Persistence Length and Finite Chain Length Effect on Characteristic Ratios

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ABSTRACT: Characteristic ratios for an unperturbed flexible chain with n bonds of length l can be defined with the mean-square end-to-end distance or the mean-square radius of gyration, $C_{r,n} \equiv \langle r^2\rangle_0/nl^2$ and $C_{s,n} \equiv \langle s^2\rangle_0/nl^2$, respectively. Their approaches to the asymptotic limits at $n \rightarrow \infty$ are found to be related by $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} = 2\{[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0} - C_{s,\infty}\}$. Real chains usually have $C_{r,\infty} > 1$ and $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} < 0$, signifying that $C_{r,n}$ makes its final approach to $C_{r,\infty}$ from below. However, some chains with $C_{r,\infty} > 1$ have values of $C_{r,n}$ that pass through a maximum at finite n and approach $C_{r,\infty}$ from *above*, $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} > 0$. Syndiotactic poly(methyl methacrylate) (*s*PMMA) is an example. In general, $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} = -2\sum_{k=1}^{\infty} k\langle \mathbf{u}_i\cdot\mathbf{u}_{i+k}\rangle_0$, where $\mathbf{u}_i \equiv \mathbf{l}_i/l_i$ denotes a unit vector parallel with the vector for bond i. Members of this sum with $15 < k < 34$ produce $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} > 0$ in *s*PMMA. These results have strong implications for the extraction of a "persistence length" from experimental data in the form $\langle s^2\rangle_0/n$ as a function of n.

A. Introduction

One of the most fundamental physical properties of a flexible chain molecule is its mean-square dimensions, expressed as either the mean-square end-to-end distance, $\langle r^2\rangle$, or the mean-square radius of gyration, $\langle s^2\rangle$. In the unperturbed, or Θ, state these properties define dimensionless characteristic ratios, C_n. For a chain with n bonds of length l they are $C_{r,n} \equiv \langle r^2\rangle_0/nl^2$ and $C_{s,n} \equiv \langle s^2\rangle_0/nl^2$, respectively. Both characteristic ratios approach asymptotic limits as n increases without limit. Over 50 years ago Debye showed these limits are related by a factor of 6, $C_{r,\infty} = 6C_{s,\infty}$.[1]

The nature of the final approach of the two C_n's to their asymptotic limit is important for theoretical and experimental reasons. On the theoretical side, some simple models of flexible chains erroneously predict the asymptotic approach of the two C_n's to their limit is controlled entirely by C_∞ itself.[2] Nature exhibits a more complex behavior, as demonstrated by the observation that polyethylene (PE) and syndiotactic poly(methyl methacrylate) (sPMMA), with nearly the same value of C_∞, have different *signs* for $[\partial C_n/\partial(1/n)]_{1/n=0}$.[3−5] Theoretical attempts to extract fundamental information about the chain from the manner in which C_n makes its final approach to C_∞ must not only confront the fact that the final approach is not controlled by C_∞ alone but also recognize that the approach can be of either sign. Several simple, but popular, models for flexible chain molecules, such as the simple wormlike chain,[6,7] are not easily reconciled with these facts.

On the experimental side, investigations of real systems usually deal with chains of finite, not infinite, degree of polymerization, and sometimes these chains are short enough so that the asymptotic limit does not apply. Chain statistics in many experimental papers is often characterized by a single parameter C_∞. This parameter, however, gives the size of the polymer coil in the limit of infinitely high molecular weight, but it is not sufficient to describe the approach to this limit by the real chains. Misunderstanding of this point leads to some confusion in the literature. For example, recent neutron[8] and probe molecule[9] experiments clearly demonstrate that polymers with similar Kuhn segment length (defined traditionally through C_∞) have strongly different dynamic bead size. A deficiency of the traditionally defined Kuhn segment length and an importance of detailed consideration of the way a chain approaches the Gaussian limit in interpretation of experimental data have been recently emphasized by Ding et al.[10] Also, Majeste et al.[11] demonstrate that in order to describe viscoelastic properties of polystyrene, one needs to take into account the proper variation of the radius of gyration with molecular weight.

Our objective here is to obtain model-independent results that identify the fundamental properties of a flexible chain that control the sign and size of $[\partial C_n/\partial(1/n)]_{1/n=0}$. We do so by starting with the definitions of the end-to-end vector, $\mathbf{r}$, and the squared radius of gyration, s^2. We then proceed from these definitions, assuming only that the chain is a flexible homopolymer with indistinguishable ends. This approach demonstrates that the values of $[\partial C_{r,n}/\partial(1/n)]_{1/n=0}$ and $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$ are not related by Debye's factor of 6. They depend in different ways on $\Sigma k\langle \mathbf{u}_i\cdot\mathbf{u}_{i+k}\rangle_0$, where $\mathbf{u}_i$ is a unit vector along bond i and the index k increases without limit. The appearance of k in front of the angle brackets plays a critical role in causing the final approaches of C_n to the asymptotic limit to be of different sign for PE and sPMMA, even though these two chains have experimentally indistinguishable values of C_∞.

