The Dimensions and Dipole Moments of Poly(propylene glycol) Chains

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ABSTRACT: Conformational energies of poly(propylene glycol) chains were calculated using classical torsional and nonbonded interaction potentials. It was shown that distinct energy minima occurred at rotational angles about the skeletal C—O bond including an asymmetric carbon, which were displaced by about -25° , 0° , and 20° (or 25° , 0° , and -20°) from the conventional symmetric positions of *trans* (*T*), *gauche* (*G*), and another *gauche* (*G'*), respectively. Two types of potential functions were used for the van der Waals interaction energy; from the comparison of experimental data for dimension and dipole moment with the theoretical values calculated in the rotational isomeric approximation, the one recommended by Scott and Scheraga and by Abe, *et al.*, was found to be appropriate for PPG chains. Calculations also showed that the mean-square moments increase with increasing syndiotacticity, although their extent was smaller than those predicted for asymmetric vinyl chains. Theory and experiment for the mean-square moments were in fair agreement in terms of their magnitude and dependence on tacticity and on molecular weight without introducing any adjustable parameter.

KEY WORDS Poly(propylene glycol) / Nonbonded Potential Function / Conformational Energy / Stereoirregular Polymer / Mean-Square Moment / End-to-End Distance / Dipole Moment /

In a recent communication,¹ one of the present authors (T.I.) and Nagai have calculated the unperturbed mean-square end-to-end distance, dipole moment, and Kerr constant for poly(oxyethylene glycol) (PEG) chains in the rotational isomeric state approximation. It seemed of interest to extend such calculations to poly(propylene glycol) (PPG) chains. The reason is twofold: PPG has a structural similarity to PEG and the effect of tacticity becomes important for PPG, which is not so for PEG. Several attempts²⁻⁵ have been reported to study theoretically the dependence of the chain conformations and mean-square moments of asymmetric vinyl chains on the stereochemical composition. Effects of *cis*—*trans* composition in diene polymers have also been investigated.⁶⁻⁸ Abe, *et al.*,⁹ were the first to calculate the unperturbed mean-square end-to-end distance and dipole moments of isotactic PPG chains using semiempirical conforma-

tional energies. They were forced to adjust some of the conformational energy parameters so that the calculated and experimental values for the mean-square moments agreed with each other, since no pertinent values were available for all the parameters. The dependence of the mean-square moments on either stereochemical composition or molecular weight has not been examined in detail.

In this study, we have attempted to calculate the conformational energies of PPG chains using appropriate interaction potentials. The result of such calculations has been used to estimate the values for the mean-square moments in the rotational isomeric state approximation. Their magnitudes, dependence on chain length or on stereochemical composition are discussed in comparison with experimental data.

Molecular Structure and Potential Function

Figure 1 shows the *trans* planar conformation

Figure 1. The *trans* planar conformation of a portion of poly(propylene glycol) chain.

Figure 2. Newman projections in the *trans* conformation for the repeating unit of the PPG chain, each consisting of three bonds, *i.e.*, C—C, C—O, and O—C. Displacement angles $\Delta\theta_a^1$, etc., for the three conformational states of each bond are defined as shown in the figure. See also text.

of a portion of a PPG chain of either *isotactic* (*IS*) or *syndiotactic* (*SY*) configuration. Here we mean by *IS* a chain configuration where two methyl groups belonging to two successive monomer units are placed on the different sides of the plane of the skeletal bond, whereas *SY* represents a chain configuration where the two methyl groups are placed on the same side. It will be convenient to introduce Newman projections as shown in Figure 2 in order to define the rotational angles about three distinct skeletal bonds, namely, C—C, C—O, and O—C. Each projection shows the *trans* conformation with respect to the skeletal bond, from which

the respective rotation angle is measured clockwise when facing the plane of the paper. This implies that a clockwise rotation of 120° produces a *gauche* conformation (*G*) and that a rotation of -120° yields another *gauche* (*G'*) one.

