Variability in the Persistence Length of an Atactic Polymer Due to Quenched Randomness, As Illustrated by Atactic Polystyrene

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ABSTRACT: The persistence lengths of atactic polystyrene (PS) have a broad distribution due to the quenched randomness of the stereochemical sequences. The breadth of this distribution, and the implications for dynamic properties, is deduced from explicit calculations of the averaged end-to-end vector, $\langle \mathbf{r} \rangle$, for all 2^x stereochemical sequences of methyl-terminated oligomers with x up to 15, where x denotes the number of phenyl side chains in the methyl-terminated oligomer. There is a large variation in the values of $\langle \mathbf{r} \rangle$ for long subchains of atactic PS, depending on the stereochemical sequence within the given subchain. Average results, and the fluctuations in these results, are obtained for PS over the entire range of the probability of a *meso* diad, p_m, with the assumption of Bernoullian statistics for the stereochemical sequences. These fluctuations are large at the intermediate values of p_m characteristic of conventional atactic PS. The results imply that beads representing Kuhn monomers in a given atactic PS chain have an extremely broad distribution for τ_0/ζ, where τ_0 is the Kuhn monomer relaxation time and ζ is the friction coefficient. This broad distribution, which is an inherent property of atactic chains, may be a contributing factor in earlier experimental observations of discrepancies in segment sizes deduced from static and dynamics measurements.

Introduction

Atactic vinyl polymers have quenched randomness in their stereochemical sequences. This quenched randomness causes vinyl polymers with $0 < p_m < 1$, where p_m denotes the probability for a *meso* diad, to be fundamentally different from chains with $p_m = 0$ or $p_m = 1$. In samples with intermediate stereochemical composition, it is unlikely that any two long chains will have exactly the same stereochemical sequence or the same conformational partition function. Therefore, Flory stated that vinyl polymers with intermediate stereochemical composition are properly considered as copolymers.[1] The quenched randomness of the stereochemical sequences in turn produces a quenched random variation in the local stiffness (persistence length, Kuhn length) as one proceeds along an atactic chain from one end to the other. Here we determine the strength of this variation for polystyrene and show that it has consequences for the dynamic properties of this polymer.

The stiffness of an unperturbed homopolymer is often characterized using average conformation-dependent physical properties in the limit as $n \rightarrow \infty$, where n denotes the number of bonds in the chain. A large value of the characteristic ratio, defined in eq 1, signifies a stiff chain.[2]

$$C_\infty \equiv \lim_{n\rightarrow\infty} \frac{\langle r^2 \rangle_0}{nl^2} \tag{1}$$

Here $\langle r^2 \rangle_0$ denotes the mean-square unperturbed end-to-end distance. The value of C_∞ is useful when the model for the chain is constructed with discrete bonds of length l.

Some coarse-grained models, such as a continuously curved (Porod−Kratky or wormlike) chain, do not employ discrete bonds.[3−5] The persistence length, a, is often employed to characterize the stiffness of the continuously curved chain. A related parameter, the Kuhn length, is twice the persistence length, $b = 2a$. For a model of a simple chain with discrete bonds, a can be approximated as the average projection, in the limit as $n \rightarrow \infty$, of the end-to-end vector for the subchain from bond i through n onto the direction of the first bond.

$$a \equiv \frac{\mathbf{l}_i}{l_i} \lim_{n\rightarrow\infty} \langle \sum_{j=i}^{n} \mathbf{l}_j \rangle \tag{2}$$

The concept of a Kuhn length is often used to determine the size of a "segment" of a coarse-grained chain. It is also sometimes used for the study of chain dynamics, through the use of a Kuhn monomer relaxation time, τ_0.[6]

$$\tau_0 \approx \frac{\zeta b^2}{k_B T} \tag{3}$$

Here ζ is the bead friction coefficient, k_B is Boltzmann's constant, and T is the absolute temperature.