B. A Simple and Accurate Expression for the Asymptotic Approach of $C_{r,n}$ to $C_{r,\infty}$

The squared end-to-end distance, r^2, for a specified conformation of a chain is defined by its n bond vectors, $\mathbf{l}_i$.

$$r^2 = \mathbf{r}\cdot\mathbf{r} = \sum_{i=1}^{n} l_i^{\,2} + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \mathbf{l}_i\cdot\mathbf{l}_j \qquad (1)$$

Taking the conformational average in the unperturbed, or Θ, state, and assuming that the bonds are of constant

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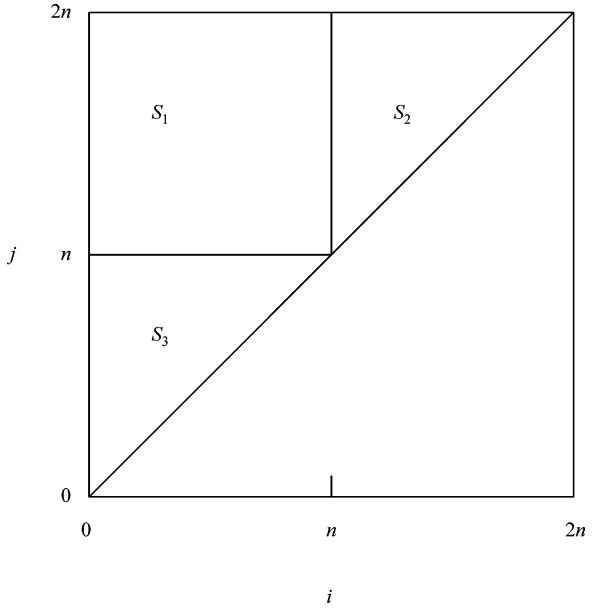

Figure 1. Ranges of the subscripts i and j for $S_{1,2n}$, $S_{2,2n}$, and $S_{3,2n}$ in a chain of $2n$ bonds.

length, $C_{r,n}$ depends on the average dot products of vectors of unit length, $\mathbf{u}_i = \mathbf{l}_i/l_i$.

$$C_{r,n} = 1 + \frac{2}{n}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0 \tag{2}$$

If n is large enough to lie within the limiting region where $C_{r,n}$ becomes linear in $1/n$,[12,13] the final approach of $C_{r,n}$ to $C_{r,\infty}$ can be written in terms of $C_{r,n}$ and $C_{r,2n}$.

$$\left[\frac{\mathrm{d}C_{r,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = \frac{C_{r,2n} - C_{r,n}}{\frac{1}{2n} - \frac{1}{n}} = -2n(C_{r,2n} - C_{r,n}) \tag{3}$$

Insight into the properties of the chain that control the sign and size of $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0}$ is obtained when the double sum in eq 2 is separated into three parts, using the ranges of the indices i and j depicted in Figure 1 for a chain of $2n$ bonds.

$$S_{1,2n} = \sum_{i=1}^{n}\sum_{j=n+1}^{2n}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0 \tag{4a}$$

$$S_{2,2n} = \sum_{i=n+1}^{2n-1}\sum_{j=i+1}^{2n}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0 \tag{4b}$$

$$S_{3,2n} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0 \tag{4c}$$

With $C_{r,2n} = 1 + (1/n)(S_{1,2n} + S_{2,2n} + S_{3,2n})$ and $C_{r,n} = 1 + (2/n)S_{3,2n}$, as required by eq 2 and eq 4, and assuming the chain has indistinguishable ends, such that identical average properties are obtained for subchains consisting of bonds 1 through n and bonds $n + 1$ through $2n$, i.e., $S_{2,2n} = S_{3,2n}$, the initial slope of $C_{r,n}$ vs $1/n$ is found to be determined completely by $S_{1,\infty} \equiv \lim_{n\to\infty} S_{1,n}$.

$$\left[\frac{\mathrm{d}C_{r,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = -2S_{1,\infty} \tag{5}$$

The intercept at $1/n = 0$ is determined by $\lim_{n\to\infty}(S_{2,n}/n) = \lim_{n\to\infty}(S_{3,n}/n)$.

$$C_{r,\infty} = 1 + 2\lim_{n\to\infty}\left(\frac{S_{3,n}}{n}\right) \tag{6}$$

The ranges for i and j are fundamentally different for these double sums, as shown by the square and triangular shapes of the regions that defines $S_{1,2n}$ and $S_{3,2n}$, respectively, in Figure 1. $C_{r,\infty}$ and $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0}$ are fundamentally different properties of the unperturbed chain.[2]

C. The Properties of $S_{1,\infty}$

The imposition of a bond angle larger than 90°, as well as the influence of short-range interactions on the population of the torsion angles, produces $C_{r,\infty} > 1$ for most chains with realistic bond angles and torsion potentials. Since, by definition, a "chain" of one bond has $C_{r,1} = 1$, this result is easily reconciled with the observation that many chains have $C_{r,n}$ that approach $C_{r,\infty}$ from below, which requires $S_{1,\infty} > 0$ in eq 5. However, eq 5 admits the possibility of chains for which $C_{r,\infty} > 1$ and $S_{1,\infty} < 0$. With this combination of $C_{r,\infty}$ and $S_{1,\infty}$, $C_{r,n}$ passes through a maximum at finite n and makes its final approach to the asymptotic limit from *above*. A chain with this behavior is defined by the six-state rotational isomeric state (RIS) model proposed by Vacatello and Flory for syndiotactic PMMA (sPMMA).[4] Their model uses realistic values of the bond angles, along with six rotational isomeric states at the bonds in the backbone, with the torsions subject to the short-range interactions determined from a careful study of atomistically detailed models of oligomers of this chain. Calculations with this model provide excellent agreement with the experimentally observed properties for PMMA.[14] The values of $C_{r,n}$ pass through a maximum when n is near 20, as shown in Figure 5. The initial slope of $C_{r,n}$ vs $1/n$ is positive (5.8), with $S_{1,\infty} = -2.9$, even though $C_{r,\infty} > 1$ ($C_{r,\infty} = 6.8$). Vacatello and Flory attributed this behavior to a tendency for formation of large loops by unperturbed *s*PMMA chains, as depicted in their Figure 9. In the next section we identify the sizes of the subchains that are responsible for the negative value of $S_{1,\infty}$ in *s*PMMA.

