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Behavior of $\langle r^2\mu^2\rangle_0$ in Several Monosubstituted Vinyl Polymers

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ABSTRACT: Generator matrix methods have been used to compute $\langle r^2\mu^2\rangle_0$, $\langle r^2\rangle_0$, and $\langle\mu^2\rangle_0$ for poly(vinyl bromide), poly(vinyl chloride), and poly(styrene) chains as functions of the stereochemical composition. The squared end-to-end distance and squared dipole moment are denoted by r^2 and μ^2, respectively, angle brackets denote the statistical mechanical average of the enclosed property, and zero as a subscript denotes the ensemble that is unperturbed by long-range interactions. The values of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ are larger than 1 for chains with a finite number of bonds, n. They approach 1 as a limit as n increases. At a specified value of n, the largest values of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ are obtained with racemic poly(vinyl chloride) chains. The tendency for a correlation of μ^2 with r^2 arises from the parallel alignment of the components of the C–Cl bond in the plane of the backbone atoms in the fully extended racemic chain. Simulations that permit the introduction of excluded volume show that $\langle\mu^2\rangle$ for all three chains is insensitive to $\langle r^2\rangle/\langle r^2\rangle_0$ unless the stereochemical composition is predominantly racemic. The response of $\langle\mu^2\rangle$ to chain expansion is more dramatic in racemic poly(vinyl chloride) than in the other two polymers.

The mean-square end-to-end distance, $\langle r^2\rangle$, is sufficient for the specification of the distribution function, $W(\mathbf{r})$, for the end-to-end vector, $\mathbf{r}$, in the special case where that distribution function is Gaussian. Expressions for $W(\mathbf{r})$ that more accurately describe the distribution function for real chains are available. A common approach is formulation of $W(\mathbf{r})$ in terms of the higher even moments of $\mathbf{r}$. In the formulation due to Nagai,[1] departures from a Gaussian distribution function are expressed by a series of terms that contain dimensionless ratios of the form $\langle r^{2\nu}\rangle/\langle r^2\rangle^\nu$. Deviation of the values of the dimensionless ratios from their asymptotic limits at large n is seen in chains of finite n. For example, $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ and $\langle r^6\rangle_0/\langle r^2\rangle_0^3$ are less than $^5/_3$ and $^{35}/_9$, respectively, for unperturbed polyethylene chains with finite n, but they approach the Gaussian limits of $^5/_3$ and $^{35}/_9$ as n becomes infinite.[2] Nagai's formulation uses the actual values of $\langle r^{2\nu}\rangle/\langle r^2\rangle^\nu$ to increase the accuracy of the expression for $W(\mathbf{r})$.

Methodology is available for the efficient computation of $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ for real unperturbed chains via the rotational isomeric state theory. The method derives from the expression of r^4 for a specified conformation as $r^2 \otimes r^2$ (where $\otimes$ denotes the direct product) and an appeal to the theorem on direct products.[3] The averaging over all conformation accessible to the unperturbed chain is obtained by the usual combination of statistical weight matrices and generator matrices that contain information about the

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bond lengths, bond angles, and dihedral angles.

This methodology has broader application because it can be utilized to ascertain whether there is a correlation between r^2 and another conformation-dependent physical property. For example, it is easily adapted to an investigation of a correlation between r^2 and the squared dipole moment, μ^2, in an unperturbed ensemble of polar chains of specified n.[4] Numerical evaluation of $\langle r^2\mu^2\rangle_0$ starts by simply writing $r^2\mu^2$ for a specified conformation as $r^2 \otimes \mu^2$, in analogy to the expression of r^4 as $r^2 \otimes r^2$. Further exploitation of the analogy leads to efficient generator matrix calculations that yield numerical values for $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$. This dimensionless ratio contains information about the correlation between r^2 and μ^2. In absence of any such correlation, $\langle r^2\mu^2\rangle_0 = \langle r^2\rangle_0\langle\mu^2\rangle_0$ and the dimensionless ratio has the value of unity. This result is expected for many real chains in the limit where n becomes infinite. However, for finite n, $\langle r^2\mu^2\rangle_0$ may be different from $\langle r^2\rangle_0\langle\mu^2\rangle_0$.[4]

