Intrinsic Flow Birefringence of Wormlike Chains

Jiro Shimada and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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ABSTRACT: The intrinsic flow birefringence of stiff chains without excluded volume is evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to wormlike cylinder models with the use of the diffusion equation of the Kirkwood type. The ratio of intrinsic flow birefringence to intrinsic viscosity is found to be almost independent of the diameter of the cylinder and also of the strength of hydrodynamic interaction. The results are applied to the determination of the dimensional and optical parameters of poly(n-butyl isocyanate) chains.

The sedimentation coefficient and intrinsic viscosity of various stiff chain macromolecules have been evaluated on the basis of continuous wormlike cylinder models, and thereby their molecular parameters have been determined reasonably.[1–4] In the present paper, a similar study of another transport property, the intrinsic flow birefringence $[n]$, is made to confirm the consistency in our theoretical procedure.

For wormlike chains without excluded volume and hydrodynamic interactions, Gotlib and Svetlov[5] have evaluated the ratio of the intrinsic flow birefringence to the intrinsic viscosity $[\eta]$. Noda and Hearst[6] have evaluated the same ratio for the Harris–Hearst chain[7] with hydrodynamic interaction, and found that it is almost independent of the amount of drainage. However, their results for the ratio $[n]/[\eta]$ are 2 and $\frac{5}{3}$ times greater than those of Gotlib and Svetlov in the coil and rod limits, respectively. Probably, these differences may arise from the variable polarizability of the segment of the Harris–Hearst chain of variable contour length. Svetlov[8] has recently obtained the same ratio by the use of the simple model of equivalent ellipsoid[9] with hydrodynamic interaction. However, the values of $[n]/[\eta]$ are appreciably lower than the corresponding values of Gotlib and Svetlov except near the rod limit. Thus, there is some controversy among the existing theories.

The flow birefringence is characterized by its intrinsic magnitude $[n]$ and the extinction angle.[10,11] Since the dynamics of wormlike chains of invariable contour length has not yet been developed, we follow the procedure of Gotlib and Svetlov.[5,12,13] That is, in steady Newtonian flow $[n]$ is evaluated by the use of the distribution function expanded to first order in rate of shear with the preaveraged Oseen hydrodynamic interaction tensor. The extinction angle is not studied in the present paper, since the distribution function of the second order in rate of shear is necessary. The effect of the internal electric field[10,11] is ignored as in the previous work cited above.[5,6,8]

In section I, the formulation is made, and in section II, numerical solutions of the derived integral equation, which cannot be solved analytically, are given. In section III, we give a method of determining the dimensional and optical parameters, and apply it to poly(n-butyl isocyanate) chains.

I. Formulation

Distribution Function. Consider a wormlike cylinder of contour length L and diameter d in the unperturbed velocity field $\mathbf{v}^0$ of solvent with viscosity coefficient η_0,

$$\mathbf{v}^0 = (\kappa y, 0, 0) \tag{1}$$

where the molecular center of mass is fixed at the origin of a Cartesian coordinate system ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$), and κ is the time-independent rate of shear.

Following the Oseen–Burgers procedure,[1–4] we replace the cylinder by a frictional force distribution $\mathbf{f}(s)$ per unit length along the cylinder axis as a function of the contour distance s from one end. Let $\mathbf{a}$ be the normal radius vector from the contour point t on the axis to an arbitrary point P which would be just located on the cylinder surface if the cylinder were present. The velocity $\mathbf{v}(\mathrm{P})$ of the solvent at the point P relative to the velocity $\mathbf{u}(\mathrm{P})$ of the cylinder at P may be expressed as the sum of the unperturbed velocity $\mathbf{v}^0(\mathrm{P})$, $-\mathbf{u}(\mathrm{P})$, and the integrated Oseen perturbations from $\mathbf{f}(s)$.

