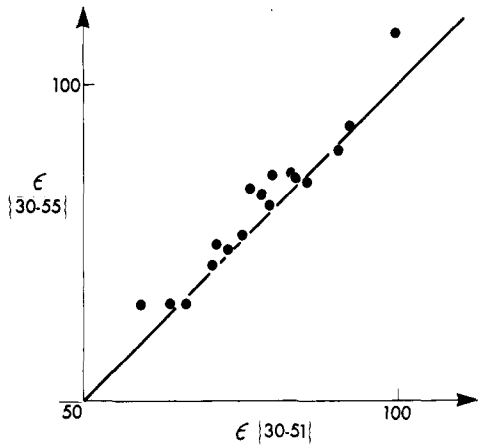

Figure 1. Energy, ϵ, in kcal/mol for 17 random conformations of trypsin inhibitor having only disulfide bridge 30–55 vs. the energies of the corresponding conformations having the bridge 30–51.

(for {51–55}). The one case of zero success, namely forming a 5–14 contact, is apparently possible by means of only *one* unique combination of conformations for residues 5 through 14, occurring only about once every 500 tries, as was discovered in another series of calculations. There are three proline residues (each having only one allowed conformation) in that short loop, which cause the difficulty in ring closure. The results, except for {5–14}, were that there was relatively little variation of w or ϵ within the individual classes and that the geometric averaged K's ranged between 0.3 and 2.8 relative to the fully reduced state. In other words, all 15 combinations should be present in comparable quantities, with the exception of perhaps {5–14}, which should have a particularly low concentration.

Conclusion

This statistical method of conformational calculation has been shown to be applicable to problems involving small proteins, particularly where the conformations involved are not very restricted. The poor convergence of the averages confine its use to situations where there is either little spread in the energies within a class or great conformational similarly between the classes. These conditions having been met in the two cases presented, the method was capable of results in agreement with, and accuracies comparable to, the semiquantitative[13] experiments. Work is now proceeding to adapt the procedure to a wider range of situations.

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Conformation Dependent Transport Coefficients of Once-Broken Rods

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ABSTRACT: A method related to that of Kirkwood and Riseman is used to calculate the steady flow intrinsic viscosity as a function of the angle χ between the two arms of a once-broken rod. The translational diffusion coefficient and sedimentation coefficient are also obtained in terms of χ. The explicit χ dependence in the results allows for the likely possibility that the two arms of a real broken rod molecule will not be connected by a perfectly flexible joint and thus that the conformation of the molecule will be described by a nonrandom distribution of χ.

I. Introduction

Some years ago the once-broken rod was offered as a theoretical hydrodynamic model for incompletely helical polypeptides or other slightly flexible linear polymers, and the intrinsic viscosity[1] $[\eta]$ and translational diffusion coefficient D (or sedimentation coefficient s)[2,3] were calculated. At about the same time, independent experimental studies[3] of the solution viscosity of poly(γ-benzyl L-glutamate) (PBLG) containing a flexible trimethylene diamine unit gave results in apparently excellent agreement with the calculated intrinsic viscosity, as compared to that for an unbroken rodlike polypeptide.

In fact, the situation requires further study. On the theoretical side, Hassager[4] has pointed out an error in some of the old calculations[1] and has corrected the result for the free-draining steady flow intrinsic viscosity. Furthermore, because the samples studied were polydisperse and possibly contaminated with unbroken rods, the experimental data[3] are also less than definitive. However, the dielectric measurements

on more nearly monodisperse samples of broken rod PPLG that have since been reported[5] represent a substantial improvement on the experimental side.

In this article we present a corrected calculation of the steady flow (zero frequency) intrinsic viscosity $[\eta]^0$ of the nondraining once-broken rod and also extend the earlier calculations[2,3] of D and s. We use a model, as in earlier work,[1,4] consisting of $2n + 1$ chain elements of molecular weight M_0 and friction constant ζ. These elements are arranged into two rigid rods of equal length that are joined at a pivotal chain element and subtend an internal angle χ. We label the elements consecutively from $-n$ to $+n$, beginning at one end and designating the pivot as 0. The total contour length L and molecular weight M of the molecule are given by

$$L = 2nb \tag{I.1}$$

and

$$M = (2n + 1)M_0 \tag{I.2}$$

where b is the distance between neighboring elements.

Deviating from the earlier work,[1-3] we avoid averaging over χ at the outset and thus obtain expressions for $[\eta]^0$, D, and s containing the explicit χ dependence. This is desirable because of the likely possibility that a real broken rod molecule will not be perfectly flexible at its joint and therefore that its conformation will be described by some nonrandom distribution of χ. The possibilities range to the extreme case of a rigid joint with a fixed value of χ and obviously encompass an infinite number of intermediate situations.

In the course of our analysis we must solve several inhomogeneous Fredholm integral equations. These equations could have been derived by the method of Kirkwood and Riseman,[6] but we have chosen a different, yet related, approach in part to illustrate its application.

II. Integral Equation Formulation

We use the coordinate system proposed by Hassager:[4] the two arms of the broken rod define a plane in which are embedded two orthogonal unit vectors $\boldsymbol{\delta}_2$ and $\boldsymbol{\delta}_3$. These vectors, along with the third member $\boldsymbol{\delta}_1$ of the orthogonal trio, define a coordinate system that rotates or tumbles with the molecule. The three Euler angles α, β, and γ are needed to specify the orientation of this coordinate system relative to a space-fixed Cartesian frame with unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$; the origins of these two-coordinate systems coincide at the center of mass of the broken rod. In the tumbling frame the position vector of a chain element, asymptotically valid for large n, is given by

$$b^{-1}\mathbf{R}_i = i\mathcal{S}\boldsymbol{\delta}_2 + (|i| - n/2)\mathcal{C}\boldsymbol{\delta}_3 \tag{II.1}$$

where $\mathcal{S} = \sin(\chi/2)$ and $\mathcal{C} = \cos(\chi/2)$.

