Table IV
A Comparison of the Experimental and Theoretical Electrophoretic Mobility Values in Several Aqueous NaCl Solutions at 0°C

N_s	$\lambda_{p,\text{theo}}$, Ω^{-1} cm^2 equiv	$U_{p,\text{theo}}$ × 10^4, cm^2 sec^{-1} v^{-1}	U_{NaAlg} × 10^4, cm^2 sec^{-1} v^{-1}	U_{NaPGal} × 10^4, cm^2 sec^{-1} v^{-1}
0.010	19.4	2.01	2.66	2.97
0.025	14.0	1.45	2.08	2.24
0.050	9.9	1.02	1.79	1.90

as the simple salt concentration increases. However, unlike the results obtained for DNA, the calculated A_p values do *not* consistantly underestimate those measured. In light of the promising correlation between the theoretical and experimental values, conductance results for other systems should be analyzed in this manner.

Since the theoretical values of the conductance parameter A_p for DNA at 5°C consistently underestimates the measured values,[45] it would be worthwhile to compare measured and calculated electric transport values obtained at 0°C. Electrophoretic mobilities U_p of NaAlg and NaPGal in aqueous NaCl solutions were determined at 0°C. The U_p values listed in Table IV were determined at infinite dilution of polyelectrolyte by extrapolating the values obtained from the ascending and descending boundaries. At each simple salt concentration the experimental U_p value for NaPGal is greater than that for NaAlg, in accord with their conductances at 25°C. From eq 8 and the relation $U_p = \lambda_p F$, theoretical values for λ_p and U_p were calculated and are listed in Table IV. It is noted from this table that the theoretical values of U_p correctly predict a decrease in U_p with an increase in simple salt concentration, but the theoretical values underestimate the experimental ones. To test Manning's theory adequately, electric transport experiments should be performed not only varying the polyelectrolyte and simple salt concentration, but also varying simple salt valence type and the temperature.

Supplementary Material Available. The conductances of aqueous NaCl solutions of sodium alginate and sodium polygalucturonate at 25°C will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number MACRO-75-789.

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Moments and Transport Coefficients of Wormlike Rings

Motoharu Fujii and Hiromi Yamakawa*

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan. *Received May 26, 1975*

ABSTRACT: The translational friction coefficient and intrinsic viscosity of ring stiff chains without excluded volume are evaluated by an application of the Oseen-Burgers procedure of hydrodynamics to ring wormlike cylinder models. The mean reciprocal distance and mean-square distance between two points on the cylinder axis, and the mean-square radius, which are required for the calculation of the transport coefficients, are evaluated in an approximate fashion. The results are applied to estimation of the molecular parameters of circular DNA.

In previous papers,[1,2] the translational friction coefficient and intrinsic viscosity of linear stiff chains without excluded volume have been evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to linear wormlike cylinder models. The light-scattering form factor of linear wormlike chains without excluded volume has also been evaluated.[3] Methods of determining a shift factor M_L, as defined as the molecular weight per unit length, and the Kuhn statistical segment length λ^{-1} have been proposed there, based on analyses of intrinsic viscosities and sedimentation coefficients and of scattered light intensities. In this paper, we make a similar study of wormlike rings.

Originally, a hydrodynamic-theoretical investigation of flexible or wormlike rings was initiated with biological interest. For example, theories of the sedimentation coefficient and intrinsic viscosity of flexible rings with excluded volume have been developed by Bloomfield and Zimm,[4] Fukatsu and Kurata,[5] and Tanaka and Yamakawa.[6] Evaluation of the sedimentation coefficient of wormlike rings with excluded volume has been carried out by Gray, Bloomfield, and Hearst.[7] In the latter, the mean reciprocal distance between two contour points has been obtained using the Gaussian approximation to the distribution function together with the cubic approximation following Hearst and Stockmayer.[8] This approximation seems to be valid for very long contour length, but not for small contour length. Further, the intrinsic viscosity of wormlike rings has not yet been evaluated. Thus, it is of interest to develop theories of the translational friction coefficient and intrinsic viscosity of ring wormlike chains in the same spirit as in the previous papers,[1] and to apply them to an analysis of circular DNA.