The origin of the qualitative differences in the behavior of $S_{1,\infty}$ and $S_{3,\infty}$ upon an increase in n becomes apparent upon examination of how $\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0$ depends on $j-i$ in a flexible chain. The dominant numerical values of $\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0$ are from pairs of i, j near the main diagonal of Figure 1 because the average dot product vanishes if the two bond vectors are connected by a sufficiently large number of bonds.

$$\lim_{k\to\infty}\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 = 0 \tag{7}$$

$S_{2,n}$ and $S_{3,n}$ increase without limit because an increase in n introduces new $\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0$ with pairs of i and j that lie near the main diagonal in Figure 1. The ratios $S_{2,n}/n$ and $S_{3,n}/n$ approach constant values as $n \to \infty$. In contrast, the value of $S_{1,n}$ itself approaches a well-defined limit as n increases. After n becomes sufficiently large, a further increase in n merely introduces new $\langle \mathbf{u}_i \cdot \mathbf{u}_j\rangle_0$ determined by pairs of i and j that lie far from the main diagonal in Figure 1, such that each new term is indistinguishable from zero.

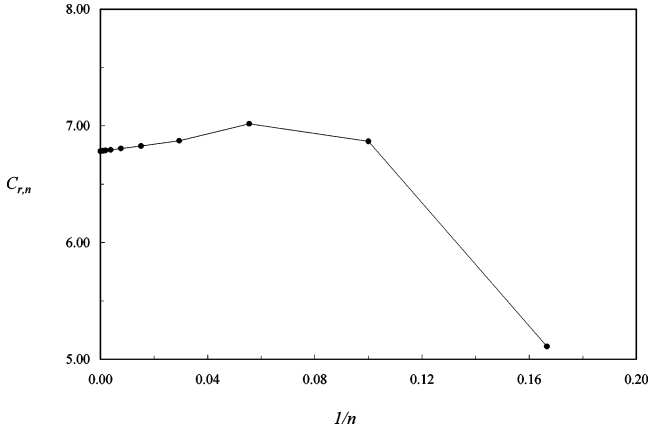

Figure 2. $C_{r,n}$ for *s*PMMA at 300 K, using the RIS model of Vacatello and Flory.[4]

The chain with $2n$ bonds has $2n - k$ combinations of $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle_0$ in $S_{1,2n} + S_{2,2n} + S_{3,2n}$ with $j - i = k$. This number decreases linearly as k increases. Much different behavior is seen with the terms that contribute to $S_{1,2n}$. Initially the number of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ in $S_{1,2n}$ *increases* linearly with an increase in k, there being k such terms if $1 \leq k \leq n$. As k increases beyond n, the number of terms decreases, with $2n - k$ terms when $n \leq k \leq 2n$. Since the $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ with $n \leq k \leq 2n$ can be ignored at sufficiently large n, for the reason stated in eq 7, the $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ with $1 \leq k \leq n$ controls the value of $S_{1,\infty}$.

$$S_{1,\infty} = \sum_{k=1}^{\infty} k \langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0 \tag{8}$$

Two simple chains demonstrate the validity of eq 8. The FJ chain, with $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0 = 0$ for $k \neq 0$, has $S_{1,\infty} = 0$, as required when $C_{r,n} = C_{r,\infty}$ at all values of n. Chains with a constant bond angle larger than 90° and free rotation (FR) about bonds have $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0 = \alpha^k$, with α denoting the cosine of the supplement of the bond angle. Then $S_{1,\infty} = \alpha(1 - \alpha)^{-2}$, which, along with $C_{r,\infty} = (1 + \alpha)/(1 - \alpha)$, produces $C_{r,\infty}^{-1}[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} = -2\alpha(1 + \alpha)^{-1}(1 - \alpha)^{-1}$, obtained previously by explicit evaluation of the derivative.[2] For these FR chains, $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ decreases monotonically as k increases, $S_{1,\infty} > 0$, and $C_{r,n}$ approaches $C_{r,\infty}$ from below.

D. Chains with Hindered Rotation

If $0 < \alpha < 90°$ and internal rotation about bonds is hindered, all $\mathbf{u}_i \cdot \mathbf{u}_{i+1} > 0$, but the status of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ with $k > 1$ is unknown until further information is available on the hindrance to rotation. Figure 3 sketches two plausible dependences of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ on k. A possible source of a monotonically decreasing curve, curve A, is a FR chain with $\theta > 90°$. The other curve, for which some of the $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ are negative, can arise if short subchains tend to follow a curved path, with this curve completing $^1/_4$ of an ellipse in m bonds, as depicted in Figure 4. For this curved subchain, $\mathbf{u}_i \cdot \mathbf{u}_{i+k}$ decreases monotonically as k increases from 1 to $m - 1$, and it reaches a value of zero when $k = m$. If the direction of curvature of the segment tends to be maintained as k becomes larger than m, $\mathbf{u}_i \cdot \mathbf{u}_{i+k}$ will become negative.

The term $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ can be computed as $\langle \mathbf{T}_i \mathbf{T}_{i+1} \ldots \mathbf{T}_{i+k-1} \rangle_{11}$ using the RIS model, where $\mathbf{T}_i$ denotes the matrix that transforms a vector from its representation

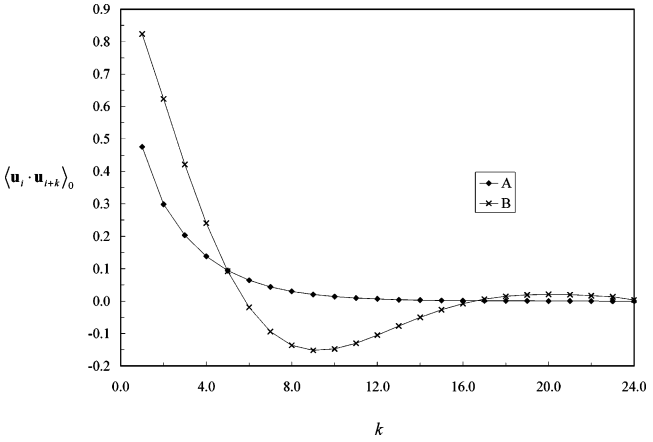

Figure 3. Sketches of two types of behavior for $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ with increasing values of k.