The structural parameters are the same as those used in our previous paper¹ on poly(oxyethylene glycol) chains, all bond angles are assumed to be tetrahedral except that $\angle\text{COH}=108^\circ$, and the following bond lengths are assumed: $b_{\text{C-C}}=1.54\text{\AA}$, $b_{\text{C-O}}=1.43\text{\AA}$, and $b_{\text{C-H}}=1.09\text{\AA}$. We also assume each bond dipole moment be placed at the center of that bond with the following magnitude: $m_{\text{C-C}}=m_{\text{C-H}}=0$, $m_{\text{C-O}}=1.0D$, and

$$m_{O-H}=1.7D.$$

The conformational energy E associated with the i -th bond is assumed to be expressible as a function of two rotation angles of consecutive skeletal bonds, θ_i and θ_{i+1} , in the form:

$$E=(1/2)[E_I(\theta_i)+E_I(\theta_{i+1})+\sum\{E_V(\theta_i)+E_V(\theta_{i+1})\}+\sum\{E_V(\theta_i,\theta_{i+1})+E_C(\theta_i,\theta_{i+1})\}] \quad (1)$$

where E_I is the intrinsic torsional energy expressed as $E_I(\theta)=(E_0/2)(1-\cos 3\theta)$, with E_0 being the torsional barrier height. The terms E_V and E_C account for the van der Waals interaction and the coulombic interaction, respectively, and the summation extends over all pairs of atoms separated by at most four bonds. The factor 1/2 in eq 1 is introduced in order to avoid dual accounting of the contributions from the one-bond interaction energy terms to the total energy. Following Scott and Scheraga,¹⁰ we neglect the coulombic interaction term in the following discussion. Two functional forms are known for the van der Waals interaction energy E_V , namely, type I:

$$a_{kl} \exp(-b_{kl}r_{kl})-c_{kl}/r_{kl}^6$$

and type II:

$$A_{kl}/r_{kl}^{12}-B_{kl}/r_{kl}^6$$

where a_{kl} , etc., are characteristic constants for a given pair of atoms k and l , and r_{kl} is the distance between the two atoms. We use both functional forms to calculate conformational energies, since at the present stage we have no definite reason to choose the one before the

other. Table I lists numerical values for the constants relevant to the two potential functions. Those for type I are taken from the paper of Scott and Scheraga¹⁰ except ones marked by*, which are the values used by Abe, *et al.*,¹¹ for the calculation of conformational energies of n -alkanes. The values for type II are those of Chen, *et al.*,¹² who used them for the determination of chain conformation of poly(α -methylvinyl methyl ether) in the crystalline state. The torsional barrier height is taken to be 3.0 kcal/mol for bond C—C and 1.07 kcal/mol for bond C—O. We have found that the latter value can also be deduced from the observed barrier height of 2.72 kcal/mol for dimethyl ether¹³ if it is corrected for the effect of nonbonded interaction with the use of type-I van der Waals potential.

Conformational Energy

Conformational energies E for PPG chains associated with rotations about two consecutive skeletal bonds have been calculated by means of eq 1 at intervals of 10° from 0 to $\pm 180^\circ$ of rotation angles, with one of C—H bonds in the methyl group affixed *trans* with respect to the C—C bond. Figures 3–5 show energy contour diagrams respectively of C—C—O, C—O—C, and O—C—C bond pairs of *IS* placement, where the figures on the contours represent the absolute energy values and the diagrams are shown only for the potential function of type I; contours above 10 kcal/mol are not shown and $\times$'s in these figures denote the minimum positions of energy domains. Table II summarizes the positions and absolute energy values for the energy

Table I. Parameters for intramolecular energy functions

Type	I ^a			II ^b	
Atom pair	$a_{kl} \times 10^{-4}$, kcal/mol	b_{kl} , Å	c_{kl} , Å ⁶ kcal/mol	$A_{kl} \times 10^{-4}$, Å ¹² kcal/mol	B_{kl} , Å ⁶ kcal/mol
H H	{ 0.917 0.995*	4.54	45.2	0.4709	49.29
C H	8.610*	4.57*	127.0*	3.9698	133.48
C C	90.860*	4.59*	363.0	29.3990	380.60
C O	41.066	4.59	275.4	16.2140	302.03
O O	13.570	4.59	217.0	8.9397	245.26
H O	2.680	4.57	90.4	1.9835	120.40

^a $a_{kl} \exp(-b_{kl}r_{kl})-c_{kl}/r_{kl}^6$.

^b $A_{kl}/r_{kl}^{12}-B_{kl}/r_{kl}^6$; the constants of type I are taken from ref 10 and ref 11 for * and those of type II are taken from ref 12.

Figure 3. Contour diagrams for the C—C—O bond pair of IS configuration of PPG chains. Total conformational energies are shown on the contours in units of kcal/mol. Computation was carried out at intervals of 10° with $E_1^{C-C} = 3.0$ kcal/mol and $E_1^{C-O} = 1.07$ kcal/mol, and with the nonbonded potential function of type I in Table I.