The mean reciprocal distance and mean-square distance between two contour points and the mean-square radius, which cannot be evaluated exactly, are required to evaluate the transport coefficients. Therefore, in section I, the asymptotic forms of the distribution functions of the distance between two contour points are derived from the Daniels[9] and WKB[10] bivariate distribution functions of both the position and the unit tangent vector at the end point for linear wormlike chains, and then the moments are obtained from them with the cubic approximation. The transport coefficients are evaluated in section II, and in section III the results are applied to estimation of the molecular parameters of circular DNA. In the Appendix, we also give the solution for the intrinsic viscosity of rigid rings with and without preaveraging the Oseen tensor. The translational friction coefficient of rigid rings has already been studied by Tchen.[11]

I. Distribution Functions and Moments

Consider two contour points 1 and 2 separated by contour length t of a wormlike ring with total contour length L. We define a conditional distribution function $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ of both the distance $\mathbf{R}$ between the points 1 and 2 and the unit tangent vector $\mathbf{u}$ at the point 2 with the unit tangent vector $\mathbf{u}_0$ at the point 1 fixed. Note that there exists no differential equation satisfied by P such as a Fokker–Planck equation for linear wormlike chains, and therefore that this P is not the Green's function. First we derive the asymptotic forms of P from the Daniels[9] and WKB[10] distribution functions. Then the moments are obtained from them. For convenience, all lengths are measured in units of λ^{-1}.

Distribution Functions. The distribution function $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ may be expressed in the form,

$$P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L) = CG(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)G(\mathbf{R},-\mathbf{u}|-\mathbf{u}_0;L-t) \quad (1)$$

with C [$=G^{-1}(0,\mathbf{u}_0|\mathbf{u}_0;L)$] the normalization constant, where $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ is the conditional distribution function of both the end-to-end distance $\mathbf{R}$ and the final unit tangent vector $\mathbf{u}$ with the initial unit tangent vector $\mathbf{u}_0$ fixed for a linear wormlike chain with contour length t. The asymptotic solutions for $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ have been obtained only in the two limiting cases: (1) $t \gg 1$[9] and (2) $t \ll 1$.[10] We may therefore derive analytical expressions for $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ only in the two cases: (1) $t \gg 1$ and $L - t \gg 1$ and (2) $t \ll 1$ and $L - t \gg 1$.

For $t \gg 1$ and $L - t \gg 1$, we use the first Daniels distribution functions[9,12] for the two G on the right of eq 1, for simplicity. Integrating $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ over $\mathbf{u}$ and $\mathbf{u}_0$, we have the distribution function $P(\mathbf{R};t,L)$ of only $\mathbf{R}$. The result is

$$\begin{aligned}P(\mathbf{R};t,L) = {}&\left[\frac{3L}{2\pi t(L-t)}\right]^{3/2}\left(1-\frac{11}{8L}\right)^{-1}\times\\ &\exp\left[-\frac{3LR^2}{2t(L-t)}\right]\left[1-\frac{5}{8t}-\frac{5}{8(L-t)}+\frac{2R^2}{t^2}+\right.\\ &\left.\frac{2R^2}{(L-t)^2}-\frac{3R^2}{2t(L-t)}-\frac{33R^4}{40t^3}-\frac{33R^4}{40(L-t)^3}+\ldots\right] \quad (2)\end{aligned}$$

where we have retained terms to order t^{-1} and $(L-t)^{-1}$.

Next we consider $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ for $t \ll 1$ and $L - t \gg 1$. In this case, we use the WKB approximation[10] to $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ and the first Daniels approximation[9] to the other G. We choose $\mathbf{u}_0$ in the direction of the z axis of a Cartesian coordinate system, and use polar coordinates $\mathbf{u} = (1,\theta,\phi)$ and Cartesian coordinates $\mathbf{R} = (x,y,z)$. Since $\theta^2 = 0(t)$, we expand $\cos\theta$ and $\sin\theta$ in the first Daniels $G(\mathbf{R},-\mathbf{u}|-\mathbf{u}_0;L-t)$ in powers of θ and retain terms to order θ^2. Then, $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ may be expressed as

$$\begin{aligned}P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L) = {}&C'(L,t)\left(\frac{3}{\pi t^3}\right)\left(\frac{45}{4\pi t^3\theta^2}\right)^{1/2}\times\\ &\exp\left[-\frac{\theta^2}{4t}-\frac{3}{t^3}\left(x-\frac{1}{2}t\theta\cos\phi\right)^2-\right.\\ &\left.\frac{3}{t^3}\left(y-\frac{1}{2}t\theta\sin\phi\right)^2-\frac{45}{4t^3\theta^2}\left(z-t+\frac{1}{6}t\theta^2\right)^2\right]\times\\ &\left[1-\frac{15}{2t\theta^2}\left(z-t+\frac{1}{6}t\theta^2\right)+\ldots\right]\times\\ &\left[1-\frac{11}{8(L-t)}-\frac{2z}{L-t}+\frac{3\theta^2}{8(L-t)}+\ldots\right] \quad (3)\end{aligned}$$