The Oseen–Burgers procedure requires that $\langle \mathbf{v}(\mathrm{P}) \rangle_{\mathbf{a}} = 0$ for all values of t ($0 \le t \le L$), where $\langle\ \rangle_{\mathbf{a}}$ designates the average over $\mathbf{a}$, assuming its uniform distribution. Since the unperturbed velocity field is linear in space, we then have

$$\int_0^L (6\pi\eta_0)^{-1} K(s, t)\mathbf{f}(s)\, \mathrm{d}s = \mathbf{u}(t) - \mathbf{v}^0(t) \tag{2}$$

with

$$K(s, t) = \langle |\mathbf{R} - \mathbf{a}|^{-1} \rangle \tag{3}$$

(see eq 6 of ref 4), where $\mathbf{R}$ is the distance between contour points t and s, and the Oseen tensor has been preaveraged, designating the two averaging processes simply by the symbol $\langle\ \rangle$.

For convenience, we replace the integral on the left of eq 2 by the sum,

$$(6\pi\eta_0)^{-1} \sum_{j=1}^{N} K_{ij}\mathbf{F}_j = \mathbf{u}_i - \mathbf{v}_i{}^0 \tag{4}$$

where

$$K_{ij} = K(iL/N, jL/N) \tag{5}$$

$$\mathbf{F}_j = (L/N)\mathbf{f}(jL/N) \tag{6}$$

Here, we suppose that the cylinder is composed of N segments, $\mathbf{u}_i$ is the velocity of the ith segment ($i = Nt/L$), $\mathbf{v}_i{}^0$ is the unperturbed solvent velocity at the location of the ith segment, and $\mathbf{F}_i$ is the frictional force exerted on the fluid by that segment. We note that the quantity $(kT/6\pi\eta_0)K_{ij}\mathbf{I}$ with k the Boltzmann constant, T the absolute temperature, and $\mathbf{I}$ the 3×3 unit tensor corresponds to the preaveraged diffusion tensor appearing in the dynamical theory of Kirkwood[14] for discrete models.

Now, the equation of continuity in the Kirkwood theory is given by

$$\frac{\partial P}{\partial t} = -\sum_{i=1}^{N} \nabla_i \cdot (P\mathbf{u}_i) \tag{7}$$

where P is the molecular distribution function at time t, and ∇_i is the differential operator with respect to the position of the ith segment. If we substitute $\mathbf{u}_i$ from eq 4 into eq 7 and make use of the force balance equation,

$$\mathbf{F}_j = -\nabla_j U - kT\nabla_j \ln P \tag{8}$$

with U the intramolecular potential, we then have the diffusion equation,

$$\frac{\partial P}{\partial t} + \sum_{i=1}^{N} \nabla_i \cdot (P\mathbf{v}_i{}^0) = \sum_{i=1}^{N}\sum_{j=1}^{N} \nabla_i \cdot [(kT/6\pi\eta_0)K_{ij}\mathbf{I}] \cdot [\nabla_j P + (kT)^{-1}P\nabla_j U] \quad (9)$$

We note that eq 9 is of the same form as the diffusion equation in the conventional theory except that the diffusion tensor is replaced by $(kT/6\pi\eta_0)K_{ij}\mathbf{I}$.

Since the diffusion tensor has been preaveraged to be independent of the coordinates, the time-independent solution of eq 9 may be obtained following the procedure of Gotlib and Svetlov,[12,13]

$$P = C\exp(-U/kT)[1 + (3\pi\eta_0\kappa/kT) \times \sum_{i=1}^{N}\sum_{j=1}^{N} (\mathbf{K}^{-1})_{ij}S_x{}^{(i)}S_y{}^{(j)} + 0(\kappa^2)] \quad (10)$$

where $\mathbf{K}^{-1}$ is the inverse of the $N \times N$ matrix $\mathbf{K} = (K_{ij})$, $S_\mu{}^{(i)}$ ($\mu = x, y$) is the μth component of the distance $\mathbf{S}^{(i)}$ between the center of resistance, which is here approximately identified with the center of mass, and the ith segment, and C is the normalization constant. Thus, we can treat an assembly of wormlike cylinders as an assembly of kinetically rigid particles whose configurational distribution is given by eq 10.[12,13]

