \alpha_A\alpha_B - \beta_A\beta_B\eta & -\alpha_A\beta_B - \alpha_B\beta_A\eta & 0 & 1-\alpha_A \\ 0 & (\alpha_B\beta_A + \alpha_A\beta_B\eta)\eta & (\alpha_A\alpha_B\eta - \beta_A\beta_B)\eta & 0 & -\beta_A\eta \\ 0 & 0 & 0 & \eta^2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{10}$$

$$(\mathbf{G}_A\mathbf{G}_B)_{D'} = \begin{bmatrix} 1 & 2(\alpha_A\alpha_B + \alpha_B - \beta_A\beta_B\eta) & -2(\alpha_A\beta_B + \beta_B + \alpha_B\beta_A\eta) & 0 & 2(1+\alpha_A) \\ 0 & \alpha_A\alpha_B - \beta_A\beta_B\eta & -\alpha_A\beta_B - \alpha_B\beta_A\eta & 0 & 1+\alpha_A \\ 0 & (\alpha_B\beta_A + \alpha_A\beta_B\eta)\eta & (\alpha_A\alpha_B\eta - \beta_A\beta_B)\eta & 0 & \beta_A\eta \\ 0 & 0 & 0 & \eta^2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{11}$$

Element by element comparison of the matrices in eq 8 and 11 shows that corresponding elements are always of the same absolute value, but four elements differ in sign. Using "+" to denote nonzero elements that are identical, "–" to denote elements that differ in sign, and "0" to denote null elements, the pattern is

$$\begin{bmatrix} + & + & - & 0 & + \\ 0 & + & - & 0 & + \\ 0 & - & + & 0 & - \\ 0 & 0 & 0 & + & 0 \\ 0 & 0 & 0 & 0 & + \end{bmatrix} \tag{12}$$

The identity of the 1,5 elements ensures that C is equal to D' when n is 2. The pattern of the +, –, and 0 in eq 12 does not change if this matrix is squared, and consequently C is also equal to D' at $n > 2$. A similar comparison of the elements in eq 9 and 10 shows that D is equal to C'.

The Freely Rotating Chain with Identical Bond Angles. In the special case of the freely rotating chain with $\theta_{ABA} = \theta_{BAB}$, the well-known expression for C is[2,3]

$$C = (1 + \alpha)/(1 - \alpha) - (2\alpha/n)(1 - \alpha^n)/(1 - \alpha)^2 \tag{13}$$

where the subscripts on α have been dropped because $\alpha_A = \alpha_B$. The definition of the didymous chain presented above immediately permits the writing of an expression for D. Since $D = C'$ and C' is obtained with $\alpha' = -\alpha$, we find, for chains with an even number of bonds

$$D = (1 - \alpha)/(1 + \alpha) + (2\alpha/n)(1 - \alpha^n)(1 + \alpha)^2 \tag{14}$$

As n becomes infinite, the asymptotic limits are related as

$$C_\infty = 1/D_\infty \tag{15}$$

It is C_∞ that will be larger than one if the bond angle is greater than $\pi/2$.

The nature of the final approach to the limit determines the values of $\partial \ln C/\partial(1/n)$ and $\partial \ln D/\partial(1/n)$, both evaluated as n goes to infinity. From eq 13 and 14, we obtain

$$[\partial \ln C/\partial(1/n)]_{n\to\infty} = -[\partial \ln D/\partial(1/n)]_{n\to\infty} = -2\alpha/(1 + \alpha)(1 - \alpha) \tag{16}$$

The two derivatives are identical in absolute value but opposite in sign. The former derivative is negative if the bond angle is greater than $\pi/2$.

Identical Bond Angles, Independent Symmetric Rotations. Another simple case is the chain in which $\theta_{ABA} = \theta_{BAB}$, and each bond is subject to the same independent,

Table I
Calculations for Poly(A–B) with Interdependent Symmetric 3-Fold Rotation Potentials[a]

statistical wt				supplements, deg		limiting values as $n \to \infty$			
ψ_A	ψ_B	ω_A	ω_B	θ_{ABA}	θ_{BAB}	C	D	$\partial C/\partial(1/n)$	$\partial D/\partial(1/n)$
0.2	0.6	0.1	0.3	60	75	7.507	1.115	−37.24	−1.24
0.2	0.6	0.1	0.3	120	105	1.192	6.743	−1.56	−28.04
0.1	0.3	0.2	0.6	120	105	1.115	7.507	−1.24	−37.24

[a] $\sigma = 0.5$, and dihedral angles for gauche placements are 110° from those for trans placements.

symmetric rotation potential. The well-known expression for the asymptotic limit for C is[4]

$$C_\infty = [(1 + \alpha)/(1 - \alpha)][(1 - \eta)/(1 + \eta)] \tag{17}$$

From the properties of the didymous chain, we can immediately write

$$D_\infty = [(1 - \alpha)/(1 + \alpha)][(1 - \eta)/(1 + \eta)] \tag{18}$$

The product of these two dimensionless ratios is completely independent of α. It is determined solely by $\langle \cos \phi \rangle$.

$$C_\infty D_\infty = [(1 - \eta)/(1 + \eta)]^2 \tag{19}$$

Unfortunately, this simple relationship between $C_\infty D_\infty$ and η is lost if $\theta_{ABA} \neq \theta_{BAB}$, if the independent rotations are not symmetric, or if the rotations are interdependent.

