termine to what degree the anisotropy becomes apparent at higher scattering angles.

Summary and Discussion

This calculation demonstrates the degree to which structures can be ordered and still conform to eq 1. With $^1/_3$ random reentry, enough disorder is present for the development of Gaussian statistics. Bonds i and j are uncorrelated for most values of i and j. The bond correlations, when properly summed, yield the characteristic ratio. The correlation range is longer in the semicrystalline state, but an appreciable fraction of these correlations are negative, since loops reverse the chain direction. Then it is not surprising that these sum to give a characteristic ratio close to the value in the melt. Equations 20 and 24 indicate that the characteristic ratio is actually lower for small crystallinities. In the limit of very thin lamellae separated by thick amorphous layers, we expect a characteristic ratio very close to the melt value, but smaller, since the chains are turned back upon themselves.

A qualitative explanation for the small change in characteristic ratio is that the chains resist long-range reorganization during quench crystallization. Phrases such as "freezing in" are often employed, implying that the chains have the same global structure before and after solidication with no detectable differences at low resolution. Yet it appears that long-range reorganization must occur, since the chains assume an anisotropic distribution after crystallization. In any case, one need not assume absence of long-range reorganization to explain the small change in C_∞.

Some comment on the range of applicability of the present model is in order. To avoid segregation, the neutron scattering experiments are performed on quench-crystallized samples. The result is a relatively low crystallinity (never much larger than 0.5 or 0.6). Implicit in this derivation is the assumption that different amorphous runs are uncorrelated, which is undoubtedly adequate for low-temperature, regime III crystallization.[17] We have also assumed $^2/_3$ near-adjacent reentry,[7] but we expect a higher degree of adjacent reentry for crystallization at higher temperatures. Therefore, the present model is probably not valid in all situations. This may explain the failure of isotactic polystyrene[6] to follow eq 1. Segregation effects are absent[6] in this polymer, and the measurements were performed on samples crystallized closer to the melting point.

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$$\langle N\rangle = n(N_c \sec\theta + \epsilon\langle M\rangle_{loop} + \delta\langle M\rangle_{tie})$$

$\langle M\rangle_{loop} = (\sec\theta)/3$ (the probability that a loop is random) times the average length of a random loop, $2N_a$ (ref 7). $\langle M\rangle_{tie}$ is N_a^2 (ref 7).
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Broken Wormlike Chain Model of Semiflexible Polymers

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Received August 2, 1985

ABSTRACT: Traditionally, the flexibility of semiflexible polymers has been explained in one of two ways, either in terms of relatively small rotational angle fluctuations giving a smoothly bending curve or in terms of abrupt breaks, or kinks, in the chain. The original wormlike chain explicitly treats only the first of these two possibilities. Here we introduce the broken wormlike chain model, which explicitly incorporates both types of flexibility by inserting breaks at random intervals into the original wormlike chain, either through a fixed angle or through a universal joint. Exact expressions for the first three even moments and the radius of gyration are derived, and the hydrodynamic radius and static structure factor are approximated. We report very little difference between properties of broken and regular wormlike chains of the same total contour length and persistence length, which implies (1) that the original wormlike chain model provides an adequate description of most experiments independent of the nature of the flexibility and (2) that it may be difficult to determine experimentally which source of flexibility is operating in any given polymer.

Introduction

A number of polymer chains, e.g., the poly(alkyl isocyanates)[1-3] or the DNA double helix,[4-7] are semiflexible, with rigid rod behavior at low molecular weights and random coil behavior at high molecular weights. The Kratky–Porod or wormlike chain model[8-11] represents a semiflexible molecule as a smoothly bending space curve characterized by two parameters, L, the contour length of the curve, and λ, the stiffness parameter, having units of reciprocal length. $(2\lambda)^{-1}$ is the correlation length or persistence length of the curve, the length over which directional correlation persists. Then the quantity $L\lambda$ is pro-

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0024-9297/86/2219-0854$01.50/0

portional to the contour length in units of the persistence length, and for appropriate values of $L\lambda$ the model comprises rigid rod ($L\lambda \ll 1$), random coil ($L\lambda \gg 1$), and all intermediate behaviors. For excellent discussions and access to the original literature, the reader is refered to Yamakawa's book[9] and his recent review article.[10]

There has been some speculation concerning the source of flexibility in such molecules. On the one hand, it is argued that the flexibility results from relatively small fluctuations of the rotational angles about the stable helical conformation, and indeed, there is ample evidence that such fluctuations can account for the observed flexibility.[6,7,12,13] On the other hand, it is argued that the flexibility results from abrupt changes in the direction of the helical conformation, brought about, for example, by polymerization "errors" or high-energy conformational states. Such arguments have been advanced for double-helical DNA,[4,5] the polyisocyanates,[1,2,14,15] and certain polysulfones.[16-18] In this paper we accept the existence of both contributions to the flexibility; one cannot deny that nature, in general, allows both possibilities. One or the other may dominate in a particular polymer but examples of both undoubtedly exist. One purpose of this paper is to identify which, if any, of the characterization tools of experimental polymer science might be sensitive to the difference between these two contributions to flexibility.