Basic Equations for [*n*]. Let α_1 be the component of polarizability per unit length along the tangent vector of the cylinder axis, and let α_2 be the values of the two equal components normal to it. We use a prime to indicate that a quantity is expressed in a Cartesian coordinate system ($\mathbf{e}_x{}'$, $\mathbf{e}_y{}'$, $\mathbf{e}_z{}'$) fixed in the macromolecule. The polarizability tensor $\mathbf{B}'$ of the whole molecule is then given by

$$B_{\mu\nu}{}' = [(\Delta\alpha)L/N]\sum_{i=1}^{N} u_\mu{}^{(i)\prime}u_\nu{}^{(i)\prime} + \alpha_2 L\delta_{\mu\nu} \quad (11)$$
$$(\mu, \nu = x', y', z')$$

where $\Delta\alpha = \alpha_1 - \alpha_2$, $u_\mu{}^{(i)\prime}$ is the μth component of the unit tangent vector $\mathbf{u}^{(i)\prime}$ associated with the ith segment, and $\delta_{\mu\nu}$ is the Kronecker δ.

Following Gotlib and Svetlov,[5] we average the polarizability tensor $\mathbf{B}$, which is expressed in the laboratory coordinate system ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$), with the distribution function P first over the orientation of the (rigid) macromolecule and then over all internal configurations to obtain the difference $\Delta\Gamma$ of the components along the principal axes of the average polarizability tensor. After averaging over the orientation, we have

$$\Delta\Gamma = \frac{\kappa}{10}\langle \mathrm{Tr}(\mathbf{B}'\cdot\mathbf{J}') - \tfrac{1}{3}(\mathrm{Tr}\mathbf{B}')(\mathrm{Tr}\mathbf{J}')\rangle + 0(\kappa^2) \quad (12)$$

where Tr indicates the trace, $\langle\ \rangle$ designates the average only over equilibrium internal configurations, and $\mathbf{J}'$ is the tensor defined by

$$J_{\mu\nu}{}' = (6\pi\eta_0/kT)\sum_{i=1}^{N}\sum_{j=1}^{N} (\mathbf{K}^{-1})_{ij}S_\mu{}^{(i)\prime}S_\nu{}^{(j)\prime} \quad (13)$$
$$(\mu, \nu = x', y', z')$$

The intrinsic flow birefringence in Newtonian flow may be expressed in terms of $\Delta\Gamma$,

$$[n] \equiv \lim_{\kappa\to 0}\frac{5N_AK\Delta\Gamma}{2\kappa\eta_0 M} = \frac{N_AK}{4\eta_0 M}\langle \mathrm{Tr}(\mathbf{B}'\cdot\mathbf{J}') - \tfrac{1}{3}(\mathrm{Tr}\mathbf{B}')(\mathrm{Tr}\mathbf{J}')\rangle \quad (14)$$

with

$$K = 4\pi(n^2+2)^2/45n \quad (15)$$

where N_A is the Avogadro number, M is the molecular weight of the macromolecule, and n is the refractive index of the solvent.

Now, we take the continuous limit, $N \to \infty$. In what follows, the primes are omitted, and unless specified otherwise, all lengths are measured in units of the Kuhn length λ^{-1}, for convenience. Then, $[n]$ (reduced by λ^4) may be expressed as

$$[n] = \frac{3\pi N_AK\Delta\alpha}{2kTM}F(L) \quad (16)$$

with

$$F(L) = \int_0^L \mathrm{d}s\int_0^L \mathrm{d}t\, K^{-1}(s,t)g(s,t) \quad (17)$$

where $K^{-1}(s, t)$ is the inverse of the kernel $K(s, t)$, for which we adopt the same approximation (eq 36–38 of ref 1) as in the case of sedimentation coefficient[1] and intrinsic viscosity,[2] and $g(s, t)$ is defined by

$$g(s,t) = \int_0^L \langle[\mathbf{u}(s_1)\cdot\mathbf{S}(s)][\mathbf{u}(s_1)\cdot\mathbf{S}(t)]\rangle\,\mathrm{d}s_1 - (L/3)\langle\mathbf{S}(s)\cdot\mathbf{S}(t)\rangle \quad (18)$$

where $\mathbf{u}(t)$ is the unit tangent vector at the contour point t and $\mathbf{S}(t)$ is its distance from the center of mass. The first term on the right of eq 18 is evaluated in the Appendix, and the second term has been given in eq 19 of ref 2. In particular, $g(s, t)$ is in the coil limit