Changes in temperature might have a negligible effect on the bond angles, but nevertheless they produce changes in C and D due to an increase in the accessible regions of ϕ at higher temperature. The changes in the distribution of accessible dihedral angles can produce a change in η. If the only effect of a change in temperature is on η, then from eq 17 and 18

$$\partial \ln C_\infty/\mathrm{d}T = \partial \ln D_\infty/\mathrm{d}T \tag{20}$$

For long chains, the temperature coefficients for C_∞ and D_∞ are identical. On the other hand, if temperature were to change α and η were temperature independent, then the temperature coefficients would be identical in absolute value but opposite in sign.

The chain length dependence of D can be extracted in a manner similar to that employed for C.[5-7] The expression for C can be written as

$$C = C_\infty - X_1 + X_2 \tag{21}$$

where C_∞ is given by eq 17 and

$$X_i = (2\lambda_i/n)(\alpha\eta + \lambda_i)(1 - \lambda_i^n)(1 - \lambda_i)^{-2}(\lambda_1 - \lambda_2)^{-1} \tag{22}$$

$$\lambda_{1,2} = \{\alpha(1 - \eta) \pm [\alpha^2(1 - \eta) + 4\eta]^{1/2}\}/2 \tag{23}$$

From the didymous chain, we find

$$D = D_\infty + X_1[(1 + \lambda_1)/(1 - \lambda_1)]^2 - X_2[(1 + \lambda_2)/(1 - \lambda_2)]^2 \tag{24}$$

Chains with Interdependent Symmetric 3-Fold Rotation Potentials

Very few real chains can be successfully treated in the approximation that their bonds are independent. However, several chains have been treated in good approximation by using interdependent symmetric 3-fold rotation potentials. Poly(oxymethylene) serves as an example.[8,9] For such chains, there is a slightly more complicated relationship between the real and didymous chain than is the case when the bonds are subject to independent symmetric rotational potentials. That relationship is described here in the approximation that $\mathbf{l}_i = \pm(l_i/m_i)\mathbf{m}_i$; i.e., the angle between $\mathbf{l}_i$ and $\mathbf{m}_i$ is either 0 or π. Acceptance of this approximation ensures that ϕ_i describes rotation about an axis that is colinear with both $\mathbf{l}_i$ and $\mathbf{m}_i$. In view of the increase in the sizes of the matrices when rotations are interdependent, the development will be based on the analysis of the results from numerical computations.

The statistical weight matrices, $\mathbf{U}$, are[1]

$$\mathbf{U}_A = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi_A & \sigma\omega_A \\ 1 & \sigma\omega_A & \sigma\psi_A \end{bmatrix} \tag{25}$$

$$\mathbf{U}_B = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi_B & \sigma\omega_B \\ 1 & \sigma\omega_B & \sigma\psi_B \end{bmatrix} \tag{26}$$

No subscript is required for σ because the first-order interactions in A–B–A–B are identical with those in B–A–B–A. The second-order interactions are those found in the fragment A–B–A–B–A (for $\mathbf{U}_A$) and B–A–B–A–B (for $\mathbf{U}_B$) and are therefore distinguished by subscripts.

The procedure for the conversion from the real to the didymous chain is documented by the results of calculations that are summarized in Table I. The first two lines present the conformational properties for two chains that differ only in the replacement of each θ by its supplement. This simple change was sufficient for generation of the didymous chain when the rotations were independent, as shown in the preceding section. The numerical entries in the first two lines of Table I show that this procedure is inadequate when the rotations become interdependent. Since the interdependence of the rotations is accomplished by assigning values different from unity for the second-order statistical weights denoted by ψ_A, ψ_B, ω_A, and ω_B, it is clear that these statistical weights must differ in the real and didymous chain. What is required is the interchange of ψ_A and ω_A and of ψ_B and ω_B, in addition to the replacement of each θ by its supplement, as shown by comparison of the first and last lines of Table I. Generator matrix calculations of the higher even moments[1] and mixed moments,[10] $\langle r^4\rangle_0/\langle r^2\rangle_0^2$, $\langle \mu^4\rangle_0/\langle \mu^2\rangle_0^2$, and $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$, as functions of n, show that in every case the property calculated for r (or μ) for the real chain is identical with the properties calculated for μm (or r') for the didymous chain. From this information we conclude that the distribution function for μ can be inferred from the distribution function for r'.