The original wormlike chain explicitly models only the first contribution to flexibility: The smoothly bending space curve of the wormlike chain naturally models flexibility due to small rotational angle fluctuations about an otherwise rigid helix. Another purpose of this paper is to determine the extent to which the second source of flexibility alters the predictions of the wormlike chain. To do this, we introduce the "broken wormlike chain model", retaining the continuous space curve of length L and stiffness parameter λ but introducing abrupt breaks in direction at random intervals of mean length b. The change in direction at each break may be either through a fixed angle ρ or through a universal joint, making an arbitrary angle.[19] Related models have been studied in the past. Yu and Stockmayer[20] examined the "once-broken rod", i.e., two rods of equal length joined through a universal joint, and an expression given for the radius of gyration of "wormlike stars" comprehends "once-broken worms" as a special case.[21]

We have been successful in obtaining exact expressions for the second, fourth, and sixth moments of the end-to-end vector and for the radius of gyration and approximations, via the Koyama distribution,[22,23] for the hydrodynamic radius and the structure factor. We find that the inclusion of abrupt breaks does little violence to the original wormlike chain model except in the most extreme cases of small b and large ρ. For this reason, we are not suggesting that the model studied here be adopted for characterization of semiflexible chains. It is only presented as a critical test of the original wormlike chain model.

We treat the broken wormlike chain as the continuous limit of a freely rotating chain of N bonds in which each bond has length l. A fraction $(1 + C)^{-1}$ of the bonds meet at an angle Z. The remaining $C(1 + C)^{-1}$ meet at an angle ρ in the fixed-angle version of the model or at an arbitrary angle in the universal joint version. Then the broken wormlike model is obtained by taking the limit $N \to \infty$, $Z \to 0$, $l \to 0$, $C \to 0$, but in such a way that $lN = L$, the total contour length, $Z^2/4l = \lambda$, the stiffness parameter, and $l/C = b$, the mean distance between breaks, are all constant. The value ρ does not change in the limiting process. In this way the intervals between breaks in the chain follow the "most probable"[24] distribution. This, of course, is appropriate to the case in which breaks occur independently and is simpler to treat than other distributions.

The findings of this work are supported by several experimental studies. These are discussed more fully in the last section.

Second Moment and Radius of Gyration

For any two bonds of the discrete chain we have[25]

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+k} \rangle = l^2 \langle \cos \theta \rangle^k \tag{1}$$

where

$$\langle \cos \theta \rangle = (1 + C)^{-1}(\cos Z + C \cos \rho) \tag{2}$$

in the fixed-angle case and

$$\langle \cos \theta \rangle = (1 + C)^{-1} \cos Z \tag{3}$$

in the universal joint case. In the continuous limit, eq 1 becomes

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(s) \rangle = e^{-2\lambda_1 s} \tag{4}$$

where

$$\lambda_1 = \lambda + (1 - \cos \rho)/2b \tag{5}$$

in the fixed-angle case and

$$\lambda_1 = \lambda + 1/2b \tag{6}$$

in the universal joint case, and where $\mathbf{u}(0)$ and $\mathbf{u}(s)$ are unit vectors tangent to the chain at positions separated by a contour distance s. It follows that the persistence length of the broken wormlike chain is $(2\lambda_1)^{-1}$. Equation 4 is sufficient to determine both $\langle R^2 \rangle$ and R_g, the mean-square end-to-end distance and the radius of gyration. In fact, eq 4 differs from the equivalent expression for the original wormlike chain only in the replacement of λ for λ_1. Therefore, the expressions for $\langle R^2 \rangle$ and R_g for the broken wormlike chain are obtained by replacing λ with λ_1 in the well-known equivalent expressions[9] for the original wormlike chain. The exponential decay of correlation automatically guarantees that $\langle R^2 \rangle$ and R_g have the same form in both models, differing only in the definition of the persistence length. Note also that the original wormlike chain expressions are obtained in the limit $\rho \to 0$ or $b \to \infty$, since $\lambda_1 \to \lambda$. Therefore, an experiment that measures only R_g, even as a function of chain length, cannot differentiate between contributions from the two sources of flexibility discussed in the Introduction. Given this fact, we week to determine if other measurements are equally insensitive.