with $C'(L,t)$ the normalization constant. It is impossible to integrate $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ over $\mathbf{u}$ and $\mathbf{u}_0$ to obtain an analytical expression for $P(\mathbf{R};t,L)$. We note that eq 3 gives the same first-order corrections to the rigid ring limiting values of all the moments as to the corresponding rigid rod limiting values,[8,10] and that the distribution function $P(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t,L)$ for $t \gg 1$ and $L - t \ll 1$ may be obtained from eq 3 by exchanging t for $L - t$.

In the following subsections, we evaluate the moments in the two cases: (1) $t \gg 1$ and $L - t \gg 1$ and (2) $t \ll 1$ and $L - t \gg 1$, using the above distribution functions. Then we give expressions for the moments approximately valid for all values of t ($0 \le t \le L/2$).

Mean-Square Distance. We obtain for the mean-square distance $\langle R^2\rangle$ in the two limits from eq 2 and 3

$$\begin{aligned}\langle R^2\rangle &= \frac{t(L-t)}{L}-\frac{1}{2}+\frac{11t(L-t)}{6L^2} \qquad \text{for } t \gg 1 \text{ and } L-t \gg 1\\ &= t^2\left(1-\frac{2}{3}t+\ldots\right) \qquad \text{for } t \ll 1 \text{ and } L-t \gg 1\end{aligned} \quad (4)$$

We join the two $\langle R^2\rangle$ given by eq 4 to complete an approximate expression for $\langle R^2\rangle$ following the procedure of Hearst and Stockmayer.[8] That is

Table I
Values of the Numerical Coefficients σ_k and f_{ijk}

	k			
	0	1	2	3
σ_k	2.18559	-4.67985×10^{-1}	4.91581×10^{-1}	-1.50334×10
f_{10k}	3.33333×10^{-1}	0	0	0
f_{11k}	-4.50040×10^{-2}	-2.75430×10^{-1}	1.19325	-5.59657
f_{12k}	-2.20160×10^{-2}	-8.22244×10^{-2}	4.57470×10^{-1}	2.97966
f_{20k}	1.19083×10^{-1}	5.30304×10^{-1}	9.99369×10^{-1}	-4.99560
f_{21k}	5.18804×10^{-3}	1.40740×10^{-1}	-2.39261	9.30255
f_{22k}	1.58136×10^{-2}	7.54396×10^{-2}	-6.20245×10^{-1}	3.39914
f_{30k}	-2.65957×10^{-2}	-1.49946×10^{-2}	-6.88179×10^{-1}	4.85298
f_{31k}	9.15166×10^{-4}	-5.33328×10^{-2}	1.03760	-4.61578
f_{32k}	-2.97808×10^{-3}	-1.87217×10^{-2}	1.93592×10^{-1}	-9.82380×10^{-1}

$$\langle R^2 \rangle = \frac{t(L-t)}{L} - \frac{1}{2} + \frac{11t(L-t)}{6L^2} \qquad \text{for } \alpha < t \leq L/2$$

$$= t^2\left(1 - \frac{2}{3}t + k_2t^2 + k_3t^3\right) \qquad \text{for } 0 \leq t \leq \alpha \tag{5}$$

where α, k_2, and k_3 are determined as functions of L in such a way that the two $\langle R^2 \rangle$ given by eq 5 have the same values and the same first and second derivatives at $t = \alpha$. The results are omitted because of their length, but we note that α increases to 1.818 as L goes to infinity.

Mean-Square Radius. The mean-square radius $\langle S^2 \rangle$ may be obtained from

$$\langle S^2 \rangle = L^{-2} \int_0^L (L-t)\langle R^2(t) \rangle \,\mathrm{d}t \tag{6}$$

Substitution of eq 5 for $\langle R^2(t) \rangle$ into eq 6 and integration leads to

$$\langle S^2 \rangle = \left(1 + \frac{11}{6L}\right)\left(\frac{L}{12} - \frac{\alpha^2}{2L} + \frac{\alpha^3}{3L^2}\right) - \frac{1}{4} + \frac{\alpha}{2L} + \frac{\alpha^3}{L}\left(\frac{1}{3} - \frac{\alpha}{6} + \frac{k_2}{5}\alpha^2 + \frac{k_3}{6}\alpha^3\right) \tag{7}$$

