Macromolecules **1987**, *20*, 1961–1964 **1961**

Flexibility in Rigid Rod Poly(*n*-alkyl isocyanates)

Robert Cook

Lawrence Livermore National Laboratory, Livermore, California 94550.

Received January 29, 1987

ABSTRACT: Poly(*n*-alkyl isocyanates) are known to be helical rigid rod polymers with persistence lengths from 20 to 60 nm, depending on the specific *n*-alkyl group and solvent. Light-scattering and viscosity measurements of well-fractionated samples have clearly shown the transition from rod-like to coil-like behavior with increasing degree of polymerization. It has been suggested that the loss of rigidity may be caused by occasional helix reversals in addition to torsional and bond angle flexibility in the backbone rotational and bond angles. We have calculated a variety of chain properties allowing only specific levels of torsional and bond angle flexibility and show that the loss of rigidity as manifest in the observed experimental measurements of persistence length, radius of gyration, and dipole moment is completely consistent with a small and physically reasonable degree of flexibility in these angles.

Introduction

Poly(*n*-alkyl isocyanates) have been known for some time to be stiff rod-like macromolecules, particularly when viewed on a short length scale.[1-4] It is generally accepted that the rod-like structure is a result of a helical twist to the chain, although the exact nature of the helix in solution is not known with certainty. The helical form is thought to be due to a combination of electronic and steric factors. In the absence of the latter we would expect the local structure of the macromolecule to be planar due to electron delocalization on the backbone carbon and nitrogen and on the pendant oxygen. The planar all-trans and alternating cis–trans geometries are shown in Figure 1. Steric interactions between the adjacent R groups in the all-trans structure or between an R group and the opposing oxygen in the cis–trans structure force a regular nonplanarity which results in a helical twist. The structure of the crystalline state also reflects this feature, exhibiting a repeat unit involving eight monomers per three twists.[5] Several workers[6-8] have attempted to determine the helical structure in solution through the study of semiempirical potential energy expressions for the local structure. A review of these studies is given by Tonelli.[8] Although the results of every study have indicated a helical conformation for the polymer, the rotational angle sequence was markedly different in each case, due to differences in the completeness of the potential energy functions used and the local geometry assumed. The different helices and local geometry parameters are given in Table I. With regard to the choice of helix, the Troxell and Scheraga[6] result is perhaps best since it alone approximates the experimentally determined dipole moment data reported by Bur and Roberts.[9] Additionally the helix is very similar to that found in the crystalline state, having close to eight residues per three turns. On the basis of these factors, we will examine only the Troxell–Scheraga helix in the calculations that follow, though we would not expect qualitatively different results for the other helices.

Solution light scattering of carefully fractionated samples has given us detailed information about the radius of gyration as a function of molecular weight or degree of polymerization.[10,11] These studies show that at low degree of polymerization the root-mean-squared radius of gyration, $\langle r_g^2\rangle^{1/2}$, is a linear function of the degree of polymerization, reflecting the relative rigidity of the macromolecular rod. However, at larger degrees of polymerization, the dependence changes over to the square root of the degree of polymerization, the expected random coil result. Thus, the rod-like properties of these systems are only a short length scale phenomena, perhaps best characterized by the persistence length, defined as[12]

$$a = \sum_{j=i}^{\infty} \frac{\langle \mathbf{b}_j \cdot \mathbf{b}_i \rangle}{b_i} \tag{1}$$

where $\mathbf{b}_i$ is a backbone bond vector interior to the chain. The averaging is taken over the allowable conformations of the chain. Using intrinsic viscosity measurements on carefully fractionated samples, Kuwata et al.[13] were able to show that the persistence length is about 35 nm in butyl chloride by application of Yamakawa–Fujii–Yoshizaki theory[14,15] for a wormlike chain model. Murakami et al.[11] used Benoit–Doty theory[16] and light-scattering measurements of the radii of gyration for fractions in hexane to determine a persistence length of 42 nm. It is on length scales much longer than these that the polymer takes on a random coil configuration.