Values of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ have been presented for a series of artificial chains.[4] Simulations show that this dimensionless ratio is more successful than $\langle \mathbf{r}\cdot\mu\rangle^2{}_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ in predicting the manner in which $\langle\mu^2\rangle$ responds to the imposition of excluded volume in these chains.[4] The artificial chains have the conformational statistics of polyethylene. They differ from polyethylene in that a dipole moment vector of unit length is rigidly attached to each bond. The dipole moment vectors are oriented so that they are perpendicular to the plane described by the chain atoms when all internal bonds adopt trans placements. This article describes the first calculation of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ for rotational isomeric state models of real chains. The chains studied are poly(vinyl bromide), poly(vinyl chloride), and poly(styrene). Simulations are also performed that show how $\langle\mu^2\rangle$ in these chains responds to the imposition of excluded volume.

Methods

Rotational Isomeric State Models. The rotational isomeric state models used are the ones described by Saiz et al.[5] for poly(vinyl bromide), by Mark[6] for poly(vinyl chloride), and by Yoon et al.[7] for poly(styrene). Simulations were also performed starting with Tonelli's model for unperturbed poly(vinyl bromide).[8] Statistical weights are assigned the values specified by these models for a temperature of 25 °C. The group dipole moments are parallel to the C–X bonds, where X is Br, Cl, or C_6H_5.

Generator Matrix Calculations. The values of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ were obtained as functions of n and p_m in the usual manner.[3-6] The stereochemical composition was assumed to be completely characterized by the probability for the meso diad, p_m, and Bernoullian statistics. Values of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ for chains with $0 < p_m < 1$ are averages over sufficiently large samples of chains of specified stereochemical sequence, which are generated by using the desired p_m and a random number generator. The typical number of chains in such samples is 99.

The computation of $\langle r^2\mu^2\rangle_0$ proceeds in the manner described recently.[4] For a specified conformation, the square of the end-to-end distance is generated as

$$r^2 = \mathbf{G}_1\,\mathbf{G}_2 \ldots \mathbf{G}_n \tag{1}$$

where the internal $\mathbf{G}_i$ are square matrices of dimensions 5 × 5, with elements determined by the length of bond i and the matrix that transforms a vector from its representation in the local coordinate system for bond $i + 1$ into its representation in the local coordinate system for bond i.[3] The terminal matrices, $\mathbf{G}_1$ and $\mathbf{G}_n$, are of the forms found in the first row and last column, respectively, of the internal $\mathbf{G}_i$. Combination of eq 1 with $r^4 = r^2 \otimes r^2$, and an appeal to the theorem on direct products, yields[3]

$$r^4 = (\mathbf{G}_1 \otimes \mathbf{G}_1)\,(\mathbf{G}_2 \otimes \mathbf{G}_2) \ldots (\mathbf{G}_n \otimes \mathbf{G}_n) \tag{2}$$

where the internal $(\mathbf{G}_i \otimes \mathbf{G}_i)$ are now of dimensions 25 × 25, and the terminal matrices are a row or column of 25 elements. With $\mathbf{H}$ as the symbol for the 5 × 5 generator matrix in which the bond vector in $\mathbf{G}$ is replaced by the group dipole moment vector, the squared dipole moment for a specified conformation is

$$\mu^2 = \mathbf{H}_1\,\mathbf{H}_2 \ldots \mathbf{H}_n \tag{3}$$

Combination of eq 1 and eq 3 with $r^2\mu^2 = r^2 \otimes \mu^2$ yields[4]

$$r^2\mu^2 = (\mathbf{G}_1 \otimes \mathbf{H}_1)\,(\mathbf{G}_2 \otimes \mathbf{H}_2) \ldots (\mathbf{G}_n \otimes \mathbf{H}_n) \tag{4}$$

where each $\mathbf{G}_i \otimes \mathbf{H}_i$ in eq 4 is of the same dimensions as the corresponding $\mathbf{G}_i \otimes \mathbf{G}_i$ in eq 2. Averaging over all chains in the unperturbed ensemble to obtain $\langle r^4\rangle_0$ is obtained by combination of eq 2 with the matrix expression for the conformational partition function, Z.[3]

$$Z = \mathbf{U}_1\,\mathbf{U}_2 \ldots \mathbf{U}_n \tag{5}$$

A perfectly analogous combination of eq 4 with Z yields $\langle r^2\mu^2\rangle_0$ for the same ensemble.