Comparison of eqs 2 and 3 implies qualitatively different dynamic behavior for simple chains, such as polyethylene (PE), and atactic vinyl polymers, such as polystyrene (PS), in which there is a quenched random variation in local stiffness as one proceeds along the atactic chain. For the simple chain, the same value of a is specified by eq 2, independent of how i is assigned and independent of which chain from a multichain ensemble is selected. Therefore, eq 3 leads to the conclusion that all coarse-grained beads, in all of these simple chains, are characterized by the same Kuhn monomer relaxation time. A very different result is obtained for a typical ensemble of atactic PS (aPS) chains due to the quenched randomness in the stereochemical sequence from one chain to the next as well as the quenched randomness in stereochemical sequences for different subchains within a given chain. The value of a obtained from eq 2 now depends both on the particular chain selected and also on the value of i used to define the particular subchain within that chain. Therefore, from eq 3, we must conclude that it can be dangerous to interpret the dynamics of aPS (or any atactic polymer) with a model that postulates a single value of τ_0 for

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all beads in the system. While such a postulate may be useful for a simple chain such as polyethylene (PE), it may become troublesome for atactic polymers. It may contribute to several experimental observations that imply a different segment size for dynamic and static properties of aPS.[7−10]

This article provides an estimate of the likely dispersion in the values of τ_0 that can arise from this source in an atactic polymer, using aPS as the specific example. We do so by study of the conformationally averaged end-to-end vector, $\langle \mathbf{r} \rangle$, for methyl-terminated oligomers of PS. The approach explicitly considers all 2^x stereochemical sequences of H−$(CH_2CHC_6H_5)_x$−CH_3 for $x = 1-15$. The 2^x conformationally averaged $\langle \mathbf{r} \rangle$ are calculated at each value of x. These discrete results are then used to determine the dispersion of a in longer PS chains over the entire physically accessible range for the probability of a *meso* diad, $0 \leq p_m \leq 1$, given the assumption of Bernoullian statistics in the averaging of the $\langle \mathbf{r} \rangle$ for the various stereochemical sequences with $0 < p_m < 1$. The dispersion of a, and hence τ_0, is large for aPS chains.

Computational Details

Conformation-dependent physical properties of PS have been studied using numerous simulation techniques, including molecular dynamics,[11−13] Monte Carlo[14] simulations of atomistically detailed models, and, more recently, simulations of coarse-grained models for this polymer.[15−18] For present purposes, the rotational isomeric state (RIS) model[19,20] is ideal because it incorporates all of the necessary structural detail and does so with a method that is computationally efficient, allowing investigation of an enormous number of different stereochemical sequences with reasonable computational resources. The RIS model is used here to calculate $\langle \mathbf{r} \rangle$ for all 2^x stereochemical sequences of unperturbed methyl-terminated oligomers of PS, H−$(CH_2CHC_6H_5)_x$−CH_3, $x = 1-15$.

The calculations are performed with the specific RIS model for PS that was described by Yoon et al.,[21] using the precise bond lengths, bond angles, torsion angles, and statistical weights specified by Rehahn et al.[22] as entry A048 in their extensive tabulation of RIS models of polymers. The temperature is 300 K. Torsion angles for *trans* and *gauche* conformations are displaced by 10° from 180° and ±60°, respectively, in the manner specified by Yoon et al.[21]

The carbon atoms in the terminal methyl groups define the length of $\mathbf{r}$. For every stereoisomer of every oligomer, $\langle \mathbf{r} \rangle$ is expressed in a local Cartesian coordinate system defined by the first two C−C bonds in the chain. The carbon atoms in the main chain are indexed from 0 to n, starting at one terminal methyl group and ending at the other terminal methyl group. Bond vector $\mathbf{l}_i$ points from chain atom $i-1$ to chain atom i. Following Flory,[19] the X axis of the internal coordinate system used for $\langle \mathbf{r} \rangle$ lies along $\mathbf{l}_1$, the Y axis is in the plane of $\mathbf{l}_1$ and $\mathbf{l}_2$, with a positive projection on $\mathbf{l}_2$, and the Z axis completes a right-handed Cartesian coordinate system. This coordinate system is depicted in Figure 1. In this coordinate system, $\mathbf{r}$ for the single conformation of 2-phenylpropane has the components presented in eq 4.

$$\mathbf{r}/l = \begin{bmatrix} 1.38 \\ 0.93 \\ 0 \end{bmatrix} \tag{4}$$

All larger oligomers have multiple stereochemical sequences, each of which has access to multiple conformations.