Fourth and Sixth Moments

Starting with the generator matrix expressions for $\langle R^4 \rangle$ and $\langle R^6 \rangle$ for arbitrary discrete chains with independent rotational potentials,[26,27] we obtained expressions for both $\langle R^4 \rangle$ and $\langle R^6 \rangle$ of the discrete broken wormlike chain and then evaluated these in the continuous limit. These derivations are extremely tedious and were performed by computer. Needless to say, it would be impossible to give the derivations here, but we will sketch the outline of the derivation of $\langle R^4 \rangle$. The derivation for $\langle R^6 \rangle$ is similar. The appropriate generator matrix equation for $\langle R^4 \rangle$ is given by Flory:[26]

$$\langle R^4 \rangle = 4[1\ 0\ 0\ 0\ \ldots][\mathbf{K}_0 + \mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3 + \mathbf{K}_4]^N \begin{bmatrix} 0 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix} \tag{7}$$

where the sum $\mathbf{K}_0 + \mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3 + \mathbf{K}_4$ is the original

generator matrix and where $\mathbf{K}_j$ includes only those portions of the matrix with units (length)^j. By expanding eq 7 we generate all possible sequences of N $\mathbf{K}$ matrices, but since the final result must have units (length)^4, we can safely retain only those sequences with the correct units. All the others must vanish. Therefore

$$\langle R^4\rangle = 4[1\ 0\ 0\ 0\ \ldots]\{\textstyle\sum_{\{ij\}_{N-1}}\mathbf{K}_0{}^i\mathbf{K}_4\mathbf{K}_0{}^j + \sum_{\{ijk\}_{N-2}}\mathbf{K}_0{}^i\mathbf{K}_1\mathbf{K}_0{}^j\mathbf{K}_3\mathbf{K}_0{}^k + \sum_{\{ijk\}_{N-2}}\mathbf{K}_0{}^i\mathbf{K}_3\mathbf{K}_0{}^j\mathbf{K}_1\mathbf{K}_0{}^k + \ldots + \sum_{\{ijklm\}_{N-4}}\mathbf{K}_0{}^i\mathbf{K}_1\mathbf{K}_0{}^j\mathbf{K}_1\mathbf{K}_0{}^k\mathbf{K}_1\mathbf{K}_0{}^l\mathbf{K}_1\mathbf{K}_0{}^m\}\begin{bmatrix}0\\0\\0\\\cdot\\\cdot\\\cdot\\1\end{bmatrix} \quad (8)$$

The symbol $\{ij\}_{N-1}$ indicates that i and j are allowed to assume all nonnegative integral values such that they sum to $N-1$, with similar notation applying to all the other sums.

To proceed, one need only begin collapsing matrix products, working from right to left. As this proceeds the number of terms grows rapidly, and a computer was used to perform the algebra. The following relationships prove necessary to the derivation:

$$\langle\mathbf{T}\rangle^n\cdot{}^3\mathbf{e}_1 = A_1{}^n\,{}^3\mathbf{e}_1 = \langle\cos\theta\rangle^n\,{}^3\mathbf{e}_1 \quad (9)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{Y}_1 = \frac{1}{3}[(2A_2{}^n + 1)\mathbf{Y}_1 + (1 - A_2{}^n)\mathbf{Y}_2] \quad (10)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{Y}_2 = \frac{1}{3}[(2 - 2A_2{}^n)\mathbf{Y}_1 + (2 + A_2{}^n)\mathbf{Y}_2] \quad (11)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{X}_1 = \frac{1}{5}[(2A_3{}^n + 3A_1{}^n)\mathbf{X}_1 + (A_1{}^n - A_3{}^n)(\mathbf{X}_2 + \mathbf{X}_3 + \mathbf{X}_4)] \quad (12)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{X}_2 = \frac{1}{5}[2(A_1{}^n - A_3{}^n)\mathbf{X}_1 + (A_3{}^n + 4A_1{}^n)\mathbf{X}_2 + (A_3{}^n - A_1{}^n)(\mathbf{X}_3 + \mathbf{X}_4)] \quad (13)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{X}_3 = \frac{1}{5}[2(A_1{}^n - A_3{}^n)\mathbf{X}_1 + (A_3{}^n + 4A_1{}^n)\mathbf{X}_3 + (A_3{}^n - A_1{}^n)(\mathbf{X}_2 + \mathbf{X}_4)] \quad (14)$$

$$\langle\mathbf{T}\otimes\mathbf{T}\otimes\mathbf{T}\rangle^n\cdot\mathbf{X}_4 = \frac{1}{5}[2(A_1{}^n - A_3{}^n)\mathbf{X}_1 + (A_3{}^n + 4A_1{}^n)\mathbf{X}_4 + (A_3{}^n - A_1{}^n)(\mathbf{X}_2 + \mathbf{X}_3)] \quad (15)$$