This procedure can be employed for numerical evaluation of the correlation between r^2 and a generalized conformation-dependent physical property, P, if P for a specified conformation can be written as a product of n matrices, as is done for μ^2 in eq 3.

Simulations. Excluded volume was introduced by the incorporation of long-range interactions in a simulation. The method is virtually identical with that recently described for the introduction of long-range interactions into chains that have the geometry and short-range interactions found in unperturbed polyethylene.[4] In the present application, a representative conformation of a chain with specified n and p_m is generated by using a random number generator and the a priori and conditional probabilities extracted from Z. A sphere of radius r^* is then centered on the chain atoms that bear the polar substituent. The number of pairs of overlapping spheres that are separated by more than six backbone bonds is denoted by n_r. The weight of the chain in the perturbed ensemble is w^{nr}. The unperturbed ensemble is preserved when $w = 1$ or when $r^* = 0$. Averages of μ^2 and r^2 for all chains in this ensemble yield $\langle\mu^2\rangle_0$ and $\langle r^2\rangle_0$. If $r^* > 0$, weighting with $w = 0$ imposes hard-sphere long-range interactions. Long-range interactions are repulsive, but not infinitely so, when $r^* > 0$ and $0 < w < 1$. Long-range interactions are attractive, and the chain contracts, when $r^* > 0$ and $w > 1$. Averages of μ^2 and r^2 for all chains in the ensembles described in the last three sentences will yield $\langle\mu^2\rangle$ and $\langle r^2\rangle$. The simulations were performed with several combinations of r^* and w that produce small expansions or contractions. The values of $\langle\mu^2\rangle/\langle\mu^2\rangle_0 = \alpha_\mu{}^2$ were plotted as a function of $\langle r^2\rangle/\langle r^2\rangle_0 = \alpha_r{}^2$, and the initial slope was evaluated at $\alpha_r{}^2 = 1$. The value of this slope is independent of r^* and w provided r^* is not much greater than the bond length and w is not much greater than 1.

Results and Discussion

Unperturbed Dimensions and Dipole Moments. Figure 1 depicts the values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle_0/xm^2$ for poly(vinyl bromide), poly(vinyl chloride), and poly(styrene) chains with a degree of polymerization, x, of 150. The length of the C–C bonds in the main chain is denoted by l, and the magnitude of the dipole moment associated with the C–X bond is denoted by m. This degree of polymerization is used in Figure 1 because it is the largest value

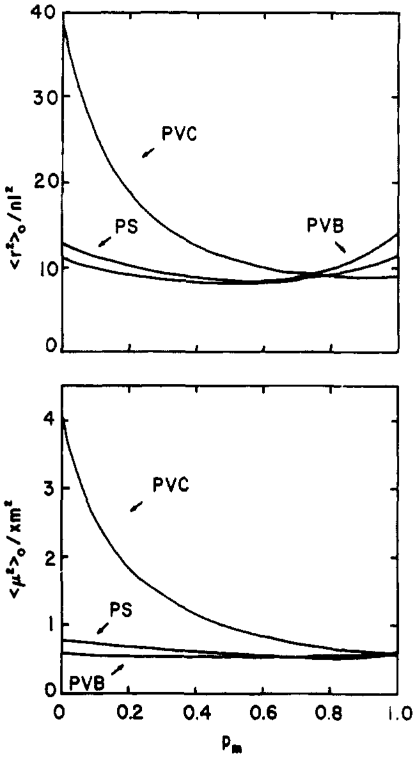

Figure 1. Dimensionless characteristic ratios for $\langle r^2\rangle_0$ (top panel) and $\langle \mu^2\rangle_0$ (bottom panel) for poly(vinyl bromide) (PVB), poly(vinyl chloride) (PVC), and poly(styrene) (PS) chains with $n = 300$ ($x = 150$) as a function of the probability for a meso diad, p_m.

of x conveniently handled in the simulations of perturbed chains, which will be described below. Only in the case of poly(vinyl chloride) at small values of p_m do the results for $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/xm^2$ in Figure 1 differ significantly from the limits as n approaches infinity. The values at $p_m = 0$ and $p_m = 1$ for poly(vinyl bromide) and poly(styrene) are in agreement with previous calculations,[5,7] and the results for poly(vinyl chloride) are also in agreement when allowance is made for the fact that Mark's calculations[6] were performed for chains with $x = 100$. The present calculations yield somewhat higher values for $\langle r^2\rangle_0/nl^2$ for poly(vinyl bromide) chains of intermediate stereochemical composition than those described previously.[5]