The stereochemical sequence of an oligomer will be expressed using *meso* (*m*) and *racemo* (*r*) diads and also using *d* and *l* pseudoasymmetric centers. Let $\mathbf{l}_i$ denote the vector for a C^α−CH_2 bond, expressed in its own coordinate system, where C^α denotes a main-chain carbon atom that bears a C_6H_5 substituent. We define C^α as a *d* (or *l*) pseudoasymmetric center if C_6H_5 lies in the positive (or negative) direction along the Z axis of this local coordinate system.

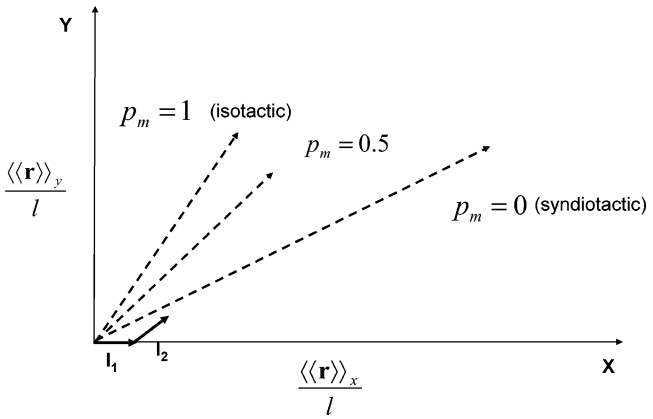

Figure 1. X and Y axes of the internal Cartesian coordinate system in which $\langle \mathbf{r} \rangle$ is expressed. The Z axis is directed toward the viewer. This coordinate system is defined by the first two bond vectors, $\mathbf{l}_1$ and $\mathbf{l}_2$. The figure also depicts asymptotic persistence vectors (normalized by l) for PS chains with $p_m = 0.0$, 0.5, and 1.0.

Table 1. Conformationally Averaged Components of $\langle \mathbf{r} \rangle$ for All Stereoisomers of 2,4-Diphenylpentane

pseudoasymmetric centers[a]	diad[b]	$\langle \mathbf{r} \rangle_X/l$	$\langle \mathbf{r} \rangle_Y/l$	$\langle \mathbf{r} \rangle_Z/l$
dd	*m*	2.03	1.54	0.95
ll	*m*	2.03	1.54	−0.95
dl	*r*	2.49	1.58	0.46
ld	*r*	2.49	1.58	−0.46

[a] Stereochemical sequence expressed using *d* and *l* pseudoasymmetric centers. [b] Stereochemical sequence expressed using *m* and *r* diads.

Table 2. Conformationally Averaged Components of $\langle \mathbf{r} \rangle$ for All Stereoisomers of 2,4,6-Triphenylheptane

pseudoasymmetric centers[a]	diads[b]	$\langle \mathbf{r} \rangle_X/l$	$\langle \mathbf{r} \rangle_Y/l$	$\langle \mathbf{r} \rangle_Z/l$
ddd	*mm*	1.81	2.12	0.95
lll	*mm*	1.81	2.12	−0.95
ddl	*mr*	2.26	2.25	1.69
lld	*mr*	2.26	2.25	−1.69
dll	*rm*	3.12	1.95	−0.21
ldd	*rm*	3.12	1.95	0.21
dld	*rr*	3.56	2.06	0.43
ldl	*rr*	3.56	2.06	−0.43

[a] Stereochemical sequence expressed using *d* and *l* pseudoasymmetric centers. [b] Stereochemical sequence expressed using *m* and *r* diads.

Components of $\langle \mathbf{r} \rangle$ for Very Short Oligomers. Tables 1 and 2 present the $\langle \mathbf{r} \rangle$ for the four and eight stereochemical sequences of 2,4-diphenylpentane and 2,4,6-triphenylheptane, the oligomers with $x = 2$ and 3. These oligomers have positive values of $\langle \mathbf{r} \rangle_X$ and $\langle \mathbf{r} \rangle_Y$. The largest value of $\langle \mathbf{r} \rangle_X$ is obtained for the completely *racemo* stereoisomers due to the strong preference by the *r* diad for propagation of sequences of *trans* conformations at the internal C−C bonds. Identical values of $\langle \mathbf{r} \rangle_X$ and $\langle \mathbf{r} \rangle_Y$ are obtained for each stereochemical sequence and its mirror image.