Table I
Poly(*n*-alkyl isocyanate) Helix Geometries from Different Theoretical and Experimental Studies

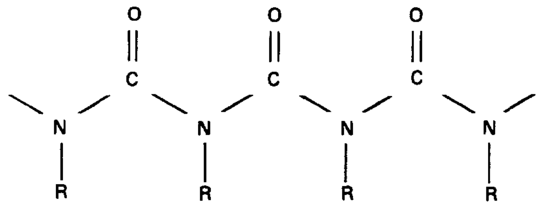
study	(ϕ_{CN},ϕ_{NC})[a]	r_{CN}, nm	r_{NC}, nm	θ_{NCN}, deg	θ_{CNC}, deg
ref 6	(−40°,160°) or (40°,200°)	0.132	0.132	120	114
ref 7	(±95°,±95°)	0.132	0.132	120	106
ref 8[b]	(±40°,±40°)	0.132	0.132	120	114
ref 5[c]	(−51.5°,162.1°) or (51.5°,197.7°)	0.141	0.139	120	129

[a] The subscripts refer to backbone atoms in the order shown in Figure 1. Rotational angles are measured from the all-trans configuration. [b] A number of local geometries were examined with the (±40°,±40°) helix. [c] The Shmueli et al.[5] paper does not give the rotational angle sequence, and the bond lengths and backbone bond angles given are only representative. The rotational angles given above are those needed to form a helix, with the backbone geometric parameters shown, that executes exactly three twists over eight monomers with an average monomeric projection of 0.194 nm.

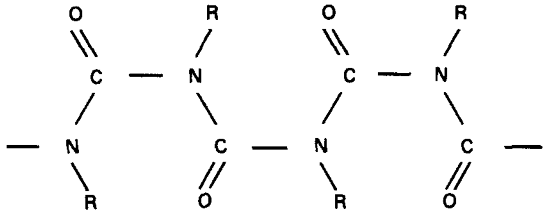
It has been suggested that this transition from rod to coil is promoted by occasional helix reversals. Tonelli[8] calculated the energy of a reversal to be about 12.6 kJ/mol. He then showed that reversals with a probability based on this energy roughly explained the decrease with increasing molecular weight of the ratio of the measured dipole moment to the degree of polymerization as measured by Bur and Roberts.[9]

We might ask, however, what the origin of the reversals is. If they are thermally activated, then we must be concerned with the barrier to reversal, which is very likely to be much higher than 12.6 kJ/mol, making thermal activation less likely. It is also possible that reversals occur during synthesis. Here it also seems likely that the barrier

0024-9297/87/2220-1961$01.50/0



All trans



Alternating cis–trans

Figure 1. All-trans and alternating cis–trans planar structures of poly(n-alkyl isocyanates). Steric repulsions between adjacent R groups in the all-trans structure or between opposing R groups and oxygen atoms in the cis–trans structure cause a helical twist in the chain.

to incorporating a reversal is higher than 12.6 kJ/mol. Either situation also begs the question as to whether or not such reversals would be mobile.

However, reversals are not the only explanation that would lead to the experimental observation of random coil behavior for large degrees of polymerization. It must be remembered that both the rotational angles and the backbone bond angles are not fixed at unique values but rather oscillate about potential minima. These fluctuations will collectively give the rod some flexibility and, as pointed out by Bur and Roberts[9] and later by Mansfield,[17] will ultimately lead, at high enough degree of polymerization, to a random coil configuration without helix reversals. This description is in fact central to the classical worm-like behavior of the Porod–Kratky chain.[18] The difficulty in resolving this question concerning the role of helix reversals and torsional flexibility has recently been addressed by Mansfield,[19] who has shown that based upon measurements of moment-dependent polymer properties such as viscosity and radius of gyration, one cannot distinguish between a flexible rod and a stiff rod with breaks.

The purpose of this paper is to thoroughly explore the role flexibility plays with respect to a specific group of rigid rod polymers, the polyisocyanates. We show that the degree of fluctuation in the rotational angles and backbone bond angles necessary to reproduce the experimental measurements of persistence length, radius of gyration, and dipole behavior is, in fact, quite small and largely independent of the particular experimental measurement and that the experimental data can easily be explained without invoking helix reversals.