Correlation of μ^2 with r^2. Figure 2 depicts the values of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ for the chains for which $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$ are described in Figure 1. This ratio is always larger than 1 in Figure 2, signifying a tendency for the more extended conformations to have larger values of μ^2 than the more compact conformations. The smallest values of $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ are obtained with chains of intermediate stereochemical composition. The general appearance of Figure 2 has much in common with the top panel in Figure 1; the order is PVB < PS ≪ PVC at $p_m = 0$, PVC < PS < PVB at $p_m = 1$, and the curves cross in the range $0.6 < p_m < 0.8$. Computations performed at other values of n (not plotted here) show that, for all chains used in Figure 2, $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ approaches 1 as a limit as n becomes infinite. At sufficiently large values of n, $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ becomes linear in $1/n$.

With the exception of poly(vinyl chloride) at $p_m < 0.18$, all of the $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ in Figure 2 fall in the range 1.032–1.066. Racemic poly(vinyl chloride) has a much larger value, 1.182, for this dimensionless ratio. The molecular origin of the large correlation of μ^2 with r^2 in racemic poly(vinyl chloride) can be traced to the strong preference for propagation of the tt conformation in this chain. In a fully extended racemic poly(vinyl chloride) chain with an even number of C–Cl bonds, there will be complete cancellation of the components of the C–Cl dipole moments perpendicular to the plane of the main-chain atoms and complete alignment of the components that are in the plane of the main-chain atoms. Complete alignment of the latter components implies that μ^2 for this fragment is proportional to the square of its degree of polymerization. The strong preference for the tt conformation in racemic poly(vinyl chloride) causes the large $\langle r^2\rangle_0/nl^2$ depicted in the top panel of Figure 1, and the alignment of the in-plane components of the C–Cl dipole moment vectors causes the large $\langle \mu^2\rangle_0/xm^2$ depicted in the bottom panel. The simultaneous occurrence of large r^2 and μ^2 in chains with long runs of trans placements is responsible for the large $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ depicted in Figure 2.

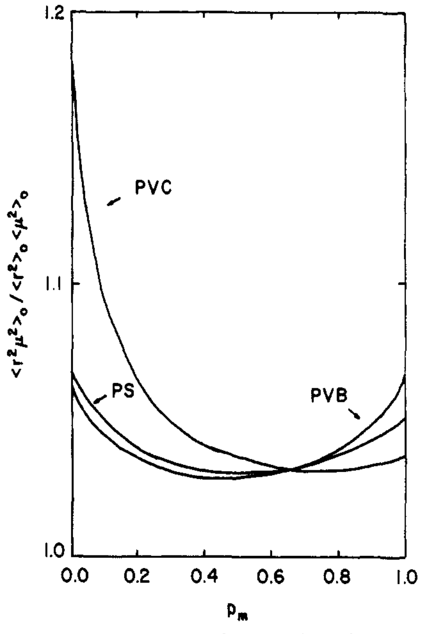

Figure 2. Dimensionless ratio $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ for PVB, PVC, and PS chains with $n = 300$, as a function of the probability for a meso diad.

While all $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0$ reported here are greater than 1, there are other chains for which this ratio can be less than one. This behavior can be observed when there is complete cancellation of two successive bond dipole moments in a fully extended chain.[4] A simple model chain that has this property is one that has the conformational properties of polyethylene, and each bond has associated with it a unit dipole moment vector that is oriented along the z axis of the local coordinate system described by Flory.[3] Since these z axes for successive bonds point in opposite directions in a chain with trans placements, segments with an even number of consecutive trans placements have no net dipole moment. The chain with $n = 300$ and the conformational statistics of unperturbed polyethylene has $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle \mu^2\rangle_0 = 0.973$.[4] If alternate bond dipole moment vectors have their directions reversed, so that all bond dipole moments are parallel when trans placements are populated exclusively, the value of $\langle r^2\mu^2\rangle_0/\langle r^2\mu^2\rangle_0$ for this chain rises to 1.011.