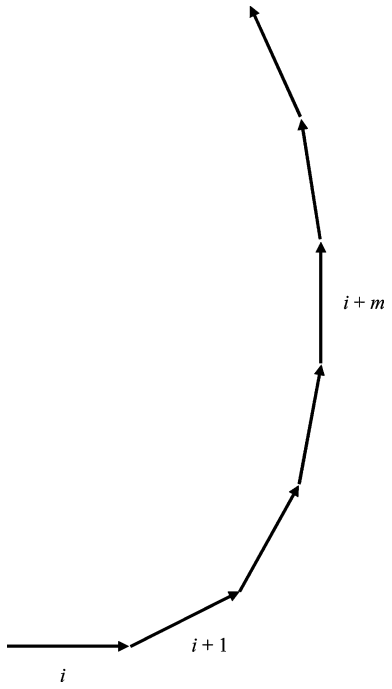

Figure 4. A curved chain segment that traces $^1/_4$ of an ellipse in m bonds. The projection of bond $i + m + 1$ onto bond i is negative.

in the local coordinate system of bond $i + 1$ into its representation in the local coordinate system of bond i.[15]

$$\langle \mathbf{T}_i \mathbf{T}_{i+1} \ldots \mathbf{T}_{i+k-1} \rangle_{11} = \langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0 = Z^{-1} \mathbf{U}_1 \mathbf{U}_2 \ldots \mathbf{U}_{i-1} \mathbf{F}_{[i} \mathbf{F}_{i+1} \ldots \mathbf{F}_{k-1]} \mathbf{U}_k \mathbf{U}_{k+1} \ldots \mathbf{U}_n \tag{9}$$

$$Z = \mathbf{U}_1 \mathbf{U}_2 \ldots \mathbf{U}_n \tag{10}$$

The conformational partition function is denoted by Z, $\mathbf{U}_i$ denotes the statistical weight matrix for bond i, and $\mathbf{F}_i$ is formulated from the transformation matrices and $\mathbf{U}_i$ using the operation Flory wrote as $(\mathbf{U}_i \otimes \mathbf{E}_3)||\mathbf{T}_i||$.[15]

Figure 5 depicts $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ as a function of k, using RIS models of Abe et al.[3] for polyethylene (PE), Flory et al.[16] for poly(dimethylsiloxane) (PDMS), and Vacatello and Flory for *s*PMMA.[4] Although the original references[3,4,16] present results for C_n, which depends on $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$, they do not present $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ explicitly. For the latter two polymers, the results are averages for the

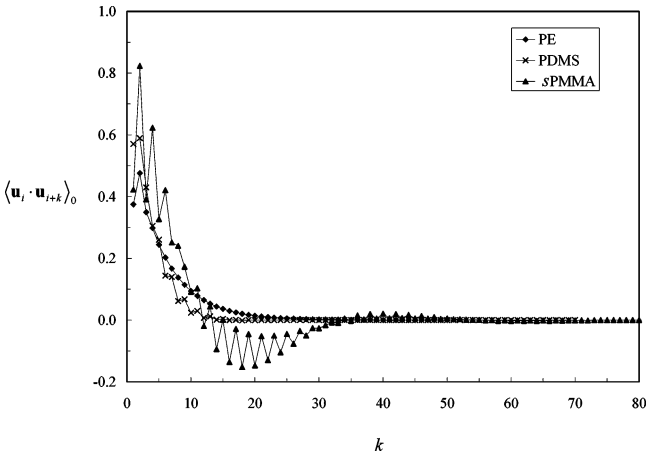

Figure 5. $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ vs k from RIS models for PE, PDMS, and *s*PMMA.

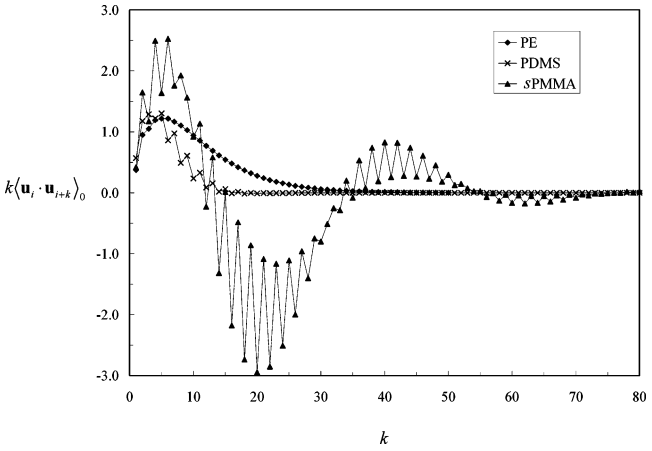

Figure 6. $k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ vs k from RIS models for PE, PDMS, and *s*PMMA.

two different choices of bond i, Si−O or O−Si for PDMS and C−CH_2 or CH_2−C for *s*PMMA. This additional averaging accounts for the different values of the Si−O−Si and O−Si−O bond angles in the former polymer and the C−CH_2−C and CH_2−C−CH_2 bond angles in the latter polymer. After an initial increase at very small k, the values of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ for PE decline continuously to zero as k increases. None of the $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ is negative in PE. A strong odd−even effect is seen in *s*PMMA. More importantly, *s*PMMA has substantial ranges of k over which $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ is negative. Negative values are obtained with $15 < k < 34$ and with $57 < k < 76$. The second negative region is not easily seen in Figure 5 because the absolute values of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ are small. PDMS shows behavior between the results for PE and *s*PMMA, with a weak odd−even effect, and a region where $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ is weakly negative. The most negative value of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ is −0.0007 at $k = 18$. It is not distinguishable from zero in Figure 5.