Mean Reciprocal Distance. The mean reciprocal distance $\langle R^{-1} \rangle$ in the two limits stated above may be derived from the distribution functions given by eq 2 and 3 as follows,

$$\langle R^{-1} \rangle = \left[\frac{6L}{\pi t(L-t)}\right]^{1/2}\left[1 - \frac{L}{40t(L-t)} - \frac{11}{120L}\right] \qquad \text{for } t \gg 1 \text{ and } L - t \gg 1$$

$$= \frac{1}{t}\left(1 + \frac{1}{3}t + \ldots\right) \qquad \text{for } t \ll 1 \text{ and } L - t \gg 1 \tag{8}$$

Note that the second line of eq 8 is the same as the assumption of Gray, et al.[7] We join the two $\langle R^{-1} \rangle$ given by eq 8 as in the case of $\langle R^2 \rangle$. The result is

$$t\langle R^{-1} \rangle = \left[\frac{6tL}{\pi(L-t)}\right]^{1/2}\left[1 - \frac{L}{40t(L-t)} - \frac{11}{120L}\right] \qquad \text{for } \sigma < t \leq L/2$$

$$= 1 + \frac{t}{3} + f_2't^2 + f_3't^3 \qquad \text{for } 0 \leq t \leq \sigma \tag{9}$$

where σ, f_2', and f_3' are determined as functions of L in such a way that the two $t\langle R^{-1} \rangle$ given by eq 9 have the same first and second derivatives at their intersection $t = \sigma$. It is clear that σ must lie between 0 and $L/2$. Then σ increases from the value 1.740, at which $\sigma = L/2$, to the value 2.186 (for linear chains) as L increases from 3.480 to ∞. We note that eq 9 and also eq 5 and 7 are valid in this range of $L \geq 2\sigma$. In what follows, we do not consider the case for smaller L except the rigid ring limit of $L = 0$.

Next we consider the mean reciprocal distance $\langle |\mathbf{R} - \mathbf{a}|^{-1} \rangle$, where $\mathbf{a}$ is the normal radius vector from the contour point 1 to a point on the surface of the ring wormlike cylinder of diameter $d = 2a$. We approximate $\langle |\mathbf{R} - \mathbf{a}|^{-1} \rangle$ by

$$\langle |\mathbf{R} - \mathbf{a}|^{-1} \rangle = \left[\frac{6L}{\pi t(L-t)}\right]^{1/2}\left[1 - \frac{L(1+5d^2)}{40t(L-t)} - \frac{11}{120L}\right] \qquad \text{for } \sigma < t \leq L/2$$

$$= \left(t^2 + \frac{d^2}{4}\right)^{-1/2}[1 + f_1(L,d)t + f_2(L,d)t^2 + f_3(L,d)t^3] \qquad \text{for } 0 \leq t \leq \sigma \tag{10}$$

where f_i are functions of L and d, and σ is assumed to equal that in eq 9. The first line of eq 10 may be derived in the same way as for linear wormlike cylinders.[1a] For later use, it is convenient to express the numerical results for σ and f_i empirically as

$$\sigma = \sum_{k=0}^{3} \sigma_k L^{-k} \tag{11}$$

$$f_i = \sum_{k=0}^{3}\sum_{j=0}^{2} f_{ijk} d^{2j} L^{-k} \tag{12}$$

where σ_k and f_{ijk} are numerical constants given in Table I.

II. Transport Coefficients

A large part of the formulation presented in previous papers[1,2] on linear wormlike cylinders remains valid for the present problem. A minimum sketch is presented which is sufficient to understand the underlying physics and stress the differences between the problems for linear and ring wormlike chains.

Basic Equations. Consider a ring wormlike cylinder of total contour length L and diameter d in the unperturbed velocity field $\mathbf{v}_0$ of solvent with viscosity coefficient η_0. Following the Oseen–Burgers procedure,[1,2] we replace the cylinder by a frictional force distribution $\mathbf{f}(x)$ per unit length along the cylinder axis as a function of the contour distance x ($-L/2 \leq x \leq L/2$) from an arbitrary contour point. Let $\mathbf{a}$ be the normal radius vector from the contour point x to an arbitrary point P which would be just located on the cylinder surface if the cylinder were present, so that

$$\mathbf{a}\cdot\mathbf{u}_0 = 0$$

$$|\mathbf{a}| = a = d/2 \tag{13}$$

with $\mathbf{u}_0$ the unit tangent vector at the point x. Let $\mathbf{R}$ be the distance between the contour points x and y. For an instantaneous configuration, the velocity $\mathbf{v}(P)$ of the solvent at the point P relative to the velocity $\mathbf{U}(P)$ of the cylinder at P may be expressed as[2]