Response of $\langle \mu^2\rangle$ to Chain Expansion. The points in Figure 3 depict the initial dependence of α_μ^2 on α_r^2, at $\alpha_r^2 = 1$, as evaluated from simulations of poly(vinyl chloride) chains with $n = 300$. Two independent simulations were performed at each of the nine values of p_m studied. The results of all simulations are shown. The simulations show that $\langle \mu^2\rangle$ for meso chains is insensitive to chain expansion, but $\langle \mu^2\rangle$ for racemic chains increases in response to the expansion of the chain that is produced by the excluded-

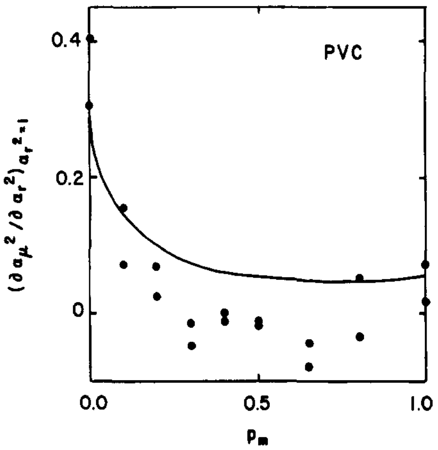

Figure 3. Initial slope of α_μ^2 versus α_r^2, at $\alpha_r^2 = 1$, for poly(vinyl chloride) chains with $n = 300$. Two independent simulations were run at each p_m investigated. The initial slope obtained from each simulation is plotted as a filled circle. The solid line is calculated with eq 6 and $K = {}^3/_2$, as described in the text.

volume effect. For chains with p_m in the range 0.4–0.5, which corresponds to the stereochemical composition determined for several samples of poly(vinyl chloride),[9-12] the simulations show that $\langle\mu^2\rangle$ is virtually unaffected by small changes of α_r^2 in the vicinity of $\alpha_r^2 = 1$.

The solid line in Figure 3 is drawn by using the generator matrix data for unperturbed poly(vinyl chloride) in Figure 2 and the expression

$$(\partial\alpha_\mu^2/\partial\alpha_r^2)_{\alpha_r^2=1} = K(\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0 - 1) \qquad (6)$$

with the value of K assigned as ${}^3/_2$. Equation 6 is an exact result for a special type of simple chain.[4] The distribution function for the end-to-end distance is

$$P(r)\,dr = [(2/\pi)(3/a^2\langle r^2\rangle_0)^3]^{1/2}\exp(-3r^2/2a^2\langle r^2\rangle_0)r^2\,dr \qquad (7)$$

and the mean-square dipole moment for chains with an end-to-end distance between r and $r + dr$ is

$$\langle\mu^2\rangle_r = \langle\mu^2\rangle_{r=0}\exp(yr^2/\langle r^2\rangle_0) \qquad (8)$$

Unperturbed chains have the $P(r)$ described by eq 7 when a^2 is one, and y in eq 8 has an absolute value that is close to zero. In spite of the simplicity of the model, it nevertheless provides a useful qualitative rationalization of the response of $\langle\mu^2\rangle$ to α_r^2 in chains that have the conformational statistics of polyethylene and bond dipole moments attached in different ways to the local coordinate systems for the bonds in the chain.[4] In general, eq 6 is most useful for chains where the response of $\langle\mu^2\rangle$ to α_r^2 is dominated by the presence of a significant correlation of μ^2 with r^2. Such correlations can exist in finite chains for which $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is rigorously equal to zero.[4] The relatively large correlation between μ^2 and r^2 in racemic poly(vinyl chloride) chains is responsible for the increase in $\langle\mu^2\rangle$ upon the imposition of excluded volume.

Similar simulations of poly(vinyl bromide) (Figure 4) show a very weak response of $\langle\mu^2\rangle$ to chain expansion when p_m is in the range 0.38–0.48, which includes the stereochemical compositions measured for several samples of this polymer.[5,10] The simulations show a larger response of $\langle\mu^2\rangle$ to α_r^2 for racemic chains when the short-range interactions are those described by Saiz et al.,[5] but the size of the response is not as large as that obtained with racemic poly(vinyl chloride). Much the same behavior is seen in the simulations of poly(styrene), the results of which are reported in Figure 5. Equation 6, with $K = {}^3/_2$, does not capture the upturn of the simulations at small p_m in these two polymers.