Individual stereoisomers have nonzero $\langle \mathbf{r} \rangle_Z$. These nonzero components are of equal absolute value, but opposite in sign, when one compares any stereochemical sequence and its mirror image. Therefore, $\langle \mathbf{r} \rangle_Z = 0$ in any racemic ensemble. The nonzero $\langle \mathbf{r} \rangle_Z$ in individual sequences is evident only when the

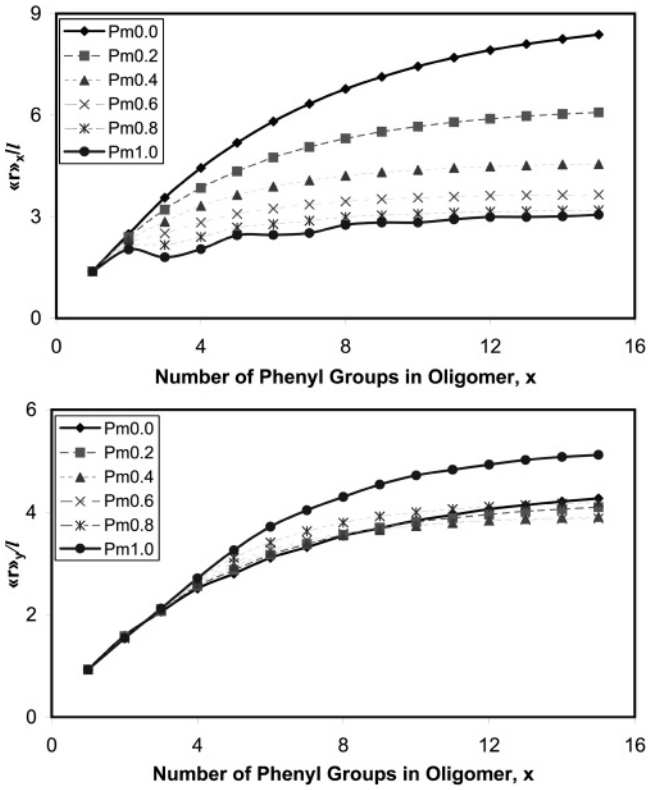

Figure 2. *X* and *Y* components of dimensionless $\langle\langle \mathbf{r} \rangle\rangle/l$ for methyl-terminated oligomers with *x* phenyl units, as a function of *x*. The *Z* component of $\langle\langle \mathbf{r} \rangle\rangle/l$ is always zero. Data are presented for the six values of p_m in the series 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0. Bernoullian statistics is assumed for the stereochemical sequences when $0 < p_m < 1$.

distinction between a stereochemical sequence and its mirror image is retained. This distinction requires expression of the stereochemical sequence as a string of *d* and *l* pseudoasymmetric centers. Information about the nonzero $\langle \mathbf{r} \rangle_Z$ components is suppressed upon averaging $\langle \mathbf{r} \rangle$ over a stereochemical sequence and its mirror image, as is done when the stereochemical sequence is expressed using *m* and *r* diads.

The sequences with the largest absolute values for $\langle \mathbf{r} \rangle_Z$ are those that contain an initial *m* diad. The *gauche* conformation in the strongly preferred *trans*−*gauche* and *gauche*−*trans* conformations within the initial *m* diad tends to displace the trajectory of the chain out of the *X*−*Y* plane. The sign of this displacement along the *Z* axis depends on whether the initial *m* diad is *dd* or *ll*. This initial displacement of the average chain trajectory out of the *XY* plane tends to be maintained if the initial *m* diad is followed by an *r* diad because the latter diad prefers the *trans*−*trans* conformation. Therefore, the $\langle \mathbf{r} \rangle_Z$ with the largest absolute values in Table 2 are obtained with the *ddl* and *lld* (*mr*) sequences.