Figure 6 depicts the values of $k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ that are required for the calculation of $S_{1,\infty}$ for PE, PDMS, and *s*PMMA via eq 8. Inspection of Figure 6 shows that $S_{1,\infty}$ must be positive for PE and PDMS, and it must be larger for PE than for PDMS. Numerical calculation yields values of $S_{1,\infty}$ that are in excellent agreement with the results reported previously for these two polymers by another method,[2] as shown in Table 1. $C_{r,n}$ makes its final approach to $C_{r,\infty}$ from below in both polymers, and this approach is steeper for PE than for PDMS.

Table 1. Comparison of the Values of $S_{1,\infty}$ Obtained by Two Methods

chain	RIS model	$C_{r,\infty}$ [a]	$S_{1,\infty}$ from $[dC_{r,n}/d(1/n)]_{1/n=0}$ [b]	$S_{1,\infty}$ from $\sum k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ [c]
PE	ref 3	6.8	17.7	17.3
PDMS	ref 16	6.3	8.8	9.3
sPMMA	ref 4	6.8	−2.9	−2.8

[a] From linear extrapolation of $C_{r,n}$ vs $1/n$ to $1/n = 0$. Data for PE and PDMS are from ref 2. Data for *s*PMMA are in Figure 2. [b] From $[dC_{r,n}/d(1/n)]_{1/n=0}$ and eq 5. Data for PE and PDMS are from ref 2. Data for *s*PMMA are in Figure 2. [c] From Figure 6 and eq 8.

Casual inspection of Figure 6 is insufficient to convincingly establish the sign of $S_{1,\infty}$ for *s*PMMA because the positive and negative contributions largely cancel one another. Numerical evaluation shows a slight excess for the negative contributions, leading to a small negative value for $S_{1,\infty}$. The value of $S_{1,\infty}$ calculated from Figure 6 and eq 8 is in good agreement with the result obtained from Figure 2 and eq 5, as shown in Table 1. Although the region of negative $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ for *s*PMMA at $15 < k < 34$ is not impressive in Figure 5, the multiplication by k in Figure 6, as required for evaluation of $S_{1,\infty}$, shows that the subchains with $15 < k < 34$ are responsible for the negative sign for $S_{1,\infty}$ in *s*PMMA, causing $C_{r,n}$ to make its final approach to $C_{r,\infty}$ from above. Syndiotactic PMMA tends to form large loops, and these loops are responsible for the negative values of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ when k is in this range.[4]

E. The Relationship between $C_{s,n}$ and $C_{s,\infty}$

An expression for $[dC_{s,n}/d(1/n)]_{1/n=0}$ is obtained by a method similar to the approach used in section B to obtain eq 5. We begin with the definition of the squared radius of gyration for a specified configuration of $n + 1$ equally weighted points, indexed from 0 to n, in terms of the squared distances between points i and j, r_{ij}^2.[17]

$$s^2 = \frac{1}{(n+1)^2} \sum_{i=0}^{n-1} \sum_{j=i+1}^{n} r_{ij}^{\,2} \tag{11}$$

With all bonds fixed at unit length, averaging in the unperturbed, or Θ, state produces the characteristic ratio defined using the mean-square unperturbed radius of gyration.

$$C_{s,n} = \frac{1}{n(n+1)^2} \sum_{i=0}^{n-1} \sum_{j=i+1}^{n} \langle r_{ij}^{\,2} \rangle_0 \tag{12}$$

If we also assume that n is large enough so that it lies in the limiting region, where $C_{s,n}$ is a linear function of $1/n$,[8,9] the initial slope of $C_{s,n}$ vs $1/n$ can be written in a manner analogous to eq 3, and that expression can be written in terms of the $\langle r_{ij}^2 \rangle_0$ by using eq 12 for $C_{s,2n}$ and $C_{s,n}$.

$$\left[\frac{dC_{s,n}}{d(1/n)}\right]_{1/n=0} = \frac{-1}{(2n+1)^2} \sum_{i=0}^{2n-1} \sum_{j=i+1}^{2n} \langle r_{ij}^{\,2} \rangle_0 + \frac{2}{(n+1)^2} \sum_{i=0}^{n-1} \sum_{j=i+1}^{n} \langle r_{ij}^{\,2} \rangle_0 \tag{13}$$

It is convenient to separate the double sums over $\langle r_{ij}^2 \rangle_0$ for the chain with $2n$ bonds into three parts, in a

manner similar to the approach employed for the $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle_0$ in eq 4.

$$S_{s,1,2n} = \sum_{i=0}^{n-1} \sum_{j=n+1}^{2n} \langle r_{ij}^2 \rangle_0 \tag{14a}$$

$$S_{s,2,2n} = \sum_{i=n}^{2n-1} \sum_{j=i+1}^{2n} \langle r_{ij}^2 \rangle_0 \tag{14b}$$

$$S_{s,3,2n} = \sum_{i=0}^{n-1} \sum_{j=i+1}^{n} \langle r_{ij}^2 \rangle_0 \tag{14c}$$

As before, the two ends of the chain are assumed to be indistinguishable, $S_{s,2,2n} = S_{s,3,2n}$.

$$\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = \frac{-(n+1)^2 S_{s,1,2n} + 2n(3n+2)S_{s,3,2n}}{(n+1)^2(2n+1)^2} \tag{15}$$

The mean-square unperturbed end-to-end distance of a subchain must depend on its number of bonds, k, but we assume that it is independent of the location of the subchain within the chain. Then $\langle r_{i,i+k}^2 \rangle_0$ is independent of i and can be represented more simply by $\langle r_k^2 \rangle_0$. This notation converts the double sums in eqs 14a and 14c into single sums with the index k.