Our calculation of $[\eta]^0$ is based on the formula[7-9]

$$[\eta]^0 = N_A kT(2M\eta_0)^{-1} \sum_{i,j}\sum \langle z_i \mathbf{e}_y \cdot \langle \mathbf{D} \rangle_{ij}^{-1} \cdot \mathbf{e}_y z_j \rangle \tag{II.2}$$

where here and elsewhere the sums range from $-n$ to $+n$ unless otherwise noted. Also, the coordinates are measured from the center of mass in the space-fixed coordinate system, the diffusion tensor $\mathbf{D}_{ij}$ has been preaveraged, N_A is Avogadro's number, k is Boltzmann's constant, and T is the absolute temperature. Both $\mathbf{D}_{ij}$ and the Oseen tensor $\mathbf{T}_{ij}$ have their usual form:

$$\mathbf{D}_{ij} = (kT/\zeta)(\delta_{ij}\mathbf{I} + \zeta\mathbf{T}_{ij}) \tag{II.3}$$

$$\mathbf{T}_{ij} = \begin{cases} (8\pi\eta_0 R_{ij})^{-1}(\mathbf{I} + R_{ij}^{-2}\mathbf{R}_{ij}\mathbf{R}_{ij}) & i \neq j \\ 0 & i = j \end{cases} \tag{II.4}$$

where $\mathbf{I}$ is the unit tensor and η_0 is the solvent viscosity coefficient.

It proves necessary to preaverage $\mathbf{D}_{ij}$ only over the Euler angles; the brackets designating the average therefore take on the significance

$$\langle(\ldots)\rangle = (8\pi^2)^{-1}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma(\ldots) \tag{II.5}$$

After averaging we find the usual result

$$\zeta\langle \mathbf{T}_{ij} \rangle = \lambda_p b R_{ij}^{-1}\mathbf{I} \tag{II.6}$$

where

$$\lambda_p = \zeta/(6\pi\eta_0 b) \tag{II.7}$$

and

$$(R_{ij}/b)^2 = (|i| - |j|)^2\mathcal{C}^2 + (i - j)^2\mathcal{S}^2 \tag{II.8}$$

Ignoring possible difficulties[10] with singularities, we proceed to formally expand $\langle \mathbf{D} \rangle^{-1}$, obtaining

$$kT\zeta^{-1}\langle \mathbf{D} \rangle_{ij}^{-1} = \delta_{ij}\mathbf{I} - \zeta\langle \mathbf{T}_{ij} \rangle + \zeta^2 \sum_k \langle \mathbf{T}_{ik} \rangle \cdot \langle \mathbf{T}_{kj} \rangle + \ldots \tag{II.9}$$

which we combine with eq II.2 and II.6 to arrive at

$$[\eta]^0 = N_A\zeta(2M\eta_0)^{-1}\sum_i \left\{ \langle z_i^2 \rangle - \lambda_p b \sum_{j\neq i} \langle z_i R_{ij}^{-1} z_j \rangle + (\lambda_p b)^2 \sum_{k\neq i}\sum_{j\neq k} \langle z_i R_{ik}^{-1} R_{kj}^{-1} z_j \rangle + \ldots \right\} \tag{II.10}$$

With[4]

$$z_i = bi\mathcal{S}\sin\beta\sin\gamma + b(|i| - n/2)\mathcal{C}\cos\beta$$

we readily average the remaining Euler angle dependence in eq II.10. Then

$$[\eta]^0 = N_A\zeta L^2(72M_0\eta_0)^{-1}(\mathcal{S}^2F_1(\lambda_p) + \mathcal{C}^2F_2(\lambda_p)) \tag{II.11}$$

where

$$F_1(\lambda) = \tfrac{3}{2}n^{-3}\sum_i i\psi_i(\lambda) \tag{II.12}$$

and

$$F_2(\lambda) = \tfrac{3}{2}n^{-3}\sum_i (|i| - n/2)\rho_i(\lambda) \tag{II.13}$$

Here,

$$\psi_i(\lambda) = i - \lambda b \sum_{j\neq i} jR_{ij}^{-1} + (\lambda b)^2 \sum_{j\neq k}\sum_{k\neq i} jR_{ik}^{-1}R_{kj}^{-1} + \ldots \tag{II.14}$$

and $\rho_i(\lambda)$ represents a similar sum. Equation II.14 may now be recognized as the iterated solution to the equation

$$\psi_i(\lambda) = i - \lambda b \sum_{j\neq i} \psi_j(\lambda)R_{ij}^{-1} \tag{II.15}$$

The analogous equation for ρ_i reads

$$\rho_i(\lambda) = |i| - n/2 - \lambda b \sum_{j\neq i} \rho_i(\lambda)R_{ij}^{-1} \tag{II.16}$$

The functions ψ_i and ρ_i are both functions of χ through R_{ij}, and thus the explicit χ dependence of $[\eta]^0$ may be calculated, provided solutions to eq II.15 and II.16 are at hand. We obtain these solutions in the form of a simple perturbation series as described in the next section.