Figure 4. Contour diagrams for the C—O—C bond pair of IS configuration of the PPG chain. Details are the same as in Figure 3.

minima appearing on the contour diagrams for both type-I and type-II potentials. One can observe in Table II that the Type-I potential

Figure 5. Contour diagrams for the O—C—C bond pair of IS configuration of the PPG chain. Details are the same as in Figure 3.

gives higher energies than the type II, although the shapes and positions of the lower energy domains were found to be similar for both types. Use of 9.17×10^3 instead of 9.95×10^3 for a_{kl} of the $H \cdots H$ interaction brought about negligible change in absolute energies in the minimum energy regions. It should be noted that the locations of distinct energy minima are displaced considerably from the conventional *trans* (0°) and two *gauche* positions ($\pm 120^\circ$); $\Delta\theta_b^1 = -25^\circ$, $\Delta\theta_b^2 = 0^\circ$, and $\Delta\theta_b^3 = 20^\circ$; $\Delta\theta_c^1 = -\Delta\theta_c^3 = -20^\circ$. Other minima are seen to undergo no detectable deviation. Cesari, *et al.*,¹⁴ determined from X-ray crystallographic analysis the deviation from the *trans* position for PPG chains in the crystalline state, with the result: $\Delta\theta_a^1 = 0^\circ$, $\Delta\theta_b^1 = -15^\circ$, and $\Delta\theta_c^1 = 15^\circ$. These crystallographic data are substantially in accord with our conformational analysis. Further inspection of the contour diagrams reveals that the *gauche* conformation for the C—O bond ($\theta_b = 120^\circ$) is energetically precluded irrespective of the conformation of neighboring bonds. This conclusion is at variance with the treatment by Abe, *et al.*,⁹ who assigned a value of about 2 kcal/mol for the interaction energy of C—O bond in the *gauche* conformation and hence did not exclude the GT states of the C—O—C bond pair. These authors also used the conventional symmetrical positions of *trans*

Table II. Stable conformation on the energy diagram of PPG chains

Rotational angle, degree		Absolute energy, kcal/mol	
θ_a	θ_b	type I ^a	type II ^a
0	-25	0.3	-0.6
0	120	2.2	-0.1
0	-100	0.2	-0.8
120	-25	0.2	-0.6
120	120	2.1	-0.1
120	-100	1.0	-0.4
-120	-25	0.3	-0.6
-120	120	6.5	2.3
-120	-100	0.2	-0.7
θ_b	θ_c	type I ^a	type II ^a
-25	0	0.6	-0.3
-25	100	1.2	0.2
-25	-100	3.3	2.1
120	0	5.5	5.9
120	100	15.4	10.6
120	-100	12.7	23.7
-100	0	0.5	-0.4
-100	100	2.2	0.6
-100	-100	1.2	0.0
θ_c	θ_a	type I ^a	type II ^a
0	0	-0.3	-1.0
0	120	-0.4	-0.9
0	-120	-0.3	-1.0
100	0	7.4	4.2
100	120	0.1	-0.8
100	-120	1.1	-0.4
-100	0	0.1	-0.9
-100	120	1.0	-0.4
-100	-120	7.4	4.2

^a These values are calculated from potential functions of types I and II in Table I, respectively.

and *gauche* for the locations of the energy minima. It is apparent that the reliability of our conclusion depends on the accuracy of the nonbonded potential parameters used and may be tested by comparison with experiment on conformation-dependent properties.

Partition Function and Mean-Square Moments

The appearance of distinct energy minima in the conformational space of PPG chains, though with slight deviations from the conventional *T* and/or *G* states, suggests that treatment of these

chains in the rotational isomeric state approximation may be justified. The conformational partition function of a PPG chain with n skeletal bonds or $N=n/3$ monomeric units is then written

$$Z = \mathbf{e}_3^T \mathbf{P}_1 \mathbf{P}_2 (\mathbf{P}_a \mathbf{P}_b \mathbf{P}_c)^{N-1} \mathbf{P}_{n-2} \mathbf{P}_{n-1} \mathbf{P}_n \mathbf{e}_3 \quad (2)$$