$$\lim_{L\to\infty} g(s,t) = \lim_{L\to\infty}\tfrac{5}{9}\langle\mathbf{S}(s)\cdot\mathbf{S}(t)\rangle = \tfrac{5}{9}\left[\frac{1}{2L}(s^2+t^2) - \frac{1}{2}(s+t) - \frac{1}{2}|s-t| + \frac{1}{3}L\right] \quad (19)$$

and in the rod limit

$$\lim_{L\to 0} g(s,t) = \lim_{L\to 0}\frac{2L}{3}\langle\mathbf{S}(s)\cdot\mathbf{S}(t)\rangle = \frac{2L}{3}\left(t-\frac{L}{2}\right)\left(s-\frac{L}{2}\right) \quad (20)$$

$F(L)$ may be expressed as

$$F(L) = \int_0^L \psi(s,s)\,\mathrm{d}s \quad (21)$$

in terms of the solution ψ of the integral equation,

$$\int_0^L K(s,t_1)\psi(t_1,t)\,\mathrm{d}t_1 = g(s,t) \quad (22)$$

We note that in the theory of $[\eta]$, we have encountered a similar integral equation, eq 15 of ref 2.

II. Solutions

Coil Limit. Since $g(s, t)$ is given by eq 19 in the coil limit, the integral eq 22 is just the same as that in the theory[2] of $[\eta]$ except a numerical factor. By the use of the previous result for $[\eta]$, we therefore readily have

$$[n]_\infty = \frac{5K\Delta\alpha}{6kT}[\eta]_\infty = \frac{5K\Delta\alpha\Phi_\infty L^{3/2}}{6kTM} \quad (23)$$

where the subscript ∞ designates the coil limit, and the Auer–Gardner value[15] for Φ_∞ is 2.862×10^{23}.

Rod Limit. Similarly, we have in the long rod limit, which we designate by the subscript 0,

$$[n]_0 = \frac{K\Delta\alpha L}{kT}[\eta]_0 = \frac{\pi N_AK\Delta\alpha}{24kTM}\,\frac{L^4}{\ln(L/d) + 2\ln 2 - \tfrac{7}{3}} \quad (24)$$

If we avoid preaveraging the Oseen tensor to use the well-known orientational distribution function for the rod[16] with the relaxation time τ obtained by Yamakawa,[4] we have

$$[n]_0 = \frac{\pi N_AK\Delta\alpha}{18kTM}\,\frac{L^4}{\ln(L/d) + 2\ln 2 - \tfrac{11}{6}} \quad (25)$$

This agrees asymptotically with the result obtained by Kuhn et al.[17] The ratios of $[n]$ and $[n]/[\eta]$ evaluated without preaveraging to those with preaveraging are asymptotically $\frac{4}{3}$ and $\frac{5}{4}$, respectively. These values are rather large compared with the corresponding ratio of $\frac{16}{15}$ for $[\eta]$. Therefore, the results for $[n]$ and $[n]/[\eta]$ evaluated with preaveraging may not be regarded as very accurate near the rod limit.

Numerical Solutions. In order to obtain the intermediate solution between $[n]_\infty$ and $[n]_0$, the integral eq 22 has been solved numerically by the use of a FACOM 230-75 digital computer at this University. The details are the same as those in the theory[2] of $[\eta]$ except that we have used the procedure of Schlitt[3,18] which may be considered to be more accurate than that of Ullman.[19]