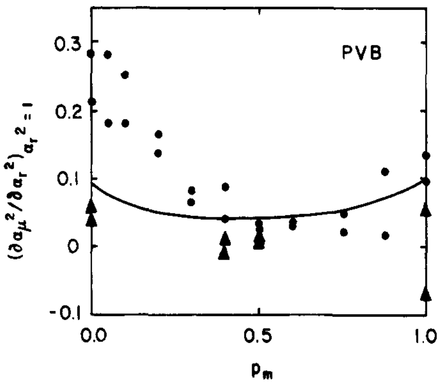

Figure 4. Initial slope of α_μ^2 versus α_r^2, at $\alpha_r^2 = 1$, for poly(vinyl bromide) chains with $n = 300$. The circles denote the results of simulations that start with the rotational isomeric state model described by Saiz et al.,[5] and the triangles are results obtained with the model described by Tonelli.[8] The solid line is calculated with $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ and $K = {}^3/_2$.

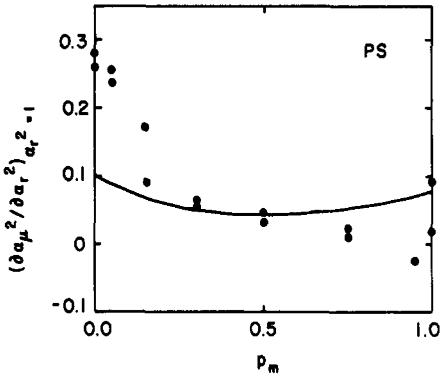

Figure 5. Initial slope of α_μ^2 versus α_r^2, at $\alpha_r^2 = 1$, for poly(styrene) chains with $n = 300$. The filled circles are the results obtained from the simulations, and the solid line is calculated from $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ and $K = {}^3/_2$.

Equation 6 had better predictive power in the recent study[4] of artificial chains with the conformational statistics of polyethylene than in the current application to vinyl polymers. One factor contributing to the different performance of this equation is the absence of a variation of $\langle r^2\rangle_0$ with p_m in the artificial chains. A change in p_m for the artificial chains was achieved by reversal of the direction of selected $\mathbf{m}_i$. There was no change in the statistical weight matrices. In all of the artificial chains, the statistical weight matrix for all internal bonds was always the one commonly used for polyethylene, and $\langle r^2\rangle_0$ was therefore independent of p_m. Consequently $\langle\mu^2\rangle_0$ and $\langle r^2\mu^2\rangle_0$, but not $\langle r^2\rangle_0$, were functions of p_m.[4,13] In contrast, a change in p_m for the vinyl polymers produces new values for $\langle r^2\rangle_0$ as well as $\langle\mu^2\rangle_0$ and $\langle r^2\mu^2\rangle_0$. The simple derivation of eq 6 does not address the circumstances where $\langle r^2\rangle_0$ is a function of p_m.

The behavior of $\langle r^2\mu^2\rangle$ will make a contribution to electric field induced light scattering.[14] At small angles, $\Delta I_{vv}/E^2$ (where ΔI_{vv} is the difference in light scattering with the electric field on and off and E is the electric field) is determined by sums over bond pairs of $\langle r_{ij}^2\rangle\langle\mu^2\rangle$, $\langle r_{ij}^2\mu^2\rangle$, and $\langle(\boldsymbol{\mu}\cdot\mathbf{r}_{ij})^2\rangle$.

When P is changed from μ^2 to $\mu^T\hat{\alpha}\mu$, where $\hat{\alpha}$ is the anisotropic part of the polarizability tensor, much larger values of $\langle r^2P\rangle_0/\langle r^2\rangle_0\langle P\rangle_0$ are obtained for poly(vinyl bromide) and poly(vinyl chloride) than the $\langle r^2\mu^2\rangle_0/\langle r^2\rangle_0\langle\mu^2\rangle_0$ reported here, as is shown by computations currently in progress. This result suggests that the dipolar contribution to the molar Kerr constant might be particularly sensitive to chain expansion in some polymers.