where $\mathbf{e}_3 = (100)^T$ and $\mathbf{e}_3^T$ is its transpose vector. The interior matrix product $\mathbf{P}_a \mathbf{P}_b \mathbf{P}_c$ is represented by $\mathbf{P}_I$ for *IS* form and by $\mathbf{P}_S$ for the *SY* form. The elements p_{kl} of $\mathbf{P}_i$ for the bond i can be obtained by the Boltzmann relation $p_{kl} = \exp(-E(\theta_k, \theta_l)/RT)$ from the energies given in Table II, which are arranged in the order of (1, 1), (1, 2), ..., (3, 3). Here R is the molar gas constant and T is the absolute temperature. The entropy contribution to p_{kl} has not been considered, because its exact estimation from the energy contour diagrams was too troublesome to be carried out in practice. $\mathbf{P}_S$ can be derived from $\mathbf{P}_I$ constructed above by interchanging the second and third rows of $\mathbf{P}_c$ in $\mathbf{P}_I$. Matrices of terminal bonds are given by

$$\mathbf{P}_1 = \mathbf{P}_2 = \mathbf{P}_{n-2} = \mathbf{P}_{n-1} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (3)$$

and $\mathbf{P}_n$ is the unit matrix of order three. Here $\mathbf{P}_2$ and $\mathbf{P}_{n-2}$ are assumed to take the above form, because none of the corresponding energy minima was found to exceed 0.1 kcal/mol.

The theoretical derivation of the mean-square moment $\langle V^2 \rangle$ related to the bond vector $\mathbf{b}$ or the bond dipole vector $\mathbf{m}$ has been discussed in detail elsewhere.^{2,15,16} The final expression relevant to our present purpose can be obtained from eq 41 or 42 in the previous paper,^{1,17} which reads

$$\langle V^2 \rangle = Z^{-1} (\mathbf{e}_s^T \times \mathbf{e}_s^T) \left[\prod_{i=1}^n \|\mathbf{H}_i\| (\mathbf{E}_s \times \mathbf{P}_i) \right] (\hat{\mathbf{e}}_s \times \mathbf{e}_s) \quad (4)$$

where s is the number of rotational states for each bond, $\hat{\mathbf{e}}_r$ is a γ -dimensional vector defined by $(000 \dots 1)^T$, and $\times$ signifies a direct product of two vectors or matrices.¹⁵ The generator matrix $\mathbf{H}_i$ has the form:

$$\mathbf{H}_i = \begin{bmatrix} 1 & 2\mathbf{v}^T \mathbf{A} & \mathbf{v}^T \mathbf{v} \\ \mathbf{0} & \mathbf{A} & \mathbf{v} \\ \mathbf{0} & \mathbf{0} & 1 \end{bmatrix}_i \quad (5)$$

with the transformation matrix A_i defined by

$$A_i = \begin{bmatrix} \alpha & \beta & 0 \\ \beta \cos \theta & -\alpha \cos \theta & \chi \sin \theta \\ \beta \sin \theta & -\alpha \sin \theta & -\chi \cos \theta \end{bmatrix}_i \quad (6)$$

where the subscript i on the brackets refers to all quantities contained therein; $\alpha = \cos \omega$ and $\beta = \sin \omega$, with ω being the supplementary bond angle; θ is the rotational angle; χ is the vectorial quantity considered; χ takes a value of $+1$ or -1 depending on whether the coordinate systems associated with two consecutive bonds are constructed on reference frames of the same handedness or not. Except for A_i about the O—C bond of SY configuration, χ should take a value of unity. The pseudodiagonal supermatrix $\|H_i\|$ is defined by

$$\|H_i\| = \begin{bmatrix} H(\theta^{(1)}) & & \\ & H(\theta^{(2)}) & \\ & & \ddots \\ & & & H(\theta^{(s)}) \end{bmatrix}_i \quad (7)$$

To a first approximation, the stereochemical composition of a PPG chain may be represented by the probability F_r of SY placement. Therefore chain configurations with different F_r values can be generated by using a table of random numbers¹⁸ from 0 to 99; numbers smaller than $100F_r$ are used to specify IS placement and those larger than $100F_r$ to specify SY one. In this way, we generated a number of such Monte Carlo chains having different F_r values and chain lengths, for which the mean-square end-to-end distance $\langle r^2 \rangle$ and the mean-square dipole moment $\langle u^2 \rangle$ were calculated by introducing relevant values for the parameters into eq 4. The averages of the values obtained for two or three Monte Carlo chains so generated were taken to be the desired ones, since no significant differences were observed in the value of F_r among them. The longest chains examined had an N of 100, which is expected to be sufficiently long for characterizing an infinite chain as will be seen below.