Theory

In addition to the persistence length, defined in eq 1, we will be interested in the mean-squared radius of gyration, $\langle r_g^2 \rangle$, where

$$\langle r_g^2 \rangle = n^{-2} \sum_{1 \le h < k \le n} \langle r_{hk}^2 \rangle \qquad (2)$$

n is the number of atoms in the chain, and r_{hk} is the distance between atoms h and k. We have used the theorem of Lagrange[20] and further have focused only on the chain backbone atoms, neglecting their mass differences. If we let $\mathbf{r}_{hk}$ be the vector from atom h to atom k, we can express $\mathbf{r}_{hk}$ in standard fashion as a sum of individual bond vectors, so that

$$\mathbf{r}_{hk} = \mathbf{b}_h + \mathbf{b}_{h+1} + \ldots + \mathbf{b}_{k-1} \qquad (3)$$

Substituting into eq 2 we have

$$\langle r_g^2 \rangle = n^{-2} \sum_{h=1}^{n-1} \sum_{k=h+1}^{n} \sum_{i=h}^{k-1} \sum_{j=h}^{k-1} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle \qquad (4)$$

Thus, the radius of gyration and persistence length can be expressed in terms of appropriate sums of average bond vector products, $\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle$. We also note that the mean-squared end-to-end distance $\langle r^2 \rangle$ can be expressed as

$$\langle r^2 \rangle = \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = (n-1) b^2 \left(\frac{2a}{b} - 1 \right) \qquad (5)$$

where the second equality is true in the limit of long chains.[12] Thus, once we have calculated the persistence length, which is independent of the degree of polymerization, we can calculate $\langle r^2 \rangle$ for very long chains and then get $\langle r_g^2 \rangle$ by remembering that $\langle r_g^2 \rangle / \langle r^2 \rangle = {}^1/_6$ in the random coil limit.

Following the approach made popular by Flory,[21] each bond vector is defined in its own reference frame. Thus, to evaluate the product $\mathbf{b}_i \cdot \mathbf{b}_j$, we must express the vector $\mathbf{b}_j$ in the ith frame. This may be accomplished by using a transformation matrix $\mathbf{T}_i$ which has the form

$$\mathbf{T}_i = \begin{pmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{pmatrix} \qquad (6)$$

We use the reference frame definitions of Flory so that θ_i is the complement of the bond angle between bonds i and $i + 1$, and ϕ_i is the rotational angle of bond i, the value of the trans state being zero. By successive application of $\mathbf{T}_i$, we can write

$$\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = \langle \mathbf{b}_i^{t} (\mathbf{T}_i \ldots \mathbf{T}_{j-1}) \mathbf{b}_j \rangle \qquad (7)$$

where the product of transformation matrices brings $\mathbf{b}_j$ into the reference frame of $\mathbf{b}_i$ and $\mathbf{b}_i^{t}$ is the transpose of $\mathbf{b}_i$. As noted earlier, the averaging indicated in eq 7 is over the various conformations of the chain. Normally this means the introduction of a statistical weight matrix to properly weight the various rotational isomeric states. In the problem at hand, however, the helix is specified by a unique sequence of rotational states, and our interest is in averaging over the fluctuations in the rotational angles (and bond angles) for the given sequence of rotational states which describe the helix. As previously shown by Cook and Moon[22] and later by Mansfield,[17] if we let δ_ϕ and δ_θ be the root-mean-squared fluctuations in the rotational angles and backbone bond angles, respectively, and if we assume that all neighboring fluctuations are independent of one another, we can preaverage the transformation matrix for these fluctuations, which results in

$$\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = \mathbf{b}_i^{t} (\langle \mathbf{T}_i \rangle \ldots \langle \mathbf{T}_{j-1} \rangle) \mathbf{b}_j \qquad (8)$$

where

$$\langle \mathbf{T}_i \rangle = \begin{pmatrix} \langle \cos\theta_i \rangle & \langle \sin\theta_i \rangle & 0 \\ \langle \sin\theta_i \rangle \langle \cos\phi_i \rangle & -\langle \cos\theta_i \rangle \langle \cos\phi_i \rangle & \langle \sin\phi_i \rangle \\ \langle \sin\theta_i \rangle \langle \sin\phi_i \rangle & -\langle \cos\theta_i \rangle \langle \sin\phi_i \rangle & -\langle \cos\phi_i \rangle \end{pmatrix} \qquad (9)$$

The averages in eq 9 are easily evaluated and yield

$$\langle \cos\omega \rangle = \cos\omega_0 \exp(-\delta_\omega^2/2) \qquad (10)$$

and

$$\langle \sin\omega \rangle = \sin\omega_0 \exp(-\delta_\omega^2/2) \qquad (11)$$