III. Perturbation Solution

For chain elements on the same arm

$$R_{ij} = b|i - j| \tag{III.1}$$

but for elements on opposing arms

$$R_{ij} = b|i-j|(1 + 4ij(i-j)^{-2}\mathcal{C}^2)^{1/2} \quad \text{(III.2)}$$

Now since

$$4ij(i-j)^{-2}\mathcal{C}^2 < 1 \quad \text{(III.3)}$$

R_{ij}^{-1} from eq III.2 may be expanded as

$$b|i-j|R_{ij}^{-1} = 1 - 2ij|i-j|^{-2}\mathcal{C}^2 + 6\,(ij|i-j|^{-2}\mathcal{C}^2)^2 + \ldots \quad \text{(III.4)}$$

The expansion should be particularly appropriate if χ does not deviate greatly from π, i.e., the conformation of the broken rod fluctuates about the fully extended form, but the results to be presented seem to indicate that much greater fluctuations are readily accommodated. Noting that the χ dependence appears as even powers of $\mathcal{C}$, we formally treat $\mathcal{C}^2$ as a small parameter and expand both ψ_i and ρ_i:

$$\psi_i = \psi_i^{(0)} + \mathcal{C}^2\psi_i^{(1)} + \mathcal{C}^4\psi_i^{(2)} + \ldots \quad \text{(III.5)}$$

$$\rho_i = \rho_i^{(0)} + \mathcal{C}^2\rho_i^{(1)} + \mathcal{C}^4\rho_i^{(2)} + \ldots \quad \text{(III.6)}$$

where the $\psi_i^{(m)}$ and $\rho_i^{(m)}$ are independent of χ. Upon substituting eq III.1, III.4, and III.5 into eq II.15 and gathering terms of the same order in $\mathcal{C}^2$, the following sequence of equations is generated:

$$\psi_i^{(0)} = i - \lambda \sum_{j \neq i} K_{ij}^{(0)}\psi_j^{(0)} \quad \text{(III.7)}$$

$$\psi_i^{(1)} = \lambda V_i - \lambda \sum_{j \neq i} K_{ij}^{(0)}\psi_j^{(1)} \quad \text{(III.8)}$$

where

$$K_{ij}^{(0)} = |i-j|^{-1} \quad \text{(III.9)}$$

$$V_i = \begin{cases} 2 \sum_{\substack{j=-n \\ \neq i}}^{0} K_{ij}^{(1)}\psi_j^{(0)} & i \geq 0 \\ 2 \sum_{\substack{j=0 \\ \neq i}}^{n} K_{ij}^{(1)}\psi_j^{(0)} & i \leq 0 \end{cases} \quad \text{(III.10)}$$

and

$$K_{ij}^{(1)} = ij|i-j|^{-3} \quad \text{(III.11)}$$

and so on. Identical maneuvers produce the corresponding hierarchy of equations for $\rho_i^{(0)}, \rho_i^{(1)}, \ldots$

$$\rho_i^{(0)} = (|i| - n/2) - \lambda \sum_{j \neq i} K_{ij}^{(0)}\rho_j^{(0)} \quad \text{(III.12)}$$

$$\rho_i^{(1)} = \lambda W_i - \lambda \sum_{j \neq i} K_{ij}^{(0)}\rho_i^{(1)} \quad \text{(III.13)}$$

where

$$W_i = \begin{cases} 2 \sum_{\substack{j=-n \\ \neq i}}^{0} K_{ij}^{(1)}\rho_j^{(0)} & i \geq 0 \\ 2 \sum_{\substack{j=0 \\ \neq i}}^{n} K_{ij}^{(1)}\rho_j^{(0)} & i \leq 0 \end{cases} \quad \text{(III.14)}$$

and so on. Equations III.5 and III.6 may also be inserted into eq II.12 and II.13, yielding

$$F_m(\lambda,\chi) = F_m^{(0)}(\lambda) + F_m^{(1)}(\lambda)\mathcal{C}^2 + \ldots \quad \text{(III.15)}$$

where

$$F_1^{(p)}(\lambda) = \tfrac{3}{2}n^{-3} \sum_i i\psi_i^{(p)}(\lambda) \quad \text{(III.16)}$$

and

$$F_2^{(p)}(\lambda) = \tfrac{3}{2}n^{-3} \sum_i (|i| - n/2)\rho_i^{(p)}(\lambda) \quad \text{(III.17)}$$

The solution of these equations and the calculation of the various F functions are described in the Appendix. In the following section we summarize the results for $[\eta]^0$ and discuss their significance.

IV. The Intrinsic Viscosity

First note that for $\chi = \pi$ eq II.11 correctly reduces to the known result $[\eta]_R{}^0$ for the preaveraged rigid rod,[11] namely

$$[\eta]_R{}^0 = N_A\zeta L^2(72M_0\eta_0)^{-1}F_1^{(0)}(\lambda_p) \quad \text{(IV.1)}$$

where $F_1^{(0)}(\lambda)$ is found in eq A.11 of the Appendix. A correct result[4] for the free-draining broken rod ($\lambda_p = 0$) may also be found.

Combining the results of eq A.16, A.28, A.34, and A.43 of the Appendix with eq II.11 and III.15 we obtain

$$[\eta]^0 = N_A\zeta L^2(288M_0\eta_0)^{-1}\Lambda(\lambda_p)[(4 - 3\mathcal{C}^2) + 4\mu(\chi)\lambda_p\Lambda(\lambda_p) + \ldots] \quad \text{(IV.2)}$$

where

$$\mu(\chi) = 14/3 + (5\ln 2 - 13/2)\mathcal{C}^2 - 5(\ln 2 - 5/8)\mathcal{C}^4 \quad \text{(IV.3)}$$

and we recall from eq A.14 that

$$\Lambda(\lambda) = (1 + 2\lambda \ln \coth (b/L))^{-1} \quad \text{(IV.4)}$$

For the physically more interesting case of complete hydrodynamic interaction with $L \gg b$ eq IV.2 simplifies with the use of eq A.44 to

$$[\eta]^0 = \pi N_A L^3[96M \ln (L/b)]^{-1}[(4 - 3\mathcal{C}^2) + 2\mu/\ln (L/b) + \ldots] \quad \text{(IV.5)}$$