Results and Discussion

In order to examine which type of potential function is more appropriate for the van der Waals interaction, we first compare the values of the characteristic ratio $\langle r^2 \rangle / nb^2$ evaluated with

the use of the two types of potential functions mentioned above, where $\bar{b}^2 = (1/3)(b_{C-O}^2 + 2b_{C-O}^2)$. The ratio $\langle r^2 \rangle / nb^2$ at 50°C is calculated to be 4.534 for IS and 5.619 for SY with a type-I potential function, whereas the corresponding values with a type-II potential function are 3.764 and 4.856, respectively. Allen, *et al.*,¹⁹ reported an experimental determination of the characteristic ratio $\langle r^2 \rangle / nb^2$ for PPG samples having different tacticities, with the following results: 5.08 deduced from the analysis of viscosity data for narrow fractions in hexane at 46°C²⁰ and 5.78(± 0.5) deduced from both viscosity and light scattering data for a number of fractionated samples in a theta solvent (isooctane at 50°C).²⁰ They have also pointed out that the characteristic ratio of PPG is insensitive to its tacticity,^{19,20} although no quantitative data for their samples has been given. Agreement between theory and experiment is fairly good, especially when the type-I potential function is assumed. However, the agreement is not necessarily satisfactory notably with the type-II potential function unless the PPG samples used by Allen and coworkers happen to be highly syndiotactic. We shall consider possible reasons for this disagreement which might be attributed to some drawbacks of the models employed.

At first the type-I potential function was found to give a value of only 2.2 kcal/mol to the energy for $G'G$ conformation of C—O—C bond pair. This value is much smaller than the >5 kcal/mol assigned to that of poly(oxyethylene glycol) chains.^{1,2} Consideration of interactions among atom pairs separated by five bonds encompassing the C—O—C bond pair, namely, $C(CH_2) \cdots C(CH_3)$, $C(CH_2) \cdots H(CH)$, and $C(CH_2) \cdots O$, should obviously increase the energy of each conformer produced by rotations about the skeletal C—C bonds. In fact, a calculation based on the type-I function gives for the corresponding interaction energies (and the distances between atom pairs in the parenthesis) at $\theta_a = 0, 120, \text{ and } -120^\circ$, values of 529 (kcal/mol) (1.615 Å), 16 (1.839 Å), and 190 (1.586 Å), respectively, all with $\theta_b = -100^\circ$ and $\theta_c = 100^\circ$. This clearly shows that both the GG' and $G'G$ conformations of C—O—C bond pair should be energetically excluded. According to an estimate based on

the type-I potential function, however, exclusion of the GG' and $G'G$ conformations has only a minor effect on the value of the characteristic ratio for both IS and SY chains.

Another difficulty arises from the fact that the energy minimum cannot be located very accurately; the precision in measuring the rotation angle is about $\pm 10^\circ$, as can be seen from the broadnesses of energy minimum regions in the contour maps (see Figures 3–5). To see the effect of this uncertainty in the locations of the energy minima, we carried out calculations with some illustrative cases. For example, it can be shown in a manner similar to that employed previously for polyethylene²¹ that a fluctuation of 15° around the T state of $O-C$ bond produced only a slight decrease in the characteristic ratio (decrease of 1% with the type-I potential). None of several trials, including adoption of $\Delta\theta_b^1 = -15^\circ$, $\Delta\theta_b^2 = 0^\circ$, and $\Delta\theta_b^3 = 10^\circ$ (2–3% decrease), was found to achieve better agreement with the experimental data. We hereafter adopt the models based on the data given in Table II excluding $G'G$ conformations of $C-O-C$ bond pair. The models with type-I and -II potential functions are designated simply as model I and model II, respectively. As far as the characteristic ratio is concerned, model I is better than model II and the van der Waals interaction potential function of type I recommended by Scott and Scheraga¹⁰ and by Abe, *et al.*,¹¹ is more appropriate for PPG chains.