$$\mathbf{v}(P) = \mathbf{v}_0(P) - \mathbf{U}(P) + \int_{-L/2}^{L/2} \mathbf{T}(-\mathbf{R} + \mathbf{a})\cdot\mathbf{f}(y)\mathrm{d}y \tag{14}$$

where $\mathbf{T}$ is the Oseen tensor,

$$\mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0 R}\left(\mathbf{I} + \frac{\mathbf{RR}}{R^2}\right) \tag{15}$$

with $\mathbf{I}$ the unit tensor.

The unperturbed velocity $\mathbf{v}_0$ is assumed to be nonexistent (for friction) or linear in space (for viscosity). Following the Oseen–Burgers procedure, we put $\langle\mathbf{v}(P)\rangle_{\mathbf{a}} = 0$ for all values of x $(-L/2 \leq x \leq L/2)$, where $\langle\ \rangle_{\mathbf{a}}$ designates the average over $\mathbf{a}$, assuming its uniform distribution subject to the conditions given by eq 13. Further, we preaverage the Oseen tensor over chain configurations. Then, an integral equation determining the frictional force $\mathbf{f}(x)$ is derived.

Translational Friction Coefficient. If the integral equation is solved in the Kirkwood–Riseman approximation,[13] we obtain for the translational friction coefficient Ξ

$$\frac{3\pi\eta_0 L}{\Xi} = \int_0^{L/2} K(t)\mathrm{d}t \tag{16}$$

Here, the kernel $K(t)$ is defined by

$$K(t) \equiv \langle|\mathbf{R} - \mathbf{a}|^{-1}\rangle \tag{17}$$

with $t = |x - y|$, where $\langle\ \rangle$ designates the average over $\mathbf{a}$ and configuration, and we have used the property of $K(t) = K(L - t)$ for rings. If we use eq 10 for $K(t)$, we have

$$\begin{aligned}\frac{3\pi\eta_0 L}{\Xi} = \left(\frac{6L}{\pi}\right)^{1/2}\Bigg[\left(1 - \frac{11}{120L}\right)\sin^{-1}\left(\frac{L-2\sigma}{L}\right) - \\ \frac{(L-2\sigma)(1+5d^2)}{20L\sigma^{1/2}(L-\sigma)^{1/2}}\Bigg] + \ln\left[\frac{2\sigma + (4\sigma^2 + d^2)^{1/2}}{d}\right] + \\ f_1\left[\left(\sigma^2 + \frac{d^2}{4}\right)^{1/2} - \frac{d}{2}\right] + \\ \frac{f_2}{2}\left\{\sigma\left(\sigma^2 + \frac{d^2}{4}\right)^{1/2} - \frac{d^2}{4}\ln\left[\frac{2\sigma + (4\sigma^2 + d^2)^{1/2}}{d}\right]\right\} + \\ \frac{f_3}{3}\left(\sigma^2 - \frac{d^2}{2}\right)\left(\sigma^2 + \frac{d^2}{4}\right)^{1/2}\end{aligned} \tag{18}$$

$$\text{for } L \geq 3.480$$

where σ and f_i are given by eq 11 and 12, respectively.

Now we calculate the coil ring limit of Ξ, which is designated by Ξ^*. The coil ring limit of the kernel $K(t)$, which we designate by $K^*(t)$, may be easily obtained by the same procedure as that in the coil limit of linear wormlike chains.[1a] Thus we have

$$K^*(t) = \frac{2}{d}\operatorname{erf}\left[\frac{3d^2L}{8t(L-t)}\right]^{1/2} \tag{19}$$

where erf (x) is an error function defined by

$$\operatorname{erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x \exp(-t^2)\mathrm{d}t \tag{20}$$

Substitution of eq 19 into 16 and integration leads to

$$\begin{aligned}\frac{3\pi\eta_0 L}{\Xi^*} = \left(\frac{3\pi}{2}\right)^{1/2} L^{1/2}\Bigg[1 - \left(\frac{3}{2\pi}\right)^{1/2}\left(\frac{d}{L^{1/2}}\right) + \\ \frac{1}{4}\left(\frac{3}{2\pi}\right)^{1/2}\left(\frac{d}{L^{1/2}}\right)^3 - \frac{3}{40}\left(\frac{3}{2\pi}\right)^{1/2}\left(\frac{\mathrm{d}}{L^{1/2}}\right)^5 + \ldots\Bigg]\end{aligned} \tag{21}$$

We therefore have

$$\lim_{L\to\infty}\Xi^* \equiv \Xi_\infty = (6\pi)^{1/2}\eta_0 L^{1/2} \tag{22}$$

This is identical with the Kirkwood–Riseman value for flexible ring polymers in the nondraining limit obtained by Bloomfield and Zimm[4] and Fukatsu and Kurata.[5] We note that the ratio $\Xi_\infty(\text{linear})/\Xi_\infty(\text{ring}) = 3\pi/8$.