Using the values of $F(L)$ obtained, we have calculated the ratio R defined by

$$R(L, d) \equiv ([n]/[\eta])/([n]_\infty/[\eta]_\infty) = (9\pi N_A/5\Phi L^{3/2})F(L) \tag{26}$$

where we have used the values obtained by Yamakawa and Fujii[2] for the viscosity constant Φ. We have found that the values of R are insensitive to the change in d and very close to the values $R_0(L)$ obtained by Gotlib and Svetlov[5] in the draining limit,

$$R_0(L) = (3L/5)[\Phi_1(2L)/\Phi_2(2L)] \tag{27}$$

with

$$\Phi_1(2L) = \frac{5}{18L^2} - \frac{2}{3L^3} + \frac{97}{108L^4} - \frac{46}{81L^5} + \left(\frac{1}{4L^4} + \frac{9}{16L^5}\right)e^{-2L} + \left(\frac{1}{108L^4} + \frac{7}{1296L^5}\right)e^{-6L} \tag{28}$$

$$\Phi_2(2L) = \frac{1}{6L} - \frac{1}{4L^2} + \frac{1}{4L^3} - \frac{1}{8L^4} + \frac{1}{8L^4}e^{-2L} \tag{29}$$

In general, the difference between our R and their R_0 values is small near the coil and rod limits, and also for small d irrespective of the value of L. For example, the difference does not exceed 3.5% for $L \gtrsim 2$ and $d \lesssim 0.06$, or $L \lesssim 2$ and $L/d \gtrsim 20$. Thus, R may well be approximated by R_0 over the whole range. Therefore, we may approximate $[n]$ by

$$[n] = \frac{5K\Delta\alpha}{6kT}R_0(L)[\eta] \tag{30}$$

where the ratio $[n]/[\eta]$ is exactly the same as that of Gotlib and Svetlov,[5] but the Yamakawa–Fujii expression[2] should be used for $[\eta]$.

III. Treatments of Experimental Data

We attempt to make an analysis of experimental data by a combination of $[n]$ and $[\eta]$. Now, it is convenient to use the unreduced $[n]$, $[\eta]$, $\Delta\alpha$, and the reduced contour length L,

$$L = \lambda M/M_L \tag{31}$$

with M_L the shift factor or the molecular weight per unit (unreduced) contour length. If we measure $[n]$ in units of cm^4 s^2/g^2 and $[\eta]$ in units of dl/g, then $[n]/[\eta]$, $[\eta]$, and $[n]$ may be written in the form,

$$\log([n]/[\eta]) = \epsilon + \log R_0(L) \tag{32}$$

$$\log[\eta] = \gamma + \tfrac{1}{2}\log L - \Gamma_1(L, d) \tag{33}$$

$$\log[n] = \epsilon + \gamma + \tfrac{1}{2}\log L - \Gamma_3(L, d) \tag{34}$$

with

$$\epsilon = \log(5K\Delta\alpha/6\lambda kT) \tag{35}$$

$$\gamma = 21.4579 - \log(M_L\lambda^2) \tag{36}$$

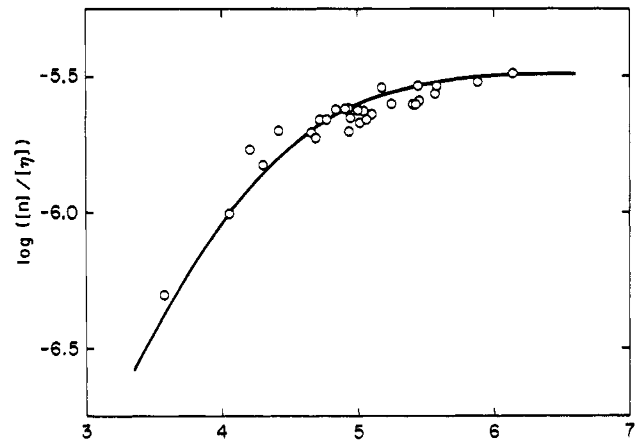

Figure 1. Analysis of the data for $[n]/[\eta]$ of poly(n-butyl isocyanate) in carbon tetrachloride at 21 °C[20] according to eq 32. The curve is displaced by $\delta = 4.48$ and $\epsilon = -5.49$.