Averages for Longer Oligomers and for the Polymer. In the remainder of this article, we will enclose **r** in single angle brackets, $\langle \mathbf{r} \rangle$, to denote a conformational average of **r** for a *single* stereochemical sequence. Double angle brackets, $\langle\langle \mathbf{r} \rangle\rangle$, will denote an additional average of the 2^x values of $\langle \mathbf{r} \rangle$ for all possible sequences of the oligomer with *x* phenyl side chains. These higher averages depend on the value of p_m used in weighting the contribution of $\langle \mathbf{r} \rangle$ from each of the 2^x stereochemical sequences. Thus, $\langle\langle \mathbf{r} \rangle\rangle$ depends on p_m, whereas the 2^x values of $\langle \mathbf{r} \rangle$ from which it is derived are independent of p_m.

The values of $\langle\langle \mathbf{r} \rangle\rangle_X$ and $\langle\langle \mathbf{r} \rangle\rangle_Y$ depend on *x* at small *x*, but they approach asymptotic limits as *x* increases, as shown in Figure 2. The tendency for propagation of a 3-fold helix in the isotactic chain is responsible for the nonmonotonic dependence of $\langle\langle \mathbf{r} \rangle\rangle_X$ on *x* at small *x* when $p_m = 1$. It is apparent that $\langle\langle \mathbf{r} \rangle\rangle_X$ tends to depend more strongly on p_m than does $\langle\langle \mathbf{r} \rangle\rangle_Y$. The largest value of $\langle\langle \mathbf{r} \rangle\rangle_X$ is obtained for the syndiotactic chain, $p_m = 0.0$, due to its strong preference for propagation of sequences of *trans* conformations at the internal C−C bonds. The preference for *trans*−*gauche* helixes in the isotactic chain, $p_m = 1.0$, produces a smaller value of $\langle\langle \mathbf{r} \rangle\rangle_X$, but this stereochemical composition produces the largest value of $\langle \mathbf{r} \rangle_Y$ in long chains. The values of $\langle\langle \mathbf{r} \rangle\rangle_Z$ are zero throughout because the averaging process assigns equal weight to any stereochemical sequence and its mirror image.

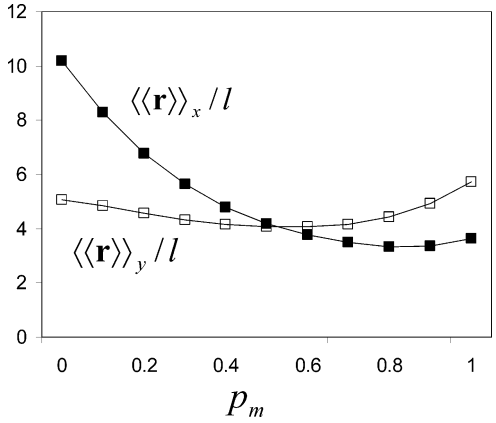

Figure 3. Asymptotic limits for the *X* and *Y* components of $\langle\langle \mathbf{r} \rangle\rangle/l$ as a function of p_m. The *Z* component is always zero.

Extrapolation of the $\langle\langle \mathbf{r} \rangle\rangle$ for each p_m to infinitely long chains was guided by the fact that C_n for a homopolymer with bonds of the same length becomes linear in $1/n$ as $n \rightarrow \infty$.[23] Since the persistence length for a relatively stiff homopolymer in which all bonds are of the same length is nearly proportional to C_∞, via $a = (l/2)(C_\infty + 1)$, we also adopt an extrapolation linear in $1/x$ for the components of the conformationally averaged end-to-end vector. The limiting values obtained by this extrapolation are depicted in Figure 3. The dependence of a component on p_m is stronger for $\langle\langle \mathbf{r} \rangle\rangle_X$ than for $\langle\langle \mathbf{r} \rangle\rangle_Y$. Since the isotactic and syndiotactic chains favor propagation of specified conformations, which are the 3-fold helix and extended chain, respectively, the components depicted in Figure 3 are relatively large at the extremes, where p_m is either 0 or 1. The largest component is $\langle\langle \mathbf{r} \rangle\rangle_X/l$ for the syndiotactic chain due to the fact that a segment of chain with all bonds in the *trans* conformation has a larger extension in the direction of the first bond. Disruption of the preferred conformations, which occurs when p_m moves toward the middle of its range, produces a decrease in the averaged components. No special significance should be attributed to the fact that both components have nearly the same value when $p_m = 0.5$ in polystyrene. Other types of atactic chains, subject to different short-range interactions, might behave otherwise. The orientation and lengths of the limiting $\langle\langle \mathbf{r} \rangle\rangle$ are emphasized in Figure 1, which includes $\mathbf{l}_1$ and $\mathbf{l}_2$, the two bond vectors that define the local Cartesian coordinate system in which $\langle \mathbf{r} \rangle$ is expressed.