In the above, ${}^k\mathbf{e}_m$ represents a unit vector of rank k, with all elements but the mth equal to 0, $\mathbf{Y}_1 = {}^9\mathbf{e}_1$, $\mathbf{Y}_2 = {}^9\mathbf{e}_5 + {}^9\mathbf{e}_9$, $\mathbf{X}_1 = {}^{27}\mathbf{e}_1$, $\mathbf{X}_2 = {}^{27}\mathbf{e}_5 + {}^{27}\mathbf{e}_9$, $\mathbf{X}_3 = {}^{27}\mathbf{e}_{11} + {}^{27}\mathbf{e}_{21}$, $\mathbf{X}_4 = {}^{27}\mathbf{e}_{13} + {}^{27}\mathbf{e}_{25}$, $A_j = \langle P_j(\cos\theta)\rangle$ for P_j the jth Legendre polynomial, and $\mathbf{T}$ is the rotation matrix discussed by Flory.[25] Equations 9–15 follow by mathematical induction once expressions for $\langle\mathbf{T}\rangle$, $\langle\mathbf{T}\otimes\mathbf{T}\rangle$, and $\langle\mathbf{T}\otimes\mathbf{T}\otimes\mathbf{T}\rangle$ are in hand, a step which, in itself, requires the computer. Finally one obtains

$$\langle R^4\rangle = \frac{40}{3}l^4\sum_{\{ijklm\}_{N-4}}A_1{}^{j+l+2} + \frac{32}{3}l^4\sum_{\{ijklm\}_{N-4}}A_1{}^{j+l+2}A_2{}^{k+1} + \text{etc.} \quad (16)$$

where "etc." represents a number of similar terms. In passing to the continuous limit, we make all the following substitutions:

$$A_j{}^{k+1} \rightarrow \exp[-j(j+1)\lambda_j s_k] \quad (17)$$

$$\sum_{k=0}^{N} \rightarrow \int_0^L ds_k/l \quad (18)$$

$$\delta_{i+j+k+l+m,N-4} \rightarrow l\delta(s_i + s_j + s_k + s_l + s_m - L) \quad (19)$$

where s_i, s_j, etc. are the continuum analogues of i, j, etc. and measure contour length along the chain. The values λ_j are chosen to satisfy eq 17 in the continuous limit:[28]

$$\lambda_n = \lambda + [n(n+1)b]^{-1}[1 - P_n(\cos\rho)] \quad (20)$$

or

$$\lambda_n = \lambda + [n(n+1)b]^{-1} \quad (21)$$

for the fixed-angle and universal joint versions, respectively, of the model. The left-hand side of eq 19 is a Kronecker δ, the right a Dirac δ. Each term of eq 16 (including all those in "etc.") carries a factor l^4. Each summation then contributes a factor l^{-1}, by eq 18, and then eq 19 also contributes a factor l to each term. Therefore, if a term has less than five summation indices, it will still carry factors of l in the continuum limit and will therefore vanish in that limit. All of the terms in eq 16 vanish in this way except those listed explicitly. This also indicates that only the last term of eq 8 survives the limiting process.

The surviving terms in eq 16 become, in the limit,

$$\langle R^4\rangle = \frac{20}{3}\int_0^L dx\ (L^2x - 2Lx^2 + x^3)e^{-2\lambda_1 x} + \frac{32}{3}\int_0^L dx\ xe^{-2\lambda_1 x}\int_0^{L-x} dy\ e^{-6\lambda_2 y}(L - x - y) \quad (22)$$

The above integrals were evaluated (again by machine) to yield

$$\langle R^4\rangle/L^4 = 5/2t_1{}^4 - 4/9t_1{}^3t_2 - 10/3t_1{}^3 - 2/27t_1{}^2t_2{}^2 + 4/9t_1{}^2t_2 + 5/3t_1{}^2 + [-5/2t_1{}^4 + 4/9t_1{}^3t_2 - 5/3t_1{}^3 + 2/27t_1{}^2t_2{}^2 + 4/9t_1{}^2t_2 + 4/27t_1t_2{}^2 - 1/54t_2{}^2t_A{}^2 + 2/27t_2{}^2t_A]e^{-2t_1} + [1/54t_2{}^2t_A{}^2]e^{-6t_2} \quad (23)$$

where $t_j = \lambda_j L$, and $2t_A = 3t_2 - t_1$. The equation for $\langle R^6\rangle$ is given in the supplementary material accompanying this article.