$$S_{s,1,2n} = \sum_{k=1}^{n} (k-1)\langle r_k^2 \rangle_0 + \sum_{k=n+1}^{2n} (2n+1-k)\langle r_k^2 \rangle_0 \tag{16}$$

$$S_{s,3,2n} = \sum_{k=1}^{n} (n+1-k)\langle r_k^2 \rangle_0 \tag{17}$$

Although the values of $\langle r_k^2 \rangle_0$ at small k do not lie in the limiting region where $C_{r,k}$ is a linear function of $1/k$, this problem becomes inconsequential if n is very large, so that $S_{s,1,2n}$ and $S_{s,3,2n}$ are dominated completely by the more numerous, and larger, values of $\langle r_k^2 \rangle_0$ that fall within the asymptotic region. With this assumption and eq 5

$$C_{r,k} = C_{r,\infty} - 2S_{1,k}/k \tag{18}$$

$$\langle r_k^2 \rangle_0 = kC_{r,\infty} - 2S_{1,k} \tag{19}$$

The $S_{1,k}$ in these two equations is the double sum over the $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle_0$ in eq 4a. Application of eq 19 to the expressions for $S_{s,1,2n}$ and $S_{s,3,2n}$ lets us write these sums in terms of n, $C_{r,\infty}$, and $S_{1,2n}$.

$$S_{s,1,2n} = n^2(n+1)C_{r,\infty} - 2n^2 S_{1,2n} \tag{20}$$

$$S_{s,3,2n} = (1/6)n(n+1)(n+2)C_{r,\infty} - n(n+1)S_{1,2n} \tag{21}$$

Combining eqs 20 and 21 with eq 16 and taking the limit as $n \rightarrow \infty$, we finally obtain a simple expression for the initial slope of $C_{s,n}$ vs $1/n$.

$$\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = C_{s,\infty} - S_{1,\infty} \tag{22}$$

Model chains demonstrate the validity of eq 22. The FJ chain has $S_{1,\infty} = 0$ because the $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k} \rangle_0$ are zero if $k \neq 0$. Therefore, $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0} = C_{s,\infty} = {}^1/_6$, which follows from the expression for the mean-square radius of gyration of this chain, $\langle s^2 \rangle_0 = (1/6)n(n+2)(n+1)^{-1}l^2$. The FR chains with $\alpha > 0$ have $C_{s,\infty} = (1/6)(1+\alpha)(1-\alpha)^{-1}$ and $S_{1,\infty} = \alpha(1-\alpha)^{-2}$. With eq 22, we recover $C_{s,\infty}{}^{-1}[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0} = 1 - 6\alpha(1+\alpha)^{-1}(1-\alpha)^{-1}$, which was obtained previously using another method.[2]

The results of calculations performed using RIS models for PE,[3] PDMS,[16] and polyisobutylene (PIB)[18] are presented in Table 2. Equation 22 reproduces quite nicely the values of $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0}$ obtained by direct calculation of $C_{s,n}$ vs $1/n$. The RIS calculations for *s*PMMA in Figure 2 specify $C_{s,\infty} = (1/6)C_{r,\infty} = 1.13$ and $S_{1,\infty} = -2.9$. From eq 22, we obtain $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0} = 4$. The positive sign deduced for $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0}$ for *s*PMMA is consistent with measurements of $\langle s^2 \rangle_0$ using nearly monodisperse samples of atactic PMMA in which 80% of the diads were racemo.[5] The measured values of $\langle s^2 \rangle_0/M$ pass through a broad maximum when M is between 10^3 and 10^4, and the final approach of $\langle s^2 \rangle_0/M$ to its asymptotic limit is from above.

Table 2. Comparison of the Values of $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0}$ Obtained by Two Methods

chain	RIS model	$C_{s,\infty}$ [a]	$S_{1,\infty}$ [b]	$C_{s,\infty} - S_{1,\infty}$	$[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0}$ [c]
PE	ref 3	1.14	18	−17	−18
PDMS	ref 16	1.05	8.8	−7.8	−8.4
PIB	ref 18	1.10	16	−15	−15

[a] From the linear extrapolation of $C_{s,n}$ vs $1/n$ to $1/n = 0$ in ref 2. [b] From eq 5 and the initial slope of $C_{r,n}$ vs $1/n$ in ref 2. [c] From the initial slope of $C_{s,n}$ vs $1/n$ in ref 2.

F. The Relationship between the Finite Chain Size Effects on $C_{r,n}$ and $C_{s,n}$

The relationship between the finite chain size effects on $C_{r,n}$ and $C_{s,n}$ is obtained by elimination of $S_{1,\infty}$ from eq 5 and eq 22.

$$\left[\frac{\mathrm{d}C_{r,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} = 2\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} - 2C_{s,\infty} \tag{23}$$

Comparison of the data in the third and final columns of Table 2 suggests there may be real flexible polymers for which a useful approximation is obtained when $2C_{s,\infty}$ is dropped from eq 23. (This simplification is not universal. It is unacceptable for the FJ chain, which has $[\mathrm{d}C_{r,n}/\mathrm{d}(1/n)]_{1/n=0} = 0$, $[\mathrm{d}C_{s,n}/\mathrm{d}(1/n)]_{1/n=0} = {}^1/_6$, and $C_{s,\infty} = {}^1/_6$.) Then a simpler approximate relationship between the initial slopes is obtained.

$$\left[\frac{\mathrm{d}C_{r,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} \cong 2\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} \tag{24}$$