Fluctuations. Although the *Z* component makes no contribution to $\langle\langle \mathbf{r} \rangle\rangle$ for racemic ensembles, this component cannot be ignored when we consider the values of $\langle \mathbf{r} \rangle$ for individual stereochemical sequences within this ensemble. This conclusion is immediately evident upon inspection of Tables 1 and 2. The range for $\langle \mathbf{r} \rangle_Z/l$, from −0.95 to +0.95 when $x = 2$, and −1.69 to +1.69 when $x = 3$, is much broader than the range for either $\langle \mathbf{r} \rangle_X/l$ or $\langle \mathbf{r} \rangle_Y/l$. If we were to consider the ensembles for 2,4-

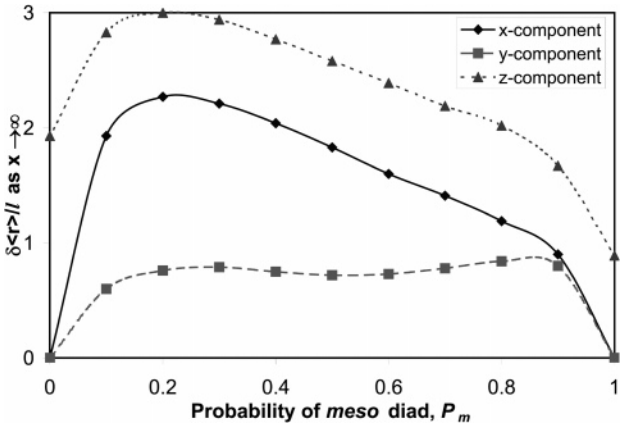

Figure 4. Fluctuations in the three components of $\langle\langle \mathbf{r} \rangle\rangle/l$, in the limit as $x \rightarrow \infty$, evaluated at intervals of 0.1 for p_m.

diphenylpentane at the extremes of stereochemical composition, where $p_m = 0$ or 1, these ensembles are composed of two stereochemical sequences with identical values for the X components of $\langle \mathbf{r} \rangle$ as well as identical values for the Y components of this vector. However, they have readily distinguishable values for $\langle \mathbf{r} \rangle_Z/l$, either ± 0.95 when $p_m = 1$ or ± 0.46 when $p_m = 0$. This variability in $\langle \mathbf{r} \rangle_Z$ can be captured by calculating a fluctuation, $\delta\langle \mathbf{r} \rangle_Z/l$, which depends on the value of p_m used for weighting the contribution of the 2^x stereochemical sequences.

$$(\delta\langle \mathbf{r} \rangle_Z/l)^2 \equiv (2l)^{-2}\{\sum p_m{}^{n_m}(1-p_m)^{x-n_m-1}\langle \mathbf{r} \rangle_Z{}^2 - [\sum p_m{}^{n_m}(1-p_m)^{x-n_m-1}\langle \mathbf{r} \rangle_Z]^2\} \quad (5)$$

The summations extend over all 2^x stereochemical sequences of the oligomer, i.e., over the four sequences listed in Table 1 when $x = 2$ and the eight sequences listed in Table 2 when $x = 3$. The numbers of m diads in each sequence is denoted by n_m. Fluctuations in the X and Y components are defined similarly.

Figure 4 depicts the dependence on p_m of the fluctuations in the three components of $\langle\langle \mathbf{r} \rangle\rangle$, in the limit as $x \rightarrow \infty$. The Z component experiences the largest fluctuations across the entire range of p_m. The X and Y components have no fluctuation when p_m is either 0 or 1, but they experience fluctuations at all intermediate values of p_m. At these intermediate values of p_m, the fluctuations decrease in the order $Z > X > Y$.