The equations for $\langle R^4\rangle$ and $\langle R^6\rangle$ successfully reproduce three known limits. For $L\lambda \gg 1$ we recover the Gaussian coil limit:

$$\langle R^4\rangle/L^4 = 5/3t_1{}^2 \quad (24)$$

$$\langle R^6\rangle/L^6 = 35/9t_1{}^3 \quad (25)$$

The original wormlike chain expressions[9,29] for $\langle R^4\rangle$ and $\langle R^6\rangle$ are recovered in the limit $\rho \rightarrow 0$ or $b \rightarrow \infty$ (equivalent to setting $\lambda_i = \lambda$). Finally, in the rigid rod limit, $L\lambda \ll 1$ and $L \ll b$, $\langle R^4\rangle = L^4$ and $\langle R^6\rangle = L^6$ are obtained. It was possible, in fact, to expand $\langle R^4\rangle$ about the rod limit:

$$\langle R^4/L^4\rangle = 1 - 8t_2/15 - 4t_1/5 + 8t_2{}^2/15 + 16t_1t_2/45 + 2t_1{}^2/5 - 16t_2{}^3/35 - 32t_1t_2{}^2/105 - 16t_1{}^2t_2/105 - 16t_1{}^3/105 + \ldots \quad (26)$$

The ability to achieve these limits is an excellent test of the validity of the equations. The rigid rod limit, for example, requires the exact cancellation of many low-order terms and it is highly improbable that it could be achieved if errors were present.

For purposes of comparison we consider broken and regular worms with the same persistence length (and therefore the same radius of gyration) and with the same contour length L. This requires that the stiffness parameters, λ, of the two chains be different, so we use λ_W and λ_B to represent the stiffness parameters of regular and broken worms, respectively. The same subscripts, W and B, will also be used for other properties in differentiating

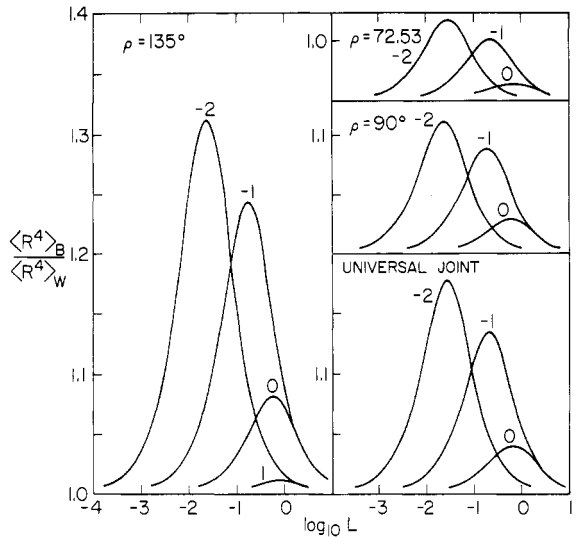

Figure 1. Ratios of fourth moments of broken and regular wormlike chains of the same contour length L and persistence length. Units of length are such that $\lambda_B = 1$. Each curve is labeled with the value log b.

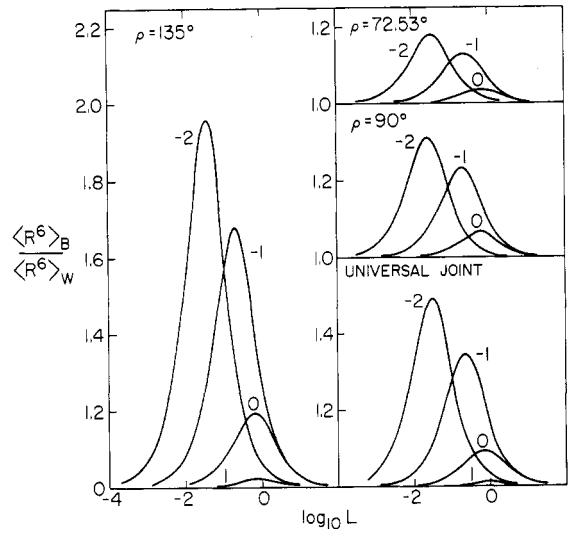

Figure 2. Same as Figure 1 but for sixth moments.

between the two models. Since the λ_j (j = 1, 2, 3, ...) of eq 20 or 21 apply only to broken worms, we can preserve that notation without confusion. The requirement of equal persistence lengths is satisfied by setting $\lambda_W = \lambda_1$. In all numerical calculations we set $\lambda_B = 1$.