Next, we evaluate the rigid ring limit of Ξ, which we designate by $\Xi^{(0)}$. The rigid ring limit of the kernel $K(t)$, which is designated by $K^{(0)}(t)$, may be expressed in the form,

$$K^{(0)}(t) = \left(\frac{\pi}{L}\right)\left[\sin^2\left(\frac{\pi t}{L}\right) + \left(\frac{\pi d}{2L}\right)^2\right]^{-1/2}\left[1 + 0\left(\frac{d^2}{L^2}\right)\right] \tag{23}$$

where we note that the contribution of neglected terms to $\Xi^{(0)}$ does not exceed 1% for $L/d \geq 20$. After substitution of eq 23 into 16, we have

$$\frac{3\pi\eta_0 L}{\Xi^{(0)}} = \left(\frac{4L^2}{4L^2 + \pi^2 d^2}\right)^{1/2} K\left[\left(\frac{4L^2}{4L^2 + \pi^2 d^2}\right)^{1/2}\right] \tag{24}$$

where $K(k)$ is the complete elliptic integral of the first kind defined by

$$K(k) = \int_0^{\pi/2}(1 - k^2\sin^2\theta)^{-1/2}\mathrm{d}\theta \tag{25}$$

For $L/d \gg 1$, eq 24 may be written as

$$\lim_{L/d\to\infty}\frac{3\pi\eta_0 L}{\Xi^{(0)}} \equiv \frac{3\pi\eta_0 L}{\Xi_0} = \ln\left(\frac{L}{d}\right) + \ln\left(\frac{8}{\pi}\right) \tag{26}$$

This is to be compared with

$$\frac{3\pi\eta_0 L}{\Xi_{0,\mathrm{l}}} = \ln\left(\frac{L}{d}\right) + 2\ln 2 - 1 \tag{27}$$

for the rigid rod in the same limit, where the subscript l refers to linear chains.

Now some comments are required on eq 26 and 27. If the Oseen tensor is not preaveraged, the translational friction coefficient may be expressed as[11]

$$\frac{3\pi\eta_0 L}{\Xi_0} = \frac{9}{10}\ln\left(\frac{L}{d}\right) + \text{constant} \tag{28}$$

for both long rigid rods and long rigid rings. The coefficient of ln (L/d) in eq 28 is not equal to that in eq 26 or 27. In the previous paper,[1a] we have used eq 27 to obtain the sedimentation coefficient for long rigid rods. From the experimental point of view, however, the sedimentation coefficient is not related to Ξ^{-1}, but rather to the translational diffusion coefficient D. We note that the relation $D = kT/\Xi$ does not hold for the exact D and Ξ for these molecules,[14,15] where kT has the usual meaning. For long rigid rods, the exact D is equal to c ln (L/d) with $c = kT/3\pi\eta_0 L$.[11] Fortunately, we may therefore relate eq 27 to the sedimentation coefficient for long rigid rods. On the other hand, the exact D for long rigid rings is equal to $c(11/12)$ ln (L/d).[11,16] Therefore, eq 26 cannot be exactly related to the sedimentation coefficient for long rigid rings.

The values of Ξ_∞/Ξ calculated from eq 18 and 22 as a function of $L^{1/2}/d$ for various values of d for $L/d \geq 10$ are plotted against the logarithm of $L^{1/2}/d$ in Figure 1. The numbers attached to the curves indicate the values of d, and the broken curve represents the coil limiting values calculated from eq 21 and 22.