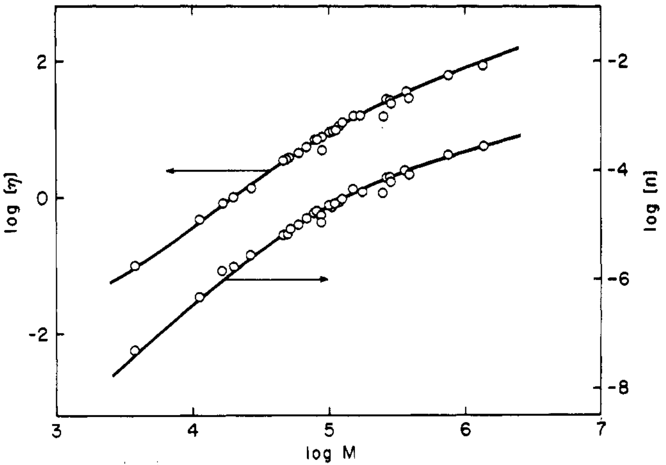

Figure 2. Analysis of the data for $[\eta]$ and $[n]$ of poly(n-butyl isocyanate) in carbon tetrachloride at 21 °C[20] according to eq 33 and 34. The curves for $[\eta]$ and $[n]$ with $d = 0.008$ are displaced by $\delta = 4.48$ and $\gamma = 1.54$, and $\delta = 4.48$ and $\epsilon + \gamma = -3.95$, respectively.

$$\Gamma_1(L, d) = \log([\eta]_\infty/[\eta]) \tag{37}$$

$$\Gamma_3(L, d) = \log([n]_\infty/[n]) = -\log R_0(L) + \Gamma_1(L, d) \tag{38}$$

where Γ_1 has been defined previously[2] (Γ_2 appearing in the sedimentation coefficient[2]).

Equations 32–38 and the fact that the quantities on both sides of eq 32 are independent of d suggest the following method of determining the dimensional and optical parameters. First, a curve of $\log R_0$ plotted against $\log L$ may be displaced by δ,

$$\delta = \log(M_L/\lambda) \tag{39}$$

in the abscissa direction and by ϵ in the ordinate direction to fit experimental plots of the quantity on the left of eq 32 against $\log M$ on the same scale. Second, as in the previous paper,[2] a curve of $\tfrac{1}{2}\log L - \Gamma_1$ for a proper value of d plotted against $\log L$ may be displaced by δ in the abscissa direction and by γ in the ordinate direction to fit experimental plots of the quantity on the left of eq 33 against $\log M$ on the same scale. These processes lead to complete estimates of the parameters. However, with the values of δ, γ, ϵ, and d thus determined, a curve of $\tfrac{1}{2}\log L - \Gamma_3$ plotted against $\log L$ may be displaced by δ in the abscissa direction and by $\epsilon + \gamma$ in the ordinate direction to confirm the curve to fit experimental plots of the quantity on the left of eq 34 against $\log M$ on the

Table I
Estimates of the Dimensional and Optical Parameters for Poly(*n*-butyl isocyanate) in Carbon Tetrachloride

Method	M_L, Å^{-1}	λ^{-1}, Å	d, Å	$\Delta\alpha$, Å^3/ (monomeric unit)
$[n] - [\eta]$[a]	42.2	710	5.7	1.5
$s - [\eta]$[b]	44.2	750	6.0	

[a] Present method. [b] See ref 2.

same scale. Thus, we may estimate M_L, λ^{-1}, and (unreduced) d from eq 36 and 39, and then $\Delta\alpha$ per monomeric unit from eq 35 using this value of M_L.

Such plots of the data obtained by Shtennikova et al.[20] for poly(*n*-butyl isocyanate) in carbon tetrachloride at 21 °C are shown in Figures 1 and 2. The curve of Figure 1 is that of log R_0 with $\delta = 4.48$ and $\epsilon = -5.49$, and the curves of Figure 2 are those of $\frac{1}{2} \log L - \Gamma_1$ and $\frac{1}{2} \log L - \Gamma_3$ with the same δ and ϵ, $\gamma = 1.54$, and $d = 0.008$. The values of M_L, λ^{-1}, (unreduced) d, and $\Delta\alpha$ (per monomeric unit) determined from these displacements are given in Table I. For the determination of $\Delta\alpha$, we have used the value 1.460 for the refractive index of the solvent and the value 99 for the molecular weight of the monomeric unit. For comparison, the estimates of M_L, λ^{-1}, and d by Yamakawa and Fujii[2] from a combination of the sedimentation and viscosity data ($s - [\eta]$) obtained by Tsvetkov et al.[21] for the same system at 20 °C are also given in the table. There is good agreement between the estimates from the two combinations.