The physical basis for the interchange of ψ_A and ω_A, and ψ_B and ω_B, in the didymous chain is presented in Table II. This table contains the three components of the end-to-end vectors and dipole moment vectors for the g^+g^+ and g^+g^- conformations of a chain of four bonds. The bond-angle supplements and angular separation of the gauche and trans states have the values found in poly(oxymethylene).[9] The first four lines present the components of $\mathbf{r}$, μ, $\mathbf{r}'$, and μ' in the g^+g^+ conformation. No two vectors are alike. The last four lines present the components of $\mathbf{r}$, μ, $\mathbf{r}'$, and μ' in the g^+g^- conformation. It can be seen that reflection through the X–Z plane would convert $\mathbf{r}/l$ for g^+g^+ into μ'/m for g^+g^-, μ/m for g^+g^+ into $\mathbf{r}'/l$ for g^+g^-, $\mathbf{r}'/l$ for g^+g^+ into μ/m for g^+g^-, and μ'/m for g^+g^+ into $\mathbf{r}/l$ for g^+g^-. Of course, the squares of the lengths

Table II
Vectors for Chains with Four Bonds[a]

conformation	vector	components *X*	*Y*	*Z*	weight
g^+g^+	$\mathbf{r}/l$	1.775	1.004	−1.607	$\sigma^2\psi$
	μ/m	−0.082	−0.072	−0.135	$\sigma^2\psi$
	$\mathbf{r}'/l$	1.436	0.685	−0.731	$\sigma^2\psi' = \sigma^2\omega$
	μ'/m	0.256	−1.617	−1.011	$\sigma^2\psi' = \sigma^2\omega$
g^+g^-	$\mathbf{r}/l$	0.256	1.617	−1.011	$\sigma^2\omega$
	μ/m	1.436	−0.685	−0.731	$\sigma^2\omega$
	$\mathbf{r}'/l$	−0.082	0.072	−0.135	$\sigma^2\omega' = \sigma^2\psi$
	μ'/m	1.775	−1.004	−1.607	$\sigma^2\omega' = \sigma^2\psi$

[a] $\theta_{ABA} = \theta_{BAB} = 68° = \pi - \theta'_{ABA} = \pi - \theta'_{BAB}$, and the gauche placements are located 110° from the trans placement.

of these vectors are unaffected by reflection through the *X*–*Z* plane. It is the squares of the lengths of the vectors that are important for the conversion of a real chain into its didymous partner.

Implications for Real Chains. In real chains subject to interdependent symmetric 3-fold rotation potentials, the second-order statistical weights for the conformations g^+g^- and g^-g^+, conventionally denoted by ω, are usually less than one.[1,9] Successive gauche placements of opposite sign are suppressed by repulsive steric interaction of atoms separated by four consecutive bonds. In the didymous chains, it is the conformations g^+g^+ and g^-g^- that must be similarly suppressed. In real chains, the second-order statistical weights for the conformations g^+g^+ and g^-g^- are often very close to one, although exceptions do occur.[11] The didymous partners of typical real chains will often have little penalty from second-order interactions for the conformations g^+g^- and g^-g^+.

The small values of C' arise from two distinct effects, both of which are illustrated by the case of poly(oxymethylene).[9] The first effect arises from the geometry of successive bonds. Typical bond angles for real chains are larger than $\pi/2$, and consequently the bond angles for didymous chains are less than $\pi/2$. In poly(oxymethylene), the bond angles are very close to 112°, and they are therefore 68° in didymous poly(oxymethylene). The second effect arises from the energetics of the second-order interactions that are responsible for the interdependence of the rotations. In the didymous chain, there is often an absence of any second-order penalty for the compact local conformations that arise from adoption of successive gauche placements of opposite sign in the didymous chain. (The compact nature of g^+g^- in the didymous chain is illustrated by the components of $\mathbf{r}'/l$ in Table II.) In real poly(oxymethylene), ψ_A and ψ_B are 1, and consequently ω_A' and ω_B' are 1 in didymous poly(oxymethylene). It is the less compact local conformations with successive gauche placements of the same sign that are penalized by the second-order interactions in the didymous chain. In poly(oxymethylene), ω_A and ω_B have values of about 0 and 0.08, and consequently ψ_A' and ψ_B' are 0 and 0.08 in didymous poly(oxymethylene).

Since C' is identical with D, the rationalization of the small values of C' in the preceeding paragraph also explains why the values for D are small.

Series expansions[12–19] that have been used to study the distribution function for $\mathbf{r}$ in unperturbed real chains with finite n can, of course, be applied to $\mathbf{r}'$ for the unperturbed didymous chain. That approach will lead directly to the distribution function for μ for the unperturbed real chain.

The nature of the didymous chain remains obscure for cases where the number of bond length vectors is different from the number of bond dipole moment vectors or where the axis for the rotation denoted by ϕ_i is not colinear with $\mathbf{l}_i$ and $\mathbf{m}_i$. In view of the anticipated effect of excluded volume on both $\langle r^2 \rangle$ and $\langle r^2 \rangle'$, the relationships described here are restricted to unperturbed chains.

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