The significance of the $[\ln (L/b)]^{-2}$ terms in eq IV.5 is hard to assess[12] in view of the artificiality of the model used and the obvious inadequacy of the treatment of hydrodynamic interaction for beads separated by small distances. The same difficulty exists in the theory of $[\eta]^0$ for both the rigid rod and rigid ring. For the former system we may compare our result, obtainable from eq IV.1, A.16, and A.44 as

$$[\eta]_R{}^0 = \pi N_A L^3[24M \ln (L/b)]^{-1}(1 + (7/3)/\ln (L/b) + \ldots) \quad \text{(IV.6)}$$

with that of Yamakawa and Fujii.[13] They applied the Burgers–Oseen method to the wormlike cylinder and found

$$[\eta]_{YF}{}^0 = \pi N_A L^3(24M)^{-1}(\ln (L/d) + 2\ln 2 - 7/3)^{-1} \quad \text{(IV.7)}$$

where d is the cylinder diameter. For a typical case with $L/b = L/d = 300$, these two equations give $[\eta]_R{}^0/[\eta]_{YF}{}^0 \approx 7/6$, a significant difference from unity. The different calculations of Paul and Mazo[9] and Fujii and Yamakawa[14] show similar discrepancies for the rigid ring.

In order to make a definite comparison with experiment, we ignore completely the ambiguous higher order terms. Then eq IV.6 reduces to

$$[\eta]_R{}^0 = \pi N_A L^3[24M \ln (L/b)]^{-1} \quad \text{(IV.8)}$$

and eq IV.5 to

$$[\eta]^0/[\eta]_R{}^0 = 1 - 3\mathcal{C}^2/4 \quad \text{(IV.9)}$$

It is noteworthy that for sufficiently long rods this ratio is just the same as that for the free-draining case. This may be rationalized physically by recalling that for a rigid rod the factor R_{ij}^{-1} controlling the strength of the preaveraged hydrodynamic interaction between a pair of segments varies as $|i-j|^{-1}$ and is thus on the verge of being a short-range effect. So, if the two parts of a once-broken rod are sufficiently long,

then for essentially all dihedral angles the interactions between segments on different arms (cross interactions) are relatively unimportant. Thus, if we simply ignore the cross-interaction terms in eq II.15 and II.16, we would still recover the proper asymptotic behavior for $[\eta]^0$, but we would now find a different and incomplete value for the coefficient of $[\ln (L/b)]^{-2}$. Our perturbative method for handling the cross interactions permits us to evaluate that term more fully, if only to compare it with results of other theoretical approaches.[12]

In view of the above discussion, we can expect that for very long once-broken rods with arms of unequal length the intrinsic viscosity ratio $[\eta]^0/[\eta]_R{}^0$ will also be that of the corresponding radii of gyration. For broken rods with arms of length $2n\sigma$ and $2n(1-\sigma)$, $0 \le \sigma \le 1$, we then readily calculate

$$[\eta]^0/[\eta]_R{}^0 = 1 - 12[\sigma(1-\sigma)\mathscr{C}]^2 \qquad \text{(IV.10)}$$

A random average of this equation over χ according to

$$\langle(\ldots)\rangle_\chi = \frac{1}{2}\int_0^\pi (\ldots)\sin\chi\, d\chi \qquad \text{(IV.11)}$$

gives

$$[\eta]^0/[\eta]_R{}^0 = 1 - 6[\sigma(1-\sigma)]^2 \qquad \text{(IV.12)}$$

If both arms are of equal length, then $\sigma = 1/2$ and $[\eta]^0/[\eta]_R{}^0 = 5/8$, which can also be obtained by averaging eq IV.9. The ratio 5/8 is too great a reduction of the intrinsic viscosity compared to experiment, but a value of $\chi = 130°$ in eq IV.9 would produce the observed decrease of approximately 14%. Being more realistic we expect that the arms will be of varying lengths. Then an arm-length distribution must be specified. The easy and oversimplified possibility that all values of σ are equally probable was invoked in the earlier analysis[3] of the sedimentation data. If we do likewise and calculate the average with

$$\langle(\ldots)\rangle_\sigma = \int_0^1 (\ldots)\, d\sigma \qquad \text{(IV.13)}$$

eq IV.10 becomes

$$[\eta]^0/[\eta]_R{}^0 = 1 - 2\mathscr{C}^2/5 \qquad \text{(IV.14)}$$

A random average of this ratio over χ gives only a 20% reduction, much closer to that observed, and a fixed angle of $\chi = 107°$ would match experiment.

The fixed angle values are intended to be merely illustrative since the real conformation of the molecule must surely fluctuate about some average value of χ. We then ought to reinterpret the fixed angle results in terms of some physically acceptable distribution of χ which would give rise to an average value of $\mathscr{C}^2 \approx 0.187$ in eq IV.9 or to an average of $\mathscr{C}^2 \approx 0.35$ in eq IV.14, for example.

To estimate the effect of the $[\ln (L/b)]^{-2}$ term on $[\eta]^0$ for the broken rod we will make one more simple calculation. After randomly averaging eq IV.5 over χ according to eq IV.11 we find[12]

$$[\eta]^0 = \pi N_A L^3[24M \ln (L/b)]^{-1}[(5/8) + 5(\ln 2 + 59/20)[12 \ln (L/b)]^{-1} + \ldots] \qquad \text{(IV.15)}$$

The first-order term thus increases the estimated value of $[\eta]^0$ for a given L/b. For example, when $L/b = 300$ we find a 42.6% increase over the value given by just the factor 5/8, but using eq IV.6 and IV.15 we now find $[\eta]^0/[\eta]_R{}^0 = 0.632$, not very different from the earlier value of 5/8. In general, $\mu(\chi)$ in eq IV.3 and IV.5 is positive and is less than 14/3 since the coefficients of $\mathscr{C}^2$ and $\mathscr{C}^4$ are negative. Comparing the first-order corrections for the broken rod and the rigid rod, we see that the latter will always be larger in magnitude although the former may constitute a larger fractional change relative to the asymptotic zeroth order result ($L \gg b$). They are clearly not negligible, and eventually a satisfactory accounting of them from theory and experiment will have to be made.