Figure 6 shows the dependence of $\langle r^2 \rangle / nb^2$ on the SY placement; the solid line is for model I and the chain line is for model II. The characteristic ratio is seen to be relatively insensitive to tacticity, being in agreement with the experimental observation by Allen, *et al.*,^{19,20} This is in contrast with asymmetric vinyl chains, for which the ratio is predicted to depend largely on the stereochemical composition.^{2–5} This difference is probably due to the structural difference in that pendant groups of the latter polymer are spaced two bonds apart, whereas those of PPG (methyl groups) are spaced three bonds apart. It is reasonable to suppose that two methyl groups located three bonds apart may have smaller steric interaction than do those two bonds apart. NMR studies^{22–24} indicated that F_r values for unfractionated acetone-soluble

Figure 6. The calculated values for $\langle r^2 \rangle / nb^2$ at 50°C of PPG chains plotted against the fraction F_r of SY configuration. The solid line is for model I and the chain line is for model II, with the values of the parameters given in Table II. Vertical segments represent the scatter of the calculated values for three Monte Carlo chains.

samples of PPG were in the range 0.43–0.47. Allen, *et al.*,¹⁹ used crystallizable and noncrystallizable fractions of PPG to obtain essentially the same characteristic ratios for both fractions. As they have suggested,¹⁹ their samples are not very different with respect to tacticity.

We next consider dipole moments of PPG and of its model compound. Use of the type-I potential function yields a value of $1.691D$ for $\langle u^2 \rangle^{1/2}$ of 1,2-dimethoxypropane. This value is in close agreement with experimental data reported by Abe, *et al.*: $1.66D$ in benzene and $1.58D$ in cyclohexane, both at 25°C . Similar calculations for PPG chains have led to the result that $\langle u^2 \rangle / nm^2 = 0.573$ and 0.641 for infinite chains of IS and SY configurations at 25°C , respectively. The former value is practically identical to experimental values of 0.54 – 0.57 reported by Abe, *et al.*,⁹ for atactic and isotactic PPG samples having high molecular weights in cyclohexane at 25°C . They obtained somewhat higher values of 0.74 – 0.75 for the same specimens in benzene at 25°C . Figure 7 demonstrates the theoretical values of $\langle u^2 \rangle / nm^2$ calculated for the two models

Figure 7. Dependence of $\langle u^2 \rangle / nm^2$ at 25°C on degree of polymerization as a function of F_r . Vertical segments attached on the curve for $F_r = 0.5$ represent the scatter of theoretical values calculated for two Monte Carlo chains. Circles and triangles denote the experimental data by Loveluck²⁵ and by Le Fevre and Sundaram,²⁶ respectively.

as functions of chain length and of F_r , where the experimental data of Loveluck²⁵ (circles) and of Le Fevre and Sundaram²⁶ (triangles) are included for comparison. These authors' data appear somewhat below the theoretical values whatever tacticities their samples may have had.

As seen in Figure 7, model I is characterized by a slight increase in $\langle u^2 \rangle / nm^2$ with increasing F_r and by a gradual decrease with increasing chain length. The former feature is consistent with the experimental finding of Abe, *et al.*,⁹ that there was no significant difference in this quantity between atactic and isotactic samples, and the latter feature is in accord with the data of Loveluck²⁵ and of Le Fevre and Sundaram.²⁶ Model II predicts $\langle r^2 \rangle / nb^2$ and $\langle u^2 \rangle / nm^2$ inconsistent with the experimental observations, and hence may be ruled out. We have also calculated the temperature coefficients of the mean-square moments for model I, typical results of which are compiled in Table III. No experimental data is as yet available to test this theoretical prediction.

Summarizing, we have attained a close agreement between theory and experiment for the mean-square end-to-end distance and the mean-square dipole moment of PPG chains assuming the van der Waals potential function recommended by Scott and Scheraga¹⁰ and by Abe, *et al.*¹¹ The mean-square moments are predicted

Table III. Effect of temperature on the mean-square moments of PPG chains as a function of the fraction of SY configuration with model I

F_r	$-d \ln \langle r^2 \rangle / dT, \times 10^{-3}$	$\langle r^2 \rangle / nb^2, 50^\circ\text{C}$	$d \ln \langle u^2 \rangle / dT, \times 10^{-3}$	$\langle u^2 \rangle / nm^2, 25^\circ\text{C}$
0.0	0.503	4.598	0.330	0.573
0.5	0.361	5.045	0.301	0.616
1.0	0.180	5.690	0.476	0.641

to increase slightly with increasing syndiotacticity, being consistent with the experimental observations.^{9,19,20} This contrast with asymmetric vinyl chains may be accounted for by the difference between their structures; pendant groups of PPG are spaced three bonds apart, whereas those for vinyl chains are spaced two bonds apart.

One of the reviewers for the present article raised the suggestion that the linkage irregularity, *e.g.*, head-to-head linkages, etc., might have more serious effects on the mean-square moments. Our calculations showed, however, that the effects were of minor importance, though not completely negligible, in comparison with the stereoregularity effect. The details will be published in a separate paper.

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