Figures 1 and 2 display the results of a comparison between fourth and sixth moments of regular and broken worms. As expected, the greatest differences are observed for large values of ρ and small values of b. For $\rho < 90°$, or in the universal joint case, and for $\lambda_B b \gtrsim 1$ the difference is rather unimportant. Also, as expected, the differences are negligible in both the rod and coil limits.

Koyama Distribution

As in the case of the original wormlike chain, exact results beyond those already given are very difficult to obtain. Instead, we employ the Koyama distribution,[22,23] an approximation to $W(R,L)$, the probability that a wormlike chain of length L has end-to-end distance R. The Koyama distribution is

$$4\pi R^2 W(R,L) = (R/2AB\pi^{1/2}) \times \{\exp[-(R-B)^2/4A^2] - \exp[-(R+B)^2/4A^2]\} \quad (27)$$

where

$$A^2 = \langle R^2\rangle(1-\eta)/6 \quad (28)$$

$$B^2 = \eta\langle R^2\rangle \quad (29)$$

and

$$\eta^2 = \frac{1}{2}(5 - 3\langle R^4\rangle\langle R^2\rangle^{-2}) \quad (30)$$

The characteristic function of $W(R,L)$ is

$$K(k) = (Bk)^{-1}\sin(Bk)\exp(-A^2k^2) \quad (31)$$

representing a hybrid of rigid rod and random coil characteristic functions. The Koyama distribution is determined completely by $\langle R^2\rangle$ and $\langle R^4\rangle$ and reproduces both these quantities (and therefore the radius of gyration) exactly.[22] It gives $\langle R^6\rangle$ for the original wormlike chain to within about 5%,[22] and the expansion of $\langle R^{-1}\rangle$ is correct asymptotically to at least two terms about the rod limit[30] and to at least one term about the coil limit[31] (i.e., first Daniel's approximation[9]). Its moments are much easier to calculated than the original wormlike chain, of which we cite two:

$$\langle R^{-1}\rangle = B^{-1}\,\mathrm{erf}\,(B/2A) \quad (32)$$

$$\langle R^6\rangle = B^6 + 42A^2B^4 + 420A^4B^2 + 840A^6 \quad (33)$$

Since the Koyama distribution is determined completely by $\langle R^2\rangle$ and $\langle R^4\rangle$, it can be applied to any semiflexible chain model once $\langle R^2\rangle$ and $\langle R^4\rangle$ are known, provided the model satisfies (see eq 30)

$$\langle R^4\rangle\langle R^2\rangle^{-2} \le 5/3 \quad (34)$$

Equation 34 holds for the original wormlike chain, with $\langle R^4\rangle\langle R^2\rangle^{-2}$ increasing monotonically from 1 in the rigid rod limit to 5/3 in the random coil limit. However, for certain values of b and ρ, $\langle R^4\rangle\langle R^2\rangle^{-2}$ for the broken wormlike chain increases from 1, passes through a maximum, and approaches 5/3 from above, violating eq 34 for all values of L above a certain cutoff. (The universal joint version always satisfies eq 34.) Since the criterion is whether $\langle R^4\rangle\langle R^2\rangle^{-2}$ approaches 5/3 from above or below in the Gaussian limit and since asymptotically we have

$$\langle (R/L)^4\rangle = (5/3t_1^2)(1 - 2/t_1 + 4/15t_2) \quad (35)$$

$$\langle (R/L)^2\rangle = t_1^{-1}(1 - 1/2t_1) \quad (36)$$

then eq 34 becomes

$$4t_1/15 \le t_2 \quad (37)$$

which is equivalent to

$$\frac{1}{44}(\cos\rho - 1)(15\cos\rho + 7) \le \lambda_B b \quad (38)$$

Equation 38 must be satisfied for the Koyama distribution to apply at large L. Figure 3 shows a plot of the left-hand side of eq 38. This quantity is negative for $\rho < \cos^{-1}(-7.15) = 117.8°$, implying that the Koyama distribution always applies for $\rho < 117.8°$. When $\rho > 117.8°$ the Koyama distribution will fail for large enough L unless $\lambda_B b$ is sufficiently large. In other words, unless the chain turns back upon itself rather severely at the breaks, the Koyama distribution can always be applied.