At the end of the next section we will compare some of these numerical conclusions with those needed to explain the sedimentation data.

V. Diffusion and Sedimentation Coefficients

We use the approximate formula of Kirkwood[15] to calculate the translational diffusion coefficient

$$(2n+1)\zeta(kT)^{-1}D = 1 + (2n+1)^{-1}\lambda_p b \sum_{i\neq j}\sum \langle R_{ij}{}^{-1}\rangle \qquad \text{(V.1)}$$

If v is the partial specific volume of the polymer and ρ_s is the density of the solvent, the additional relation

$$s = M(1 - v\rho_s)(N_A kT)^{-1}D \qquad \text{(V.2)}$$

can be used to calculate the sedimentation coefficient s. As in the preceding viscosity calculation we may defer the explicit average over the internal angle χ and thereby obtain D and s as functions of χ. In the present case it is also easy to take into account the possibility that the two arms of the broken rod may be of unequal length.

The expressions for R_{ij} are given in eq III.1 and III.2. We then decompose the required double sum into three restricted sums:

$$b\sum_{i\neq j}\sum R_{ij}{}^{-1} = X_{11} + X_{22} + 2X_{12} \qquad \text{(V.3)}$$

$$X_{11} = \sum_{i=1}^{2n\sigma}\sum_{j=1}^{2n\sigma}(1-\delta_{ij})|i-j|^{-1} \qquad \text{(V.4)}$$

$$X_{22} = \sum_{i=1}^{2n(1-\sigma)}\sum_{j=1}^{2n(1-\sigma)}(1-\delta_{ij})|i-j|^{-1} \qquad \text{(V.5)}$$

$$X_{12} = \sum_{i=0}^{2n\sigma}\sum_{j=0}^{2n(1-\sigma)}(1-\delta_{i0}\delta_{j0})(i^2+j^2-2ij\cos\chi)^{-1/2} \qquad \text{(V.6)}$$

Two of these sums, X_{11} and X_{22}, have been evaluated[3] previously and will be reproduced later. The third sum can be evaluated as follows. Treat i and j as continuous variables, and let

$$i = 2n\sigma x, \quad j = 2n\sigma y \qquad \text{(V.7)}$$

then

$$X_{12} = 2n\sigma\int_0^1 dx\int_0^{(1-\sigma)/\sigma} dy(x^2+y^2-2xy\cos\chi)^{-1/2} \qquad \text{(V.8)}$$

After transforming into polar coordinates (r,θ) and performing the easy r integration, we find

$$(2n(1-\sigma)\sigma)^{-1}X_{12} = \int_0^1((1-\sigma)^2u^2 - 2(1-\sigma)\sigma u\cos\chi + \sigma^2)^{-1/2}\,du + \int_0^1(\sigma^2v^2 - 2(1-\sigma)\sigma v\cos\chi + (1-\sigma)^2)^{-1/2}\,dv \qquad \text{(V.9)}$$

Where the further changes of variables $u = \sigma(1-\sigma)^{-1}\tan\theta$ and $v = u^{-1}$ were used to write eq V.9. After the remaining integrals are performed we obtain

$$(2n)^{-1}X_{12} = \sigma\ln[(1-2\sigma\mathscr{C}^2 + Z(\sigma,\chi))(2\sigma\mathscr{S}^2)^{-1}] + (1-\sigma)\ln[(1-2(1-\sigma)\mathscr{C}^2 + Z(\sigma,\chi))(2(1-\sigma)\mathscr{S}^2)^{-1}] \qquad \text{(V.10)}$$

where

$$Z(\sigma,\chi) = (1 - 4(1-\sigma)\sigma\mathscr{C}^2)^{1/2} \qquad \text{(V.11)}$$

and from the earlier work[3] we have

$$X_{11} = 4n\sigma(\ln(2n) + \ln\sigma + \gamma - 1) \quad \text{(V.12a)}$$

and

$$X_{22} = 4n(1-\sigma)(\ln(2n) + \ln(1-\sigma) + \gamma - 1) \quad \text{(V.12b)}$$

where γ is Euler's constant. For $\chi = \pi$ the sum of X's in eq V.3 reduces to the correct result for an unbroken rigid rod. Further, a random average of X_{12} over χ also yields an expression obtained[3] earlier:

$$\frac{1}{2}\int_0^\pi X_{12}\sin\chi\,d\chi = 2n(1-\sigma)(2 + \ln\sigma - \ln(1-\sigma)) \quad \text{(V.13)}$$

(Note the misprints in ref 3.) This latter average may perhaps be most easily performed by use of eq V.9.