Figure 5 presents a graphic depiction of the importance of the fluctuations in the three components of $\langle \mathbf{r} \rangle$ when $p_m = 0.5$. The Cartesian coordinate system is the one defined by the first two bonds. The major axes of the ellipsoid drawn about $\langle\langle \mathbf{r} \rangle\rangle$ have the values determined by the fluctuation in each component. This ellipsoid has its center in the XY plane. The size of the ellipsoid emphasizes the broad variation in $\langle \mathbf{r} \rangle$ for the various stereochemical sequences.

If the same algorithm were used to analyze a simple chain such as PE, it would find zero fluctuation for all three components of $\langle \mathbf{r} \rangle$. The fluctuations depicted in Figures 4 and 5 arise from the fact that PS chains of specified x can have different stereochemical sequences, each with its own value of $\langle \mathbf{r} \rangle$. A simple chain such as PE does not have access to such variability in $\langle \mathbf{r} \rangle$.

Distribution of Kuhn Monomer Relaxation Times. The $\langle \mathbf{r} \rangle$ calculated with the rotational isomeric state model contains more detail that does the persistence length because $\langle \mathbf{r} \rangle$ can have nonzero components in all directions. A simple wormlike chain model, in which the direction of the instantaneous curvature is random, cannot produce a $\langle \mathbf{r} \rangle$ with nonzero components

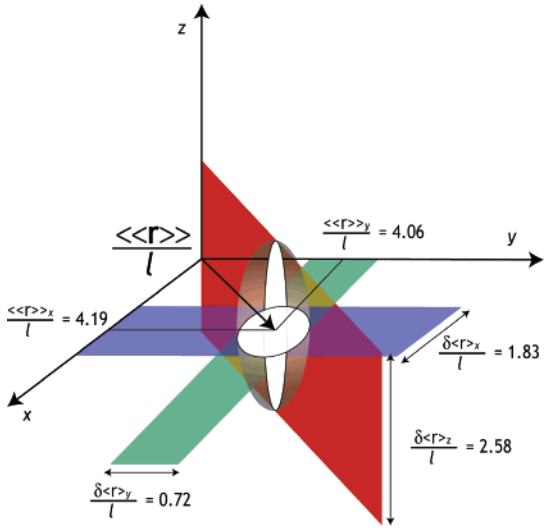

Figure 5. Ellipsoid with major axes specified by the fluctuations in $\langle \mathbf{r} \rangle/l$ when $p_m = 0.5$. The ellipsoid is centered on $\langle\langle \mathbf{r} \rangle\rangle/l$.

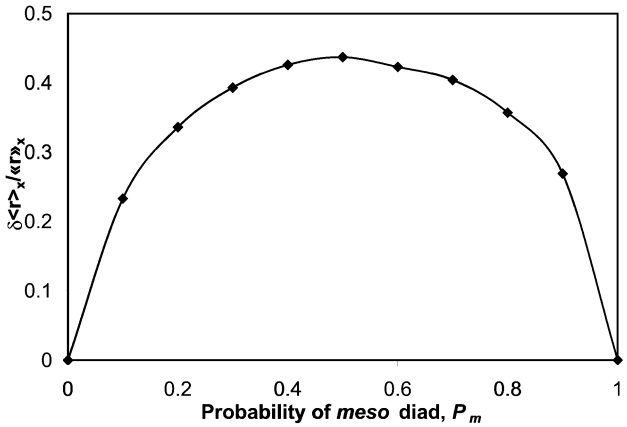

Figure 6. Ratio of the fluctuation in the X component of $\langle \mathbf{r} \rangle$ in various stereochemical sequences to the average value obtained considering the same stereochemical sequences, at intervals of 0.1 for p_m.

perpendicular to the direction of the initially chosen line segment of length dl. If one interprets the persistence length as being the average projection of the end-to-end vector onto the direction of the first bond, only the X component of $\langle \mathbf{r} \rangle$ is pertinent to the discussion of the persistence length. Then the severity of the fluctuation in the local stiffness of the chain, arising from differences in the stereochemical sequences, is measured by $\delta\langle \mathbf{r} \rangle_X/\langle\langle \mathbf{r} \rangle\rangle_X$, where both terms are evaluated for the same value of p_m, in the limit as $x \rightarrow \infty$. The numerator is the fluctuation in the X component, arising from the different stereochemical sequences. The dominator is the average value of the X component, with the average extending over all stereochemical sequences. The results are depicted in Figure 6.