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Notes

Anionic Polymerization of N-Substituted Maleimide. 4. "Living" Characteristics of Anionic Polymerization of *N*-Phenylmaleimide

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Introduction

A number of vinyl monomers possessing one carbonyl group such as acrylates and vinyl ketones can be polymerized with appropriate anionic initiators and the polymerization mechanism of such monomers has been studied quite intensively and systematically.[1-4] Some vinylidene monomers having the 1,1-dicarbonyl substituted or similar structure such as methylene malonates are also known to be easily polymerized with the initiators of low basicity.[5,6] However, for the anionic polymerization of vinylene monomers having a 1,2-dicarbonyl substituted structure, no detailed study has been carried out until 1985, not only on the mechanism of polymerization but also even on the polymerization reactivity of monomers to the initiators, because only a few vinylene monomers can be polymerized with basic initiators.[7-9] Dialkyl fumarates, for instance, are reported to give no polymer with typical anionic initiators such as butyllithium.[10] In previous papers[11-14] we first reported some new results that various anionic initiators—alkali-metal *tert*-butoxides, Grignard reagents, ate complexes, and organozinc compounds—as well as butyllithium, can polymerize *N*-phenylmaleimide (*N*-PMI) and *N*-ethylmaleimide and give corresponding homopolymers which are soluble in THF, 1,4-dioxane, dichloromethane, DMSO, and DMF, though an early report indicated that poly(*N*-PMI) produced with butyllithium could not be dissolved in any solvents. The polymerization of *N*-PMI initiated with potassium *tert*-butoxide in THF was suggestive of an extremely stable propagating species and afforded poly(*N*-PMI) in quantitative yield. Good agreement between the degree of polymerization and initial monomer/initiator molar ratio was also observed for alkali-metal *tert*-butoxides.

On the basis of these results, it seemed to be valuable to investigate the mechanism of anionic polymerization of *N*-PMI initiated with alkali-metal *tert*-butoxides in detail.

Experimental Section

Reagents. *N*-PMI (from Japan Catalytic Chemical Ind.) was purified by recrystallization several times from purified cyclohexane and dried in vacuo at room temperature. It was further dried at 80 °C in vacuo before use. THF was purified by distillation under purified nitrogen atmosphere after being dried by refluxing with sodium benzophenone ketyl before use. Potassium, sodium, and lithium *tert*-butoxides were purified by sublimation under reduced pressure. Sodium *tert*-butoxide and lithium *tert*-butoxide were synthesized from 2-methyl-2-propanol and sodium or lithium metal, respectively. THF solutions of *N*-PMI and alkali-metal *tert*-butoxides were prepared under purified nitrogen before use.

Procedures. The polymerization reaction was carried out in a sealed glass ampule under purified nitrogen atmosphere. After appropriate time intervals polymerization was terminated with hydrochloric acid/methanol and then the reaction mixture was poured into a large amount of an ether/methanol (volume ratio 3/1) mixture. The white precipitate was collected by filtration, washed with ether, methanol, water, and methanol again, and dried at 110 °C in vacuo to constant weight.

Measurements. Vapor pressure osmometry (VPO) was carried out with a Corona 117 vapor pressure osmometer, using THF as solvent. Gel permeation chromatography (GPC) was measured with a Toyo Soda HLC-802A apparatus at 38 °C with TSK gel G4000HXL-G3000HXL-G2000HXL column series, using THF as eluent (flow rate 1.0 mL/min). Molecular weight measured by GPC was calculated from the calibration curve which was corrected[15] by referring to the data of $\bar{M}_w$'s with low-angle light-scattering photometry and of $\bar{M}_n$'s with VPO for four poly(N-PMI) samples with different molecular weights. Low-angle light-scattering photometry was measured with a Toyo Soda LS-8000 light-scattering photometer. ^{1}H NMR was recorded at 279.05 MHz on a JEOL JNM-GX270 at 40 °C using deuteriated dichloromethane as a solvent and dichloromethane as an internal reference. All chemical shifts given in parts per million were transformed to the TMS scale (δ scale) by employing 5.30 ppm as the chemical shift of dichloromethane from TMS. ^{13}C NMR was measured at 67.80 MHz on a JEOL JNM-GX270 at 40 °C under proton decoupling conditions using deuteriated dichloromethane as a solvent and an internal reference. Chemical shifts of each carbon in parts per million were transformed to the TMS scale (δ scale) by employing 53.6 ppm as the chemical shift of the central peak of deuteriated dichloromethane from that of TMS.

Results and Discussion

Reaction Mode of the Polymerization. Figure 1 shows ^{1}H NMR (A) and ^{13}C NMR (B) of poly(*N*-PMI) obtained with lithium *tert*-butoxide as initiator in THF at −72 °C. In Figure 1A the signals observed from 6 to 8 ppm are assigned to phenyl protons. The broad and

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