We now consider the χ dependence of s for just two particular distributions of σ. First, when the two arms of the broken rod are of equal length, i.e., when $\sigma = \frac{1}{2}$, the expression for s becomes quite simple. Upon combining eq V.1–V.3 and V.10–V.12 we find

$$s = C\ln M + C' + C\,d(\chi) \quad \text{(V.14)}$$

where

$$C = 2\lambda_p(1 - v\rho_s)M_0(N_A\zeta)^{-1} \quad \text{(V.15)}$$

$$C' = C[(2\lambda_p)^{-1} + \gamma - 1 - \ln M_0] \quad \text{(V.16)}$$

and

$$d(\chi) = -\ln[2\mathcal{S}/(1+\mathcal{S})] \quad \text{(V.17)}$$

Second, as in the preceding section we just average s uniformly over σ:

$$\langle s\rangle_\sigma = \int_0^1 s\,d\sigma \quad \text{(V.18)}$$

The integrals involving X_{11} and X_{22} are easy, and they give

$$\langle X_{11}\rangle_\sigma + \langle X_{22}\rangle_\sigma = 4n(\ln 2n + \gamma - 3/2) \quad \text{(V.19)}$$

The average of X_{12} is more troublesome. Let us define

$$2nJ = \langle X_{12}\rangle_\sigma \quad \text{(V.20)}$$

Then, beginning with eq. V.9 it is possible to write

$$J = 2\int_0^1 d\sigma \int_0^1 dy\,\sigma(1-\sigma)[\sigma^2y^2 - 2\sigma(1-\sigma)y\cos\chi + (1-\sigma)^2]^{-1/2} \quad \text{(V.21)}$$

We proceed by setting $\cos\chi = 2\mathcal{C}^2 - 1$. After completing the square in y we may expand the integrand and perform the double integrals term by term. The result is a convergent series that can be resummed to give

$$J = (2\mathcal{C})^{-1}\ln\cot(\chi/4) \quad \text{(V.22)}$$

We combine eq V.1–V.3 with the above results to write

$$\langle s\rangle_\sigma = C\ln M + C' + C(J - 1/2) \quad \text{(V.23)}$$

We may readily ascertain that both eq V.14 and V.23 correctly yield the rigid rod limit with $\chi = \pi$, the σ average being inconsequential then. A random average of eq V.23 over χ also gives a result

$$s = C\ln M + C' + 0.20C \quad \text{(V.24)}$$

found earlier.[3] Since this expression adequately accounts for the sedimentation data,[3] we might now ask for the values of χ which make eq V.14 and V.23 numerically equal to eq V.24. We find that $\chi = 88°$ makes $d \approx 0.20$ in eq V.14, but a random average of d according to eq IV.11 gives

$$\langle d(\chi)\rangle_\chi = 1 - \ln 2$$

which is too high. In eq V.23 we find that $\chi = 71°$ produces the numerical equivalence. Values of χ greater than these lead to s values smaller than are required by eq V.24.

Thus, this oversimplified interpretation of the results for $[\eta]^0$ and s is inconsistent. This is not surprising in view of the polydispersity of the samples, the use of an oversimplified arm-length distribution, and the lack of precise knowledge of the conformational preferences of the broken rod molecules. More work is needed to clarify the situation.

One final remark should be made. Equations V.14 and V.23 are singular for $\chi = 0$. Mathematically, this results from the singular nature of terms like $R_{i,-i}^{-1}$ as $\chi \to 0$. Physically, it is a consequence of the inadequate treatment of hydrodynamic interaction for small particle separations. Of course, in real molecules excluded volume forces prevent χ from vanishing and this conformation never occurs, or it occurs with zero probability in any averaging over conformations.

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Appendix. Solution of Integral Equations

We require the solutions of eq III.7, III.8, III.12, and III.13. The same general method is used repeatedly. We first let

$$i = nx, \quad j = ny \quad \text{(A.1)}$$

in each equation, and then treat x and y as continuous variables. Doing so produces integral equations which, following Ullman,[11] we further transform by putting

$$x = \tanh(u/2), \quad y = \tanh(v/2) \quad \text{(A.2)}$$

The resulting equations are then susceptible to standard Fourier transform techniques.

Thus, eq III.7 first becomes

$$\psi^{(0)}(x) = nx - \lambda\int_{-1}^1 K^{(0)}(x-y)\psi^{(0)}(y)\,dy \quad \text{(A.3)}$$

where

$$K^{(0)}(x) = \begin{cases} |x|^{-1} & |x| \geq \epsilon = 2b/L \\ 0 & |x| < \epsilon \end{cases} \quad \text{(A.4)}$$

This equation has also appeared in the earlier work of Kirkwood, Riseman, and Auer.[11,16,17] After changing variables according to eq A.2, and with

$$\psi^{(0)}(u) = \phi^{(0)}(u)\cosh(u/2) \quad \text{(A.5)}$$

Fourier transformation yields

$$\phi^{(0)}(u) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} e^{iku}\hat{\phi}^{(0)}(k)\,dk \quad \text{(A.6)}$$

where

$$\hat{\phi}^{(0)}(k) = in(4\pi)^{1/2}k\,\mathrm{sech}(k\pi)U(k,\lambda) \quad \text{(A.7)}$$

and

$$U(k,\lambda) = (1 + \lambda g(k))^{-1} \quad \text{(A.8)}$$

Here $i = (-1)^{1/2}$ and

$$g(k) = 2\int_\epsilon^\infty \cos(2ku)\,\mathrm{csch}(u)\,du \quad \text{(A.9)}$$

where $(2/\pi)^{1/2}g(k)$ is the Fourier transform of the kernel $G(u)$ of the integral equation in u,v variables:

$$G(u) = \begin{cases} |\mathrm{csch}(u/2)| & |u| \geq 2\epsilon \\ 0 & |u| < 2\epsilon \end{cases} \quad \text{(A.10)}$$

Equations A.5–A.7 and III.16 may be combined to give the following expression for $F_1^{(0)}$:

$$F_1^{(0)}(\lambda) = 12\pi \int_0^\infty k^2 \operatorname{sech}^2(k\pi) U(k,\lambda)\, dk \quad (A.11)$$

We now evaluate this integral to what will ultimately prove to be order $[\ln(L/b)]^{-2}$. First note that

$$g(k) = 2 \ln \coth(b/L) - 4 \int_\epsilon^\infty \sin^2(kz) \operatorname{csch}(z)\, dz \quad (A.12)$$