If data are normalized so that all of the intercepts at $1/n = 0$ are equal to 1, the comparison is altered by the factor of 6 that comes from $C_{s,\infty} = (1/6)C_{r,\infty}$, reproducing a relationship noted previously.[2]

$$\frac{1}{C_{r,\infty}}\left[\frac{\mathrm{d}C_{r,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} \cong \frac{1}{3C_{s,\infty}}\left[\frac{\mathrm{d}C_{s,n}}{\mathrm{d}(1/n)}\right]_{1/n=0} \tag{25}$$

G. Implications for the Interpretation of Experimental Data: The "Persistence Length"

$S_{1,\infty}$ is accessible from measurement of $\langle s^2 \rangle_0$ as a function of M. $C_{s,\infty}$ is obtained from the intercept at $1/n$

$= 0$ in a plot of $C_{s,n}$ vs $1/n$. With this value of $C_{s,\infty}$ and the initial slope, the value of $S_{1,\infty}$ is obtained using eq 22. The measurement of $C_{s,n}$ as a function of n then leads directly to $[dC_{r,n}/d(1/n)]_{1/n=0}$ via eq 23.

The inequality of the values of $[dC_{r,n}/d(1/n)]_{1/n=0}$ and $[dC_{s,n}/d(1/n)]_{1/n=0}$ has implications for the interpretation of experimental results that measure the finite chain effect. Techniques for experimental measurements of the mean-square unperturbed dimensions rarely measure $\langle r^2\rangle_0$ directly. They are more likely to measure $\langle s^2\rangle_0$. Conversion between the two measures of the mean-square unperturbed dimensions is simple in the asymptotic limit as $n \rightarrow \infty$, where $\langle r^2\rangle_0 \rightarrow 6\langle s^2\rangle_0$ can be assumed with confidence.[1] But eq 23 shows a significantly different relationship between the approaches to the asymptotic limit for these two measures of the mean-square unperturbed dimensions. It is dangerous to blindly use theoretical equations derived specifically for $\langle r^2\rangle_0$ to interpret a finite chain size effect characterized by experimental measurement of $\langle s^2\rangle_0$.

Measurements of the finite chain size effect on the characteristic ratio are sometimes used to estimate a value of the persistence length, a_{cc}, for the continuously curved, wormlike, or Porod−Kratky chain,[6,7] using something like

$$C_{r,n}/C_{r,\infty} = 1 - a_{cc}(1/r_{max}) \tag{26}$$

where r_{max}, the contour length, is proportional to n. The data in Table 1 stress the danger of this approach. Three chains with nearly identical $C_{r,\infty}$ have drastically different initial slopes of $C_{r,n}/C_{r,\infty}$ vs $1/n$. Interpretation of the data for these three chains using eq 26 leads to the uncomfortable conclusion that either the persistence length or contour length is *negative* for one of these chains.

The origin of the failure of eq 26 is easily seen. The continuously curved wormlike chain has the same curvature everywhere, and the *direction* of that curvature decorrelates over an infinitesimally small increment in the contour length. That rapid decorrelation in the direction of the curvature is contradicted by the schematic model depicted in Figure 4, where the direction of the curvature tends to be maintained for a significant number of bonds, leading to $\mathbf{u}_i \cdot \mathbf{u}_{i+k} < 0$. Real chains, such as *s*PMMA, may require many bonds before decorrelation of the direction of curvature is achieved. This behavior has a direct impact on the behavior of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ and hence $S_{1,\infty}$. It should not be surprising to learn that nonsense follows from an attempt to interpret the properties of such chains with the model of the continuously curved chain because that model ignores the slow decorrelation in the direction of curvature of the real chain.

It is worthwhile to examine another property of the chain that has some of the attributes of a persistence length. Let a_d denote the average projection of the end of a long unperturbed chain onto bond i. (This a_d is not identical with the persistence length a_{cc} defined for the continuously curved wormlike chain,[6,7] because a continuously curved chain is not composed of discrete bonds, and the angle between a discrete bond and the "contour" at that location is not well-defined. The "d" and "cc" in the subscripts emphasize this distinction in the definitions of a.) The contribution made to a_d by bond $i + k$ is the average projection of bond vector $\mathbf{l}_{i+k}$ onto bond i. This term depends on the length of bond $i + k$, denoted l_{i+k}, and the average projection of the corresponding unit vector, written in the previous sections as $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$.

Table 3. Values of a_d for RIS Models of Three Unperturbed Chains

chain	$\sum_{k=1}^{\infty}\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$	l, nm	a_d, nm	$C_{r,\infty} = 6C_{s,\infty}$
PE	2.9	0.154	0.45	6.8
PDMS	2.6	0.164	0.43	6.3
sPMMA	2.8	0.154	0.43	6.8

$$a_d = \sum_{k=1}^{\infty} l_{i+k}\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 \tag{27}$$

Comparison with eq 8 shows that a_d and $S_{1,\infty}$ are identical only when $l_{i+k} = k$, which is unlikely in any real chain, where l_{i+k} is real but k is an integer.

There are real polymers for which it is acceptable to assume that all of the bonds in the chain are of the same length, l. For these chains the defining expression for a_d becomes

$$a_d = l\sum_{k=1}^{\infty}\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 \tag{28}$$

For PE, PDMS, and *s*PMMA, the value of a_d specified by eq 28 is the length of a C−C or Si−O bond multiplied by the area under the appropriate curve in Figure 5. This figure specifies nearly identical numerical values of a_d for these three polymers, as shown in Table 3. The similar values of a_d for these three chains are consistent with their nearly identical $C_{r,\infty}$. In contrast, the a_{cc} defined by eq 26 for the same three chains differ strongly, with one of these a_{cc} being negative if contour lengths are defined to be positive.