When p_m is in the range found for typical samples of aPS, the fluctuation in the persistence length, arising from different stereochemical sequences, exceeds 40% of the value of the persistence length averaged over all stereochemical sequences. This fluctuation would be zero for a simpler chain, such as PE, and it is also zero for the PS chains at the extremes of stereochemical composition, where p_m is either 0 or 1.

The consequences for the Kuhn monomer relaxation time defined by eq 3 are demonstrated by examination of the distribution function for the persistence length, $a = b/2$, for the atactic chain. We do so by selecting $p_m = 0.5$ and identifying the persistence length with the X component of $\langle \mathbf{r} \rangle$ for all sequences. Figure 7 depicts the distribution function for a^2 under

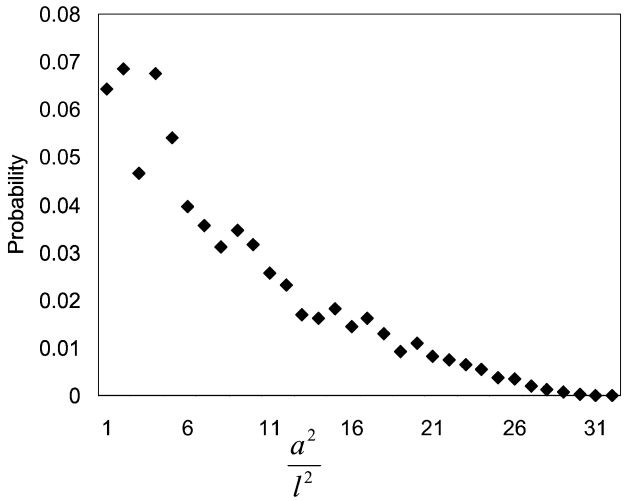

Figure 7. Distribution function for a^2/l^2 for aPS with $p_m = 0.5$, where a for any stereochemical sequence is identified with the X component of $\langle \mathbf{r} \rangle$. The bin size for a^2/l^2 is 2.

these conditions. Via eq 3, it becomes a distribution function for $(k_B T/4)(\tau_0/\zeta)$ at the temperature of the simulation, 300 K. Since T is constant, the figure essentially presents the distribution function for (τ_0/ζ) for aPS, in the approximation that the polymer is treated as a string of Kuhn monomers. If this same treatment were applied to a simpler chain, such as PE or PS at the extremes of stereochemical composition, the distribution function would be a delta function, with a single value of (τ_0/ζ) for all Kuhn monomers. The heterogeneity in the stereochemical sequences for aPS yields a much different picture, with a broad range of (τ_0/ζ) for the Kuhn monomers in a given chain.

The implications of this broad distribution of (τ_0/ζ) for a particular dynamic property of a chain will depend on whether that property is most sensitive to the fastest or slowest relaxing Kuhn monomer. Obviously, the distribution is of little significance for a static property, such as the mean-square radius of gyration, which does not depend on either τ_0 or ζ. A different conclusion is obtained for dynamic properties. Significant translation of the center of mass requires motion of all of the Kuhn monomers in the chain, and that motion must wait for the slowest moving Kuhn monomer. Figure 7 shows that the slowest Kuhn monomer has (τ_0/ζ) several times longer than the average Kuhn monomer. Therefore, it is not surprising that the literature contains examples of experimental measurements where sizes of Kuhn monomers deduced from a static measurement are incompatible with the sizes deduced from dynamic measurements for aPS. The heterogeneity in the stereochemical sequence of aPS, leading to a heterogeneity in (τ_0/ζ), will produce this result. Since the mean-square unperturbed dimensions of atactic polystyrene are observed to have a weak temperature dependence,[24] the distribution depicted in Figure 7 should also have a weak temperature dependence.

Other atactic polymers may also be susceptible to this effect. The strength of that effect, as reflected by the breadth of the distribution for a^2, will depend on p_m, whether or not the stereochemical sequence is Bernoullian, and on the short-range interactions in the particular atactic polymer of interest.

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