We calculated $\langle R^6\rangle$ for the broken wormlike chain by eq 33 and compared these values to the exact values of $\langle R^6\rangle$. The Koyama approximation for $\langle R^6\rangle$ becomes progressively poorer for either increasing ρ or decreasing b, but the error is always less than 11% for $\rho \le 135°$ and $\lambda_B b \ge 10^{-2}$ in the fixed-angle case and never much larger than 7% for $\lambda_B b \ge 10^{-2}$ in the universal joint case. These

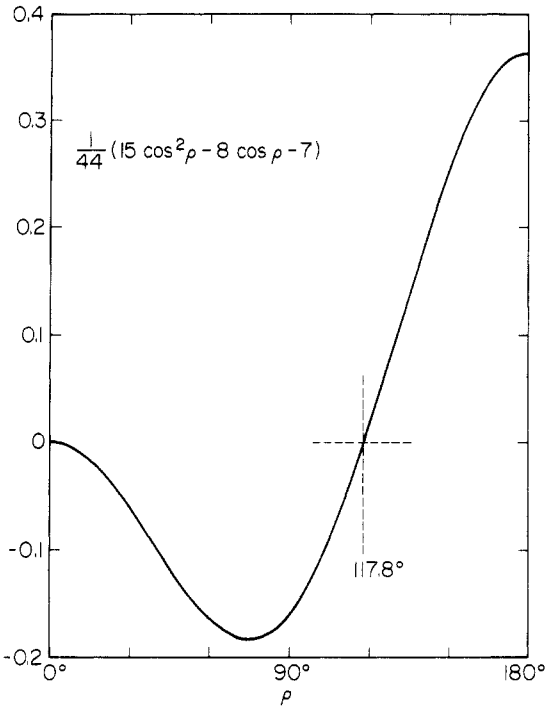

Figure 3. $(15\cos^2\rho - 8\cos\rho - 7)/44$ plotted as a function of ρ. If the product $\lambda_B b$ falls below this curve for fixed-angle broken worms, the Koyama distribution will be inapplicable at large L. This only becomes a problem for acutely bent worms ($\rho > 117.8°$).

results strongly suggest that the Koyama distribution is a good approximation for both the original and the broken wormlike chain models.

The Koyama distribution is exact for the case of a chain composed of a rigid rod of length B joined to a completely flexible coil of gyration radius A. This may be shown by computing the characteristic function of such a chain, obtaining eq 31. The ability of this chain to closely reproduce properties of wormlike models is another example of insensitivity to the nature of flexibility.

Hydrodynamic Radius

We estimate the hydrodynamic radius in the Kirkwood approximation:[9]

$$R_H^{-1} = 2L^{-2}\int_\Gamma^L ds\ (L - s)\langle R(s)^{-1}\rangle \tag{39}$$

where $\langle R(s)^{-1}\rangle$ represents the mean reciprocal end-to-end distance of chains of length s. The quantity Γ is a lower cutoff designed to prevent divergence of the integral and represents an effective hydrodynamic radius of the chain. Physically, we expect $\Gamma \ll L$. $\langle R(s)^{-1}\rangle$ is approximated by eq 32.

It is possible to obtain an asymptotic expansion of eq 39 near the rod limit in the Koyama approximation for both regular and broken worms. For regular worms near the rod limit we have

$$s^{-2}\langle R(s)^2\rangle_W = 1 - 2s\lambda_W/3 + s^2\lambda_W^2/3 \tag{40}$$

$$s^{-4}\langle R(s)^4\rangle_W = 1 - 4s\lambda_W/3 + 58s^2\lambda_W^2/45 \tag{41}$$

from which it follows that

$$\eta_W = 1 - 2s^2\lambda_W^2/15 \tag{42}$$

$$sB_W^{-1} = 1 + s\lambda_W/3 + s^2\lambda_W^2/15 \tag{43}$$

and

$$s^{-1}A_W = 45^{-1/2}s\lambda_W(1 - s\lambda_W/3 + s^2\lambda_W^2/9) \tag{44}$$

It follows that $B_W/A_W = \mathcal{O}(s\lambda_W)^{-1} \gg 1$, permitting us to neglect the erf $(B/2A)$ term in eq 32. Then by substituting eq 43 into eq 39 and assuming $L \gg \Gamma$, we obtain

$$2R_{H\text{-}W} = L[\ln(L/e\Gamma) + (L\lambda_W/6)(1 + L\lambda_W/15)]^{-1} \tag{45}$$

Likewise for broken worms, beginning from eq 40 but with λ_1 replacing λ_W, and from eq 26 we obtain

$$sB_B^{-1} = 1 + (8\lambda_1/15 - \lambda_2/5)s \tag{46}$$

and

$$2R_{H\text{-}B} = L[\ln(L/e\Gamma) + L(4\lambda_1/15 - \lambda_2/10)]^{-1} \tag{47}$$

The first term of either eq 45 or 47 represents the rigid rod result; the additional terms are small corrections due to flexibility. The ratio of hydrodynamic radii of two chains with the same L and the same persistence length is

$$R_{H\text{-}B}/R_{H\text{-}W} = 1 - L\sin^4(\rho/2)[10b\ln(L/e\Gamma)]^{-1} \tag{48}$$

for the fixed-angle case and

$$R_{H\text{-}B}/R_{H\text{-}W} = 1 - L[30b\ln(L/e\Gamma)]^{-1} \tag{49}$$

for the universal joint case.