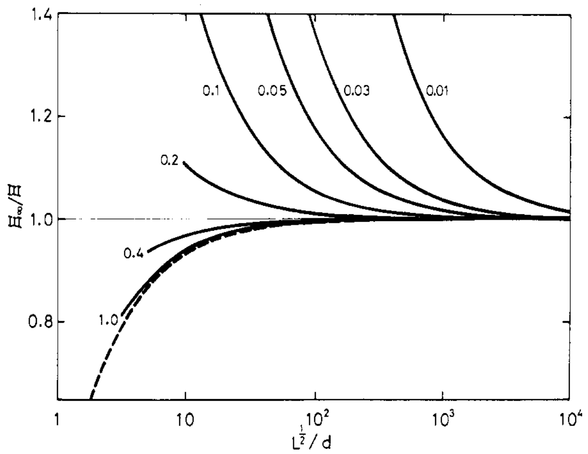

Figure 1. The ratio Ξ_∞/Ξ plotted against the logarithm of $L^{1/2}/d$. The numbers attached to the curves indicate the values of d. The broken curve represents the coil ring limiting values Ξ_∞/Ξ^*.

Table II
Values of $\Phi^* \times 10^{-23}$ as a Function of $L^{1/2}/d$

$L^{1/2}/d$	$\Phi^* \times 10^{-23}$	$L^{1/2}/d$	$\Phi^* \times 10^{-23}$
20	2.350	400	1.8776
40	2.131	1000	1.8661
62	2.020	2000	1.8603
100	1.9579	4000	1.8574
200	1.9031	10000	1.8557

Intrinsic Viscosity. We may evaluate the intrinsic viscosity $[\eta]$ in the same way as in the case of linear wormlike chains. The details are omitted here. The result may be written in the form,

$$[\eta] = \frac{N_A L}{M} \int_{-1}^{1} \psi(x,x)\mathrm{d}x \tag{29}$$

where N_A is the Avogadro number, M is the molecular weight, and ψ satisfies the integral equation

$$\int_{-1}^{1} K(x,\xi)\psi(\xi,y)\mathrm{d}\xi = g(x,y) \tag{30}$$

with

$$g(x,y) = \frac{\pi}{L}\left[\langle S^2\rangle - \frac{1}{2}\left\langle R^2\left(\frac{L}{2}|x-y|\right)\right\rangle\right] \tag{31}$$

where the kernel $K(x,\xi)$ in eq 30 is given by eq 10 and 17 with $2t = L|x - \xi|$, and $\langle S^2\rangle$ and $\langle R^2(t)\rangle$ are given by eq 7 and 5, respectively.

The integral eq 30 cannot be solved analytically. It has been solved numerically by the use of a FACOM 230-75 digital computer at this University. The details are the same as before[1b] except that we have used the procedure of Schlitt[17] which may be considered to be more accurate than that of Ullman.[18] The value thus obtained for the viscosity constant $\Phi = [\eta]M/L^{3/2}$ in the limit $L \to \infty$ agrees with the exact corresponding value of 1.854×10^{23}.[4-6] We note that for linear wormlike chains, the values of $[\eta]$ obtained by the present procedure are very close to those by the previous procedure[1b,18] except near the rigid rod limit; the two results in this limit agree to within 2%.

The present numerical results may be expressed empirically as

$$[\eta] = \frac{\Phi_\infty L^{3/2}}{M} \frac{1}{1 + \sum_{i=1}^{4} c_i L^{-i/2}} \tag{32}$$

$$\text{for } L \geq 3.480$$

with $\Phi_\infty = 1.854 \times 10^{23}$. c_i are functions of d and given by

$$\begin{aligned} c_1 &= 0.809231 - 40.8202d - 483.899d^2 - (2.53944 + 339.266d^2)\ln d \\ c_2 &= -13.7690 + 380.429d + 5197.48d^2 + (0.818816 + 3517.90d^2)\ln d \\ c_3 &= 35.0883 - 1079.70d - 14530.3d^2 - (1.44344 + 9855.73d^2)\ln d \\ c_4 &= -28.6643 + 927.876d + 12010.0d^2 + (0.571812 + 8221.82d^2)\ln d \end{aligned} \tag{33}$$

$$\text{for } 0.001 \leq d \leq 0.1$$

and

$$\begin{aligned} c_1 &= -2.17381 - 11.3578d + 249.523d^2 - 729.371d^3 + 489.172d^4 - (3.58885 - 74.3257d^2 + 335.732d^4)\ln d \\ c_2 &= 112.769 - 851.870d - 21390.1d^2 + 56909.8d^3 - 34787.5d^4 + (41.8243 - 9944.26d^2 + 22067.0d^4)\ln d \\ c_3 &= -1680.23 + 24753.1d + 498848d^2 - 1314310d^3 + 792477d^4 - (526.628 - 244353d^2 + 497280d^4)\ln d \\ c_4 &= 7043.32 - 142907d - 2883470d^2 + 7668650d^3 - 4648720d^4 + (2177.01 - 1407520d^2 + 2937180d^4)\ln d \end{aligned} \tag{34}$$

$$\text{for } 0.1 < d < 1.0$$

The error in the value of $[\eta]$ calculated from eq 32 (compared with the numerical solution) does not exceed 2% for $0.001 \leq d \leq 0.1$ and $L \geq 3.480$, and 1% for $0.1 < d < 1.0$ and $L \geq 90$.