In conclusion, the transport properties of poly(*n*-butyl isocyanate) chains may be consistently interpreted on the basis of the wormlike cylinder model. However, the light-scattering study of this polymer by Fetters and Yu[22] seems to show the existence of a maximum in the ratio of the mean-square radius of gyration to M as a function of M. This is inconsistent with the wormlike chain model, and the conformational and transport behavior of this polymer might be interpreted more satisfactorily by the helical wormlike chain model recently introduced by Yamakawa and Fujii.[23] This is a problem in the future.

Appendix

The first term on the right of eq 18 may be reduced to

$$\begin{aligned} g_1(s, t) = {} & \int_0^L \mathrm{d}s_1 \langle [\mathbf{u}(s_1) \cdot \mathbf{S}(s)][\mathbf{u}(s_1) \cdot \mathbf{S}(t)] \rangle \\ = {} & \frac{1}{2L} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}t_1 \langle \{\mathbf{u}(s_1) \cdot [\mathbf{S}(s) \\ & - \mathbf{S}(t_1)]\}^2 + \{\mathbf{u}(s_1) \cdot [\mathbf{S}(t) - \mathbf{S}(t_1)]\}^2 \rangle \\ & - \frac{1}{2L^2} \int_0^L \mathrm{d}t_1 \int_0^L \mathrm{d}s_2 \int_0^{\mathrm{L}} \mathrm{d}s_1 \langle \{\mathbf{u}(s_1) \cdot [\mathbf{S}(t_1) \\ & - \mathbf{S}(s_2)]\}^2 \rangle - \frac{1}{2} \int_0^L \mathrm{d}s_1 \langle \{\mathbf{u}(s_1) \cdot [\mathbf{S}(s) - \mathbf{S}(t)]\}^2 \rangle \end{aligned} \quad \text{(A1)}$$

For example, the first term of the integrand in the second equality of eq A1 may be rewritten as

$$\begin{aligned} & \langle \{\mathbf{u}(s_1) \cdot [\mathbf{S}(s) - \mathbf{S}(t_1)]\}^2 \rangle \\ & \quad = \int_{t_1}^{s} \mathrm{d}s_2 \int_{t_1}^{s} \mathrm{d}t_2 \langle [\mathbf{u}(s_1) \cdot \mathbf{u}(s_2)][\mathbf{u}(s_1) \cdot \mathbf{u}(t_2)] \rangle \end{aligned} \quad \text{(A2)}$$

The integrand on the right of eq A2 may be evaluated by the use of the conditional distribution function $G(\mathbf{u}|\mathbf{u}_0;t)$ of the unit tangent vector $\mathbf{u}$ at the end point with the initial unit tangent vector $\mathbf{u}_0$ fixed for the wormlike chain of contour length t,[24]

$$G(\mathbf{u}|\mathbf{u}_0;t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} e^{-l(l+1)t} Y_l^m(\theta, \phi) Y_l^{-m}(\theta_0, \phi_0) \quad \text{(A3)}$$

where $\mathbf{u} = (1, \theta, \phi)$ and $\mathbf{u}_0 = (1, \theta_0, \phi_0)$ in spherical polar coordinates, and Y_l^m are the normalized spherical harmonics.

The other terms may be evaluated in a similar way, and the result is

$$\begin{aligned} g_1(s, t) = {} & (1/2L)[f_1(s) + f_1(L - s) + f_1(t) + f_1(L - t)] \\ & - f_2(L) - f_3(s - t) - f_4(s, t) - f_4(L - t, L - s) \end{aligned} \quad \text{(A4)}$$