For $L \gg b$ $\ln \coth(b/L)$ will dominate, and we may expand $U(k,\lambda)$ as

$$U(k,\lambda)/\Lambda(\lambda) = 1 + 4\lambda\Lambda(\lambda) \int_\epsilon^\infty \sin^2(kz) \operatorname{csch}(z)\, dz + \ldots \quad (A.13)$$

where

$$\Lambda(\lambda) = (1 + 2\lambda \ln \coth(b/L))^{-1} \quad (A.14)$$

Then, since

$$12\pi \int_0^\infty k^2 \operatorname{sech}^2(k\pi)\, dk = 1 \quad (A.15)$$

eq A.11 and A.13 give

$$F_1^{(0)}(\lambda)/\Lambda(\lambda) = 1 + a_1\lambda\Lambda(\lambda) + \ldots \quad (A.16)$$

where

$$a_1 = 48\pi \int_\epsilon^\infty dz \int_0^\infty dk\, [k \operatorname{sech}(k\pi) \sin(kz)]^2 \operatorname{csch}(z) \quad (A.17)$$

We can evaluate this integral with the result that

$$a_1 = 14/3 + \mathcal{O}(\epsilon) \quad (A.18)$$

We now turn our attention to eq III.8 for $\psi^{(1)}$. After the required transformations are performed we find

$$\phi^{(1)}(u) = \lambda f(u) - (\lambda/2) \int_{-\infty}^\infty G(u - v)\phi^{(1)}(v)\, dv \quad (A.19)$$

where

$$\psi^{(1)}(u) = \phi^{(1)}(u) \cosh(u/2) \quad (A.20)$$

$$4f(u) = \sinh(u) \int_0^\infty \phi^{(0)}(v) \sinh(v) H(u,v)\, dv \quad (A.21)$$

and

$$H(u,v) = \begin{cases} [G(u+v)]^3 & u \geq 0 \\ [G(u-v)]^3 & u \leq 0 \end{cases} \quad (A.22)$$

Fourier transformation of eq A.19 gives

$$\hat{\phi}^{(1)}(k) = inq(k)U(k,\lambda) \quad (A.23)$$

where

$$q(k) = -\lambda(8n^2\pi)^{-1/2} \int_0^\infty \int_0^\infty \sin(ku) \sinh(u) \times \sinh(v)\phi^{(0)}(v)H(u,v)\, du\, dv \quad (A.24)$$

Next, with eq A.20 and A.23 it is possible to transform eq III.16 to read

$$F_1^{(1)}(\lambda) = 6\pi \int_0^\infty k \operatorname{sech}(k\pi) q(k) U(k,\lambda)\, dk \quad (A.25)$$

Now we use eq A.6, A.7, and A.13 to calculate

$$\phi^{(0)}(u) = n\Lambda(\lambda) \tanh(u/2) \operatorname{sech}(u/2) + \ldots \quad (A.26)$$

which may be combined with eq A.24 and A.13 to simplify eq A.25. To order $[\ln(L/b)]^{-2}$ the result is

$$F_1^{(1)}(\lambda) = 6\lambda\Lambda^2(\lambda) \int_0^1 \int_0^1 x^2y^2(x+y)^{-3}\, dx\, dy \quad (A.27)$$

The double integral is readily performed, and we obtain

$$F_1^{(1)}(\lambda) = 4(\ln 2 - 5/8)\lambda\Lambda^2(\lambda) \quad (A.28)$$

We now focus on eq III.12. After the necessary changes of variables and with

$$\rho^{(0)}(u) = P^{(0)}(u) \cosh(u/2) \quad (A.29)$$

we find for the Fourier transform of $P^{(0)}(u)$:

$$\hat{P}^{(0)}(k) = n2^{1/2}p(k)U(k,\lambda) \quad (A.30)$$

where

$$p(k) = (\pi)^{-1/2} \int_0^\infty \cos(ku) \times (\tanh(u/2) - 1/2) \operatorname{sech}(u/2)\, du \quad (A.31)$$

With this result we find that eq III.17 may be cast in the form

$$F_2^{(0)}(\lambda) = 3 \int_0^\infty [p(k)]^2 U(k,\lambda)\, dk \quad (A.32)$$

Once again we expand $U(k,\lambda)$ and since

$$4 \int_0^\infty [p(k)]^2\, dk = \int_0^1 (2y-1)^2\, dy \quad (A.33)$$

we find through order $[\ln(L/b)]^{-2}$

$$4F_2^{(0)}(\lambda)/\Lambda(\lambda) = 1 + a_2\lambda\Lambda(\lambda) + \ldots \quad (A.34)$$

where

$$a_2 = 48 \int_\epsilon^\infty dz \int_0^\infty dk\, [p(k) \sin(kz)]^2 \operatorname{csch}(z) \quad (A.35)$$

Evaluation of this integral gives

$$a_2 = 4 \ln 2 + 8/3 + \mathcal{O}(\epsilon) \quad (A.36)$$

Finally we need to solve eq III.13. Using the same transformations again we find

$$\rho^{(1)}(u) = P^{(1)}(u) \cosh(u/2) \quad (A.37)$$

$$P^{(1)}(u) = 4n\pi^{-1/2} \int_0^\infty \cos(ku) w(k) U(k,\lambda)\, dk \quad (A.38)$$

and

$$w(k) = -\lambda(8n)^{-1}\pi^{-1/2} \int_0^\infty \int_0^\infty \cos(ku) \sinh(u) \times \sinh(v) P^{(0)}(v) H(u,v)\, du\, dv \quad (A.39)$$