Next we consider the coil ring limit $[\eta]^*$ of the intrinsic viscosity. The kernel in eq 30 is given by eq 19 and the g function on the right of eq 30 is given by

$$g^*(x,y) = \frac{\pi}{8}\left[\frac{2}{3} - 2|x-y|\left(1 - \frac{|x-y|}{2}\right)\right] \tag{35}$$

The solution for $[\eta]^*$ has been obtained numerically. The values of Φ^* corresponding to $[\eta]^*$ as a function of $L^{1/2}/d$ are given in Table II.

The solution for the rigid ring limit $[\eta]^{(0)}$ ($L,d,t \to 0$) has also been obtained numerically by the use of the $K^{(0)}$ given by eq 23 and

$$g^{(0)}(x,y) = \left(\frac{L}{4\pi}\right)\cos \pi|x-y| \tag{36}$$

Further, we define $[\eta]_0$ by

$$\lim_{L/d \to \infty} [\eta]^{(0)} \equiv [\eta]_0 \tag{37}$$

which corresponds to Ξ_0 in the previous subsection. The analytical solution for $[\eta]_0$ may be obtained by a Fourier expansion method, as shown in the Appendix. The result is

$$[\eta]_0 = \frac{N_A L^3}{8\pi M} \frac{1}{\ln(L/d) + \ln(8/\pi) - 2} \tag{38}$$

This is to be compared with the result derived (in the Appendix) without preaveraging the Oseen tensor

$$[\eta]_0 = \frac{N_A L^3}{8\pi M}\left(\frac{17}{15}\right)\frac{1}{\ln(L/d) + \ln(8/\pi) - (144/85)} \tag{39}$$

The values of $[\eta]^{(0)}/[\eta]_0$ with the $[\eta]_0$ given by eq 38 are 0.9977, 0.9997, and 1.000 at L/d = 20, 25, and 50, respectively.

The values of $[\eta]/[\eta]_\infty = \Phi/\Phi_\infty$ are plotted against the logarithm of $L^{1/2}/d$ for various values of d in Figure 2. The numbers attached to the curves indicate the values of d

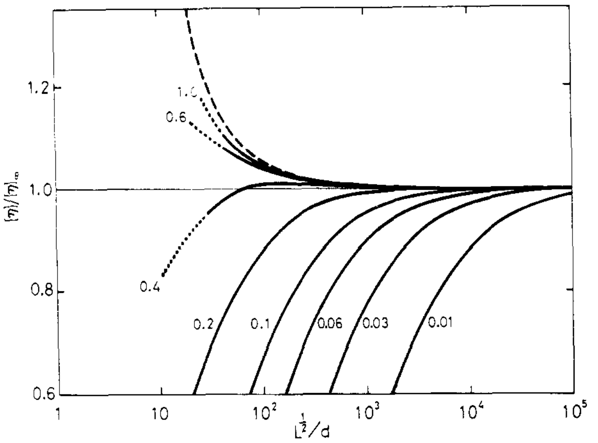

Figure 2. The ratio $[\eta]/[\eta]_\infty = \Phi/\Phi_\infty$ plotted against the logarithm of $L^{1/2}/d$. The numbers attached to the curves indicate the values of d. The broken curve represents the coil ring limiting values $[\eta]^*/[\eta]_\infty$.

and the broken curve represents the values of the ratio $[\eta]^*/[\eta]_\infty$.

III. Application to Circular DNA

In previous papers,[1] we have applied our theories of the sedimentation coefficient s and intrinsic viscosity of linear wormlike chains to estimation of the molecular parameters of linear DNA. We make a similar analysis of circular DNA, using the results obtained in the previous section.

It is known that M_L is 195 daltons/Å for DNA. Therefore, we first attempt to estimate λ^{-1} and d from only the sedimentation coefficient data[19–26] for circular DNA in the same way as before.[1a] The values of λ^{-1} and d thus estimated are 1300 ± 100 Å and 26 ± 3 Å, respectively. Figure 3 shows double-logarithmic plots of s (