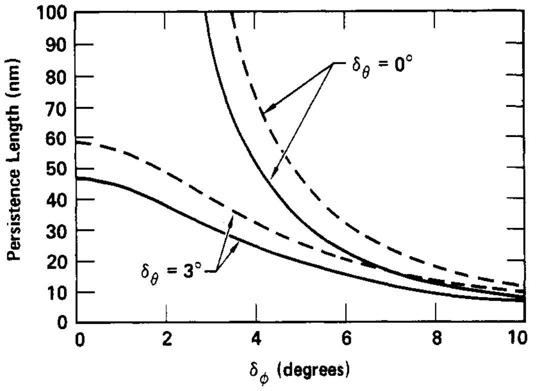


Figure 2. Plot of persistence length, *a*, as a function of torstional angle flexibility, δ_ϕ. Results for both the Troxell–Scheraga geometry (solid lines) and the Shmueli geometry (dashed lines) are shown for two different values of the backbone bond angle flexibility parameter, δ_ϕ. Table I details the geometries used.

where ω_0 is the rotational angle or backbone bond angle around which the oscillations occur. Thus, using this modified transformation matrix, we can calculate the desired average bond vector products and compute average helix properties for varying degrees of flexibility in the rotational angles and backbone bond angles. The results of these calculations follow.

Results and Discussion

In Figure 2 we have plotted the persistence length as a function of δ_ϕ for values of δ_θ equal to zero and three. In order to span the possible geometries, we have done calculations on both the Troxell–Scheraga geometry (solid lines) and the Shmueli geometry (dashed lines) for the Troxell–Scheraga helix. Note first and most importantly that the persistence length is extremely sensitive to the flexibility parameters of the chain. This sensitivity explains in part the strong solvent and pendant group dependence of *a*, since we would expect the torsional flexibility to be strongly affected by these factors.[23] If we take 40 nm as the experimental value we wish to match, one can also see that the degree of torsional and bond angle flexibility needed to achieve this value depends somewhat on the geometry picked. However, what is most significant is that even in the case where we allow no backbone bond angle flexibility, we only need a value of δ_ϕ between 5° and 6° to reproduce the experimental result. This is clearly an upper limit, since any flexibility in the backbone bond angles will reduce the needed rotational angle flexibility. We note here that this result agrees well with that obtained by Mansfield.[17]

It is fair to ask what magnitude of rotational angle flexibility we might expect. In his potential energy calculations, Tonelli[8] modeled the rotational potental as

$$V_\phi = (V_\phi{}^0/2)(1 - \cos 2\phi) \qquad (12)$$

with values of $V_\phi{}^0$, the intrinsic barrier to rotation, up to 83.7 kJ/mol. At this level, the calculated δ_ϕ would be 7.0°. Temperature-dependent nuclear magnetic resonance studies on urea and 1-methylurea give values of $V_\phi{}^0$ of 46.0 and 31.4 kJ/mol, respectively,[24,25] which correspond to δ_ϕ values of 9.4° and 11.4°. Values of δ_ϕ based only on the intrinsic rotational potential are, of course, upper limits, since the Coulombic and van der Waals interactions are not included and would certainly act to restrict the flexibility in local chain motion. Tonelli gives some detailed total energy data around the $(\phi_{\mathrm{CN}}, \phi_{\mathrm{NC}}) = (\pm 40°, \pm 40°)$ helix in Table II of his paper.[8] A crude extraction of δ_ϕ from this data for $V_\phi{}^0$ equal to 41.8 kJ/mol gives a value of about 4°. This value is probably low, since it is extracted from data for a pair of bonds rotating together from equilibrium, a higher energy situation than for a single rotation. Thus, the conclusion to be drawn is that the values of rotational angle flexibility necessary to reproduce the experimentally determined persistence lengths are certainly within the scope of reasonable values and perhaps may be smaller than one would expect, particularly if one allows some backbone bond angle flexibility. This may be reasonable if there is significant correlation between fluctuations on neighboring bonds, a feature explicitly ignored in our preaveraged transformation matrix approach.