Hydrodynamic radius values for the two models were compared, either with the use of eq 48 or 49 or by numerical integration of eq 39. As usual we found that the difference between the two models increases for either increasing ρ or decreasing b. The difference also increases with increasing Γ. However, the difference always proved to be slight, never more than about 3% for $\rho \le 135°$, $\lambda_B b \ge 10^{-2}$, and $\lambda_B\Gamma = 10^{-6}$ or 10^{-5}. Increasing Γ further could have increased these differences, but probably not too strongly in light of the logarithmic dependence in eq 48 or 49.

Static Structure Factor

The light scattering structure factor is given by an appropriate integration of eq 31:

$$S(k) = 2L^{-2}\int_0^L ds\ (L - s)[B(s)k]^{-1}\sin[B(s)k]e^{-[A(s)k]^2} \tag{50}$$

This integral was performed numerically and values for the two models were compared. Since we only compare models with the same radii of gyration, $S(k)$ values agree very well when $S_W(k) \simeq 1$. The discrepancy between $S_W(k)$ and $S_B(k)$ increases with increasing k, reaches a maximum, and decreases again in the tails. In all cases examined the discrepancy is less than about 20% for all k values such that $0.1 < S_W(k) < 1$. Values of k for which $S_W(k) < 0.1$ were not considered. Once again, this includes values of $\rho \le 135°$ and $\lambda_B b \ge 10^{-2}$.

Summary and Discussion

At least in the range of model parameters examined, neither the hydrodynamic radii nor the structure factors show important differences between the two models. Evidently, one could achieve more important differences by going to either larger ρ or smaller b values, but it is meaningless to consider nonphysical values of the parameters. To compute either R_H or $S(k)$, one must sum over all pairs of segments within the polymer, and since the discrepancies between the two models extend only over a limited range of length scales, we expect discrepancies in the sums of even smaller magnitude than those seen in Figure 1. We conclude, therefore, that the original wormlike chain, in spite of the absence of abrupt breaks, is an adequate model of semiflexible polymers, especially for

those properties, such as R_H or $S(k)$, involving sums over all pairs of segments of the chain. This probably includes intrinsic viscosity and the first cumulant of the dynamic structure factor as well.

Unfortunately, this also implies that it should be difficult to distinguish between flexibility due to abrupt breaks and flexibility due to fluctuations in rotational angles. System-specific experiments might, in certain cases, be capable of detecting abrupt breaks, but we conclude on the basis of these calculations that general experimental techniques are insensitive.

Hays and Zimm[32] report viscosity and sedimentation experiments on nicked DNA samples. These are DNA molecules with single-strand breaks introduced enzymatically at random intervals along the chain and, therefore, are probably well represented by this model, at least if we assume that the DNA undergoes only smooth bending between nicks. The extent of nicking can be measured independently, providing estimates of b, the mean length between nicks. Hays and Zimm report insignificant changes in persistence length induced by the nicking, even when b is as small as one-half to one-fifth the persistence length of unnicked DNA. then eq 5 indicates that $\langle \cos \rho \rangle$ is near unity or, in other words, that the bending at the nicks is not too severe. This agrees with the conclusion of Hays and Zimm that the nicks are not universal joints. This set of measurements indicates that the broken wormlike chain model can provide useful geometrical information about breaks in the chain if the presence of breaks can be established independently.

Another experimental study with at least peripheral relevance is the study by Pfannemüller et al.[21] of a once-broken wormlike chain. Both light scattering and viscosity measurements were unable to detect a flexible joint at the center of the chain. Only by observing a shift in the dielectric loss peak could the presence of the joint be detected.

Acknowledgment. The author thanks Dr. R. L. Jernigan for supplying excerpts of his doctoral dissertation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The computer time for this research was supported in full through the facilities of the Computer Science Center of the University of Maryland. Partial support was also provided by the National Science Foundation under Grant No. DMR 8451928.

Supplementary Material Available: Equation for $\langle R^6 \rangle$ (1 page). Ordering information is given on any current masthead page.

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