With these results eq III.17 may be brought into the form

$$F_2^{(1)}(\lambda) = 6 \int_0^\infty w(k)p(k)U(k,\lambda)\, dk \quad (A.40)$$

After expanding $U(k,\lambda)$, Fourier inversion of eq A.30 gives

$$P^{(0)}(u) = n\Lambda(\lambda)(|\tanh(u/2)| - 1/2) \operatorname{sech}(u/2) + \ldots \quad (A.41)$$

We use this result and eq A.13 in order to reduce eq A.40 to

$$2F_2^{(1)}(\lambda) = -3\lambda\Lambda^2(\lambda) \int_0^1 \int_0^1 xy(2x-1) \times (2y-1)(x+y)^{-3}\, dx\, dy \quad (A.42)$$

to order $[\ln(L/b)]^{-2}$. After calculation of the double integral we find

$$F_2^{(1)}(\lambda) = -(\ln 2 - 5/8)\lambda\Lambda^2(\lambda) \quad (A.43)$$

Finally, we need only to note that

$$\Lambda(\lambda) \sim [2\lambda \ln (L/b)]^{-1} \qquad (A.44)$$

for $L \gg b$.

In his review of this article, Professor H. Yamakawa pointed out a potential mathematical difficulty involving the cut-off limits in eq A.10. Regarding this we comment as follows.

The results in this section depend on the evaluation of the Fourier transform of integrals such as $\int_{-\infty}^{\infty} d\upsilon\, \phi(\upsilon)G(u-\upsilon)$. In u,υ variables the precise cut-off for the vanishing of the kernel G becomes the requirement that $|\tanh(u/2) - \tanh(\upsilon/2)| < \epsilon$. With this restriction the Fourier transform of the above integral can be written as

$$\int_{-\infty}^{\nu} d\upsilon\, e^{ik\upsilon}\phi(\upsilon) \int_{\alpha-\upsilon}^{\infty} du\, e^{iku}G(u) + \int_{-\nu}^{\infty} d\upsilon\, e^{ik\upsilon}\phi(\upsilon) \int_{-\infty}^{\beta-\upsilon} du\, e^{iku}G(u)$$

where $\nu = 2\tanh^{-1}(1-\epsilon)$, $\alpha = 2\tanh^{-1}(\tanh(\upsilon/2)+\epsilon)$, and $\beta = 2\tanh^{-1}(\tanh(\upsilon/2)-\epsilon)$. Then, as $\epsilon \to 0$, $\nu \to \infty$, $\alpha - \upsilon \to 2\epsilon$, $\beta - \upsilon \to -2\epsilon$, the integral asymptotically becomes factorable, only now permitting the easy solution for $\hat{\phi}$.

The asymptotic nature of this result suggests that the term of order $[\ln (L/b)]^{-2}$ presented in section IV is still incomplete, rendering its significance even more ambiguous.

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Conformational Characteristics of Poly(alkyl vinyl ether)'s

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ABSTRACT: Conformational energies were estimated for the poly(alkyl vinyl ether) chain using semiempirical energy expressions. The results were tested for NMR data on 2,4-dimethoxypentane. The 3×3 statistical weight matrices derived therefrom were applied to the analysis of various configuration-dependent properties of these polymers: H+CH_2–CH(OR)+$_x$$CH_3$, R = methyl, ethyl, isopropyl, isobutyl, (*S*)-1-methylpropyl and (*S*)-2-methylbutyl groups. The characteristic ratio of the unperturbed dimension (C_∞ = 6.1–8.0) estimated from fractionated samples of poly(methyl vinyl ether) in a good solvent was reproduced in a moderately isotactic region. Experimental values of the mean-square dipole moment per repeat unit $\langle\mu^2\rangle/x$ for isotactic samples of poly(isopropyl vinyl ether) (0.67) and poly(isobutyl vinyl ether) (0.97–1.35) were also found to be in agreement with those calculated in a reasonable range of tacticity. These properties are quite insensitive to the extra stabilization energy associated with "gauche oxygen" placements. The fraction of helical conformations was estimated for asymmetric side chains, indicating that the large enhancement in optical activity arises from the neighbor-dependent character of the polymer chain.

Configuration-dependent properties of poly-α-olefins, hydrocarbon analogues of poly(alkyl vinyl ether)'s, have been successfully treated within the framework of the rotational isomeric state approximation.[1] These include characteristic ratios C_∞,[2,3] optical anistropy,[4] interpretation of NMR spectra,[5] and optical rotation.[6,7] Recently Suter and Flory[8] carried out detailed calculations of conformational energies of polypropylene using semiempirical expressions. Large displacements of high-energy conformations from the perfectly staggered position were taken into account in their five-state matrix scheme, which thereby offers more exact representation of the energy contour map. Stereochemical equilibrium data[7] and characteristic ratios C_∞ are satisfactorily treated on this basis. They concluded on the other hand that the widely adopted three-state model is useful as well, the statistical weight ω associated with second-order interactions being treated as a somewhat arbitrarily adjustable parameter.[2,3]

Conformational energies of poly(alkyl vinyl ether)'s are more complicated, due to the presence of oxygen atoms. The semiempirical expressions customarily formulated were found to give somewhat higher estimates for conformational energies associated with "gauche oxygens" in the poly(alkylene oxide) chains.[1,9] Such gauche oxygen effects[10] will be discussed in the text. The dipole moments associated with side chains provide information which is obviously not available from the hydrocarbon polymers. The theory[11] set forth previously for the dipole moment of vinyl polmyers with flexible side chains is applicable to such properties.

Alkyl vinyl ethers CH_2=CHOR such as R = methyl, ethyl, isopropyl, or isobutyl have been known to give isotactic polymers when polymerized with homogeneous cationic catalysts.[12-14] Natta and co-workers[13,14] concluded from their

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