Of course, it is the area under the curve in Figure 6 that determines the value of $S_{1,\infty}$ and hence $[dC_{r,n}/d(1/n)]_{1/n=0}$. From eq 8 and eq 28, $S_{1,\infty}$ is related to a_d/l by

$$S_{1,\infty} = a_d/l + \sum_{k=1}^{\infty}(k-1)\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 \tag{29}$$

If all bonds are of the same length, the general relationships between a_d and the initial slopes are obtained from eqs 5, 22, and 29.

$$\frac{a_d}{l} = -\frac{1}{2}\left[\frac{dC_{r,n}}{d(1/n)}\right]_{1/n=0} - \sum_{k=1}^{\infty}(k-1)\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 = -\left[\frac{dC_{s,n}}{d(1/n)}\right]_{1/n=0} + C_{s,\infty} - \sum_{k=1}^{\infty}(k-1)\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0 \tag{30}$$

An inquiry into the numerical importance of the troublesome summation that appears explicitly in eq 30 can utilize simple analytical expressions if attention is restricted to FR chains. Then this sum is equal to $-\alpha^2(1-\alpha)^{-2}$, and the remaining terms in eq 30 are $-(1/2)[dC_{r,n}/d(1/n)]_{1/n=0} = -[dC_{s,n}/d(1/n)]_{1/n=0} + C_{s,\infty} = \alpha(1-\alpha)^{-2}$. Two important conclusions arise. First, with $0 < \alpha < 1$, the explicit sum is of opposite sign from the remaining expressions in eq 30. Failure to consider the explicit sum leads to an overestimation of the value of a_d for FR chains. Second, the relative size of the error depends on the stiffness of the chain. The ratio of the incorrect value of a_d (deduced by ignoring the explicit sum) to its true value is $\alpha(1-\alpha)^{-2}\,[\alpha(1-\alpha)^{-2}$

Table 4. RIS Data Relevant to the Relationship between a_d and the Initial Slopes

chain	$(1/2)[dC_{r,\infty}/d(1/n)]_{1/n=0}$	$[dC_{s,n}/d(1/n)]_{1/n=0} - C_{s,\infty}$	$\sum_{k=1}^{\infty}(k-1)\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$
PE	−17	−17	14
PDMS	−9.0	−9.4	6.7
sPMMA	2.8	2.9	−5.6

$-\alpha^2(1-\alpha)^{-2}]^{-1} = (1-\alpha)^{-1}$. The relative error becomes more severe as α increases, i.e., as the chain becomes stiffer.

Some pertinent data for RIS chains are presented in Table 4. Of course, the signs of the terms for sPMMA in Table 4 have no counterpart in the FR chains. Nevertheless, these three RIS chains share with FR chains the property that the explicit sum in eq 30 is of opposite sign from the remaining terms. The RIS chains show that severe consequences for the estimate of a_d can occur if the explicit sum is ignored. The error can exceed 100% in the RIS chains, all three of which have values of a_d/l in the range 2.6−2.9.

The numerical impact of the explicit sum in eq 30 complicates the task of extracting a reliable value of a_d from measurements of the M dependence of $C_{s,n}$. That information could be determined by the following approach. The experimental measurements of $C_{s,n}$ vs $1/n$ provide an excellent data set for the validation of a proposed RIS model for the chain. All values of $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ are then available from that validated model through eq 9, and these $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ lead directly to a_d through eq 28.

We close with a conjecture that is suggested by the contrast in important attributes of $S_{1,\infty}$, a_d, and a_{cc}. Of these three properties, only $S_{1,\infty}$ is easily accessible from well-defined experiments and has a straightforward relationship to the unperturbed dimensions of finite chains. In contrast, the route to an experimental value of a_d is much less direct because this property is less directly tied to the finite chain size effect on the unperturbed dimensions. The persistence length for the continuously curved chain, a_{cc}, is even worse because it is negative for some real chains. For these reasons, might the rationalization of some physical properties of polymers that depend on the finite chain effect be more easily, or accurately, accomplished in terms of $S_{1,\infty}$, instead of in terms of a_{cc} or a_d? The initial slope of $C_{r,n}$ vs $1/n$ is indeed of fundamental significance, but it is misleading, and wrong, to interpret this fundamental property as being determined by a persistence length. The controlling physical property is $S_{1,\infty} = \sum_{k=1}^{\infty} k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$.

H. Conclusions

Starting from the definitions of the end-to-end vector and the squared radius of gyration, and assuming only a flexible homopolymer with indistinguishable ends, we obtain simple expressions for the final asymptotic approach of $C_{r,n}$ and $C_{s,n}$ to their asymptotic limits. For many chains, the relationship of $[\partial C_{r,n}/\partial(1/n)]_{1/n=0}$ and $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$ is approximately a factor of 2, but other values are possible. The final approach of $C_{r,n}$ to its limit is determined completely by $\sum k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$, and the final approach of $C_{s,n}$ to its limit is determined jointly by this same sum and $C_{s,\infty}$. Since $\sum k\langle \mathbf{u}_i \cdot \mathbf{u}_{i+k}\rangle_0$ can be either positive or negative, both $[\partial C_{r,n}/\partial(1/n)]_{1/n=0}$ and $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$ can be either positive or negative. Two different chains may have indistinguishable values of $C_{r,\infty}$ (or $C_{s,\infty}$) and yet have different *signs* for $[\partial C_{r,n}/\partial(1/n)]_{1/n=0}$ (or $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$). Polyethylene and syndiotactic poly(methyl methacrylate) are a pair of real chains that exhibit this behavior. Attempts to extract structural parameters from measured values of $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$ should recognize that chains with the same value of $C_{s,\infty}$ can have different sizes (and signs) for $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$. Acceptable theoretical treatments for the mean-square unperturbed dimensions should also be consistent with this behavior of $C_{s,\infty}$ and $[\partial C_{s,n}/\partial(1/n)]_{1/n=0}$.

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