where

$$\begin{aligned} f_1(s) = {} & \left(\frac{L}{6} + \frac{5}{18}\right) s^2 - \left(\frac{L}{6} + \frac{4}{9}\right) s + \frac{L}{12} + \frac{49}{162} \\ & - \left(\frac{s}{6} + \frac{L}{12} + \frac{43}{144}\right) e^{-2s} - \frac{1}{72} e^{-4(L-s)} - \left(\frac{s}{108} + \frac{5}{1296}\right) e^{-6s} \\ & - \left(\frac{s}{54} - \frac{1}{81}\right) e^{-6(L-s)} + \frac{1}{648} e^{-6L} \\ f_2(s) = {} & \frac{s^2}{18} + \frac{s}{108} - \frac{5}{36} + \frac{167}{648s} - \frac{46}{243s^2} \\ & + \left(\frac{1}{8s} + \frac{3}{16s^2}\right) e^{-2s} + \left(\frac{1}{324s} + \frac{7}{3888s^2}\right) e^{-6s} \\ f_3(s) = {} & \frac{1}{6} s^2 + \frac{7}{36} |s| - \frac{13}{54} + \frac{1}{4} (|s| + 1) e^{-2|s|} - \frac{1}{108} e^{-6|s|} \\ f_4(s, t) = {} & \frac{1}{6} \left(s - t - \frac{1}{2} + \frac{1}{2} e^{-2s+2t}\right) t \\ & - \frac{1}{72} (e^{-2s+2t} - e^{-2s-4t}) + \frac{1}{216} (e^{-6s+6t} - e^{-6s}) \\ & + \frac{1}{108} (1 - e^{-6t}) \qquad \text{for } s \geq t \\ = {} & f_4(t, s) \qquad \text{for } t > s \end{aligned} \quad \text{(A5)}$$

References and Notes

(1) H. Yamakawa and M. Fujii, *Macromolecules*, **6**, 407 (1973).
(2) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).
(3) M. Fujii and H. Yamakawa, *Macromolecules*, **8**, 792 (1975).
(4) H. Yamakawa, *Macromolecules*, **8**, 339 (1975).
(5) Yu. Ya. Gotlib and Yu. Ye. Svetlov, *Dokl. Akad. Nauk SSSR*, **168**, 621 (1966).
(6) I. Noda and J. E. Hearst, *J. Chem. Phys.*, **54**, 2342 (1971).
(7) R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595 (1966).
(8) Yu. Ye. Svetlov, *Vysokomol. Soedin., Ser. A*, **16**, 2593 (1974).
(9) Yu. Ya. Gotlib and Yu. Ye. Svetlov, *Vysokomol. Soedin., Ser. A*, **9**, 1150 (1967).
(10) V. N. Tsvetkov, "Newer Methods of Polymer Characterization", B. Ke, Ed., Interscience, New York, N.Y., 1964.
(11) H. Janeschitz-Kriegl, *Adv. Polym. Sci.*, **6**, 170 (1969).
(12) Yu. Ya. Gotlib and Yu. Ye. Svetlov, *Vysokomol. Soedin.*, **8**, 1517 (1966).
(13) M. Fixman and W. H. Stockmayer, *Annu. Rev. Phys. Chem.*, **21**, 407 (1971).
(14) J. G. Kirkwood, *Recl. Trav. Chim. Pays-Bas*, **68**, 649 (1949).
(15) P. L. Auer and C. S. Gardner, *J. Chem. Phys.*, **23**, 1546 (1955).
(16) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).
(17) W. Kuhn, H. Kuhn, and P. Buchner, *Ergeb. Exakten Naturwiss.*, **25**, 1 (1951).
(18) D. W. Schlitt, *J. Math. Phys. (N.Y.)*, **9**, 436 (1968).
(19) R. Ullman, *J. Chem. Phys.*, **49**, 5486 (1968).
(20) I. N. Shtennikova, V. N. Tsvetkov, T. V. Peker, Ye. I. Ryumtsev, and Yu. P. Getmanchuk, *Vysokomol. Soedin., Ser. A*, **16**, 1086 (1974).
(21) V. N. Tsvetkov, I. N. Shtennikova, Ye. I. Ryumtsev, and Yu. P. Getmanchuk, *Eur. Polym. J.*, **7**, 767 (1971).
(22) L. J. Fetters and H. Yu, *Macromolecules*, **4**, 385 (1971).
(23) H. Yamakawa and M. Fujii, *J. Chem. Phys.*, to be published.
(24) H. Yamakawa, *J. Chem. Phys.*, **59**, 3811 (1973).