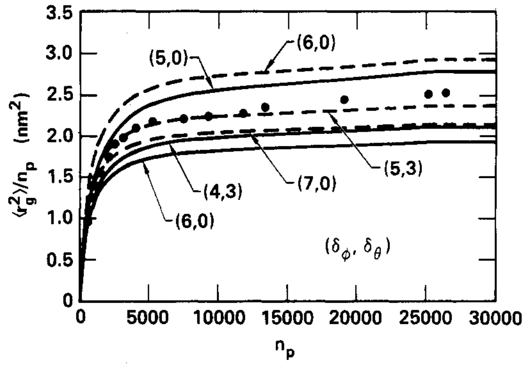


Figure 3. Plot of the mean-squared radius of gyration, $\langle r_g{}^2\rangle$, divided by the degree of polymerization, n_p, as a function of n_p. Results for both the Troxell–Scheraga (solid lines) and Shmueli (dashed lines) are shown for several $(\delta_\phi,\delta_\phi)$ pairs. The experimental data of Murakami et al.[11] are also shown as solid circles.

The persistence length is, of course, not dependent on the degree of polymerization as is the mean-squared radius of gyration, $\langle r_g{}^2\rangle$. Thus, it is of interest to see if our approach to rod flexibility follows the transition from rod to coil behavior accurately. We have plotted our calculated $\langle r_g{}^2\rangle/n_p$, where n_p is the degree of polymerization, vs. n_p in Figure 3 for the Troxell–Scheraga geometry (solid lines) and for the Shmueli geometry (dashed lines). In each case the Troxell–Scheraga helix (−40°,160°) is used, and curves for several combinations of δ_ϕ and δ_θ are shown. Also shown are the experimental data of Murakami et al.[11] for fractionated samples of poly(*n*-hexyl isocyanate) in hexane. It is not our objective to "fit" these data exactly, and the calculated curves serve only to define the range. We see again that, depending somewhat on the geometry chosen, the data are well represented by values of δ_ϕ between 5° and 7° or less if flexibility is allowed in the backbone bond angles.

As mentioned earlier, experimentally measured dipole moments exist as a function of molecular weight for poly(*n*-butyl isocyanate).[9] Since the chain dipole moment is proportional to the end-to-end length, we can write $\mu \propto \langle r^2\rangle^{1/2}$, where μ is the magnitude of the dipole moment and $\langle r^2\rangle^{1/2}$ is the root-mean-squared end-to-end length. At low molecular weight when the polymer is more rod-like, we might expect $\langle r^2\rangle^{1/2}$ to be proportional to the degree of polymerization, n_p, and thus μ/n_p should be equal to a constant, determined experimentally by Bur and Roberts[9] and reported to be 1.13 D per residue. In fact, any degree of flexibility is manifest, even at low n_p, by a decrease in the ratio of μ/n_p with increasing n_p, the decreased being more steep the greater the flexibility. A reinterpretation of the Bur and Roberts data in this context leads to a limiting value in excess of 1.25 D per residue. In Figure 4 we plot the experimental data of Bur and Roberts (expressed as μ/n_p) along with our calculated values of $A\langle r^2\rangle^{1/2}/n_p$ vs. n_p for several values of δ_ϕ for both

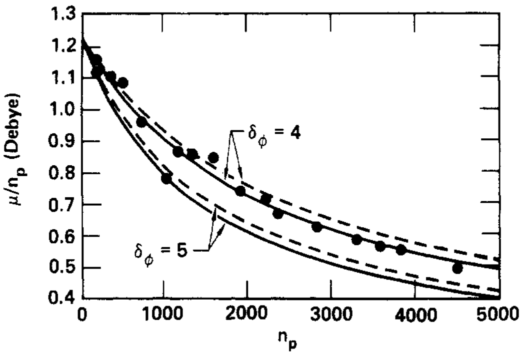


Figure 4. Plot of the chain dipole, μ, divided by n_p as a function of n_p where μ is calculated from the mean-squared end-to-end length, $\langle r^2 \rangle$, and limiting dipole per residue, A, as $A\langle r^2 \rangle^{1/2}/n_p$. Different geometries and degrees of flexibility are shown as in Figure 3. The experimental data for Bur and Roberts[9] are also shown as solid circles.

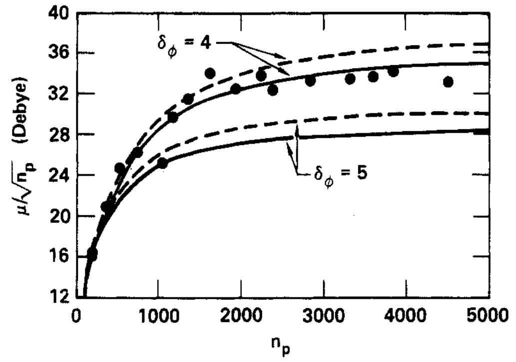


Figure 5. Same as Figure 4 except the ordinate is now $\mu/n_p^{1/2}$.

the Troxell–Scheraga (solid lines) and Shmueli (dashed lines) geometries. The value of A is determined to reproduce a limiting value of 1.25 D per residue and is computed for each geometry by dividing 1.25 D by the projection length per residue for the perfectly stiff rod. What we see is that torsional (and backbone bond angle) flexibility is sufficient to accurately map the decrease in μ/n_p with increasing degree of polymerization.

As n_p becomes large and the polymer assumes random coil behavior, $\langle r^2 \rangle$ becomes proportional to n_p, and thus we would expect $\mu/n_p^{1/2}$ to approach a constant for large n_p. In Figure 5, we plot $A\langle r^2 \rangle^{1/2}/n_p^{1/2}$ vs. n_p for several values of δ_ϕ for the two geometries along with the experimental data of Bur and Roberts (expressed as $\mu/n_p^{1/2}$). Again we see reasonable agreement with the experimental data. Particularly noteworthy is the fact that the value of A taken to fit the low molecular weight data leads to accurate predictions of the high molecular weight data.

What we have shown is that the observed experimental properties of the poly(n-alkyl isocyantes) can be completely and consistently explained by taking into account a small and reasonable degree of torsional and bond angle flexibility. We cannot claim on the basis of this study that helix reversals are not present, only that they are not necessary to explain the data. Certain experiments on specific systems may, in fact, be able to distinguish between contributions from flexibility and reversals. Work in this area will be reported shortly.

Acknowledgment. I thank Prof. Mark M. Green of Polytechnic University and Dr. Lucy Lucht of LLNL for several useful discussions and also Dr. Alan E. Tonelli of AT&T Bell Laboratories for access to his notes on his 1974 paper. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

References and Notes

(1) Shashoua, V. E.; Sweeney, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.
(2) Berger, M. N.; Tidswell, B. M. *J. Polym. Sci., Polym. Symp.* **1973**, *42*, 1063.
(3) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727.
(4) Green, M. M.; Gross, R. A.; Crosby, C.; Schilling, F. C. *Macromolecules* **1987**, *20*, 992.
(5) Shmueli, U.; Traub, W. Rosenheck, K. *J. Polym. Sci, Part A-2* **1969**, *7*, 515.
(6) Troxell, T. C.; Scheraga, H. A. *Macromolecules* **1971**, *4*, 528.
(7) Han, C. C.-C.; Yu, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1973**, *14*, 121.
(8) Tonelli, A. E. *Macromolecules* **1974**, *7*, 628.
(9) Bur, A. J.; Roberts, D. E. *J. Chem. Phys.* **1969**, *51*, 406.
(10) Rubingh, D. N.; Yu, H. *Macromolecules* **1976**, *9*, 681.
(11) Murakami, H.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 345.
(12) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969; p 111.
(13) Kuwata, M.; Murakami, H.; Norisuye, T.; Fujita, H. *Macromolecules* **1984**, *17*, 2731.
(14) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(15) Yamakawa, H.; Yoshizaki, T. *Macromolecules* **1980**, *13*, 633.
(16) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(17) Mansfield, M. L. *Macromolecules* **1983**, *16*, 1863.
(18) Reference 12, pp 401–403.
(19) Mansfield, M. L. *Macromolecules* **1986**, *19*, 854.
(20) Reference 12, pp 383–384.
(21) Reference 12, Chapter 1.
(22) Cook, R.; Moon, M. *Macromolecules* **1980**, *13*, 1537.
(23) Green, M. M., private communication.
(24) Filleux-Blanchard, M. L.; Duranol, A. *J. Magn. Reson.* **1971**, *3*, 187.
(25) Walter, W.; Schaumann, E.; Rose, H. *Tetrahedron* **1972**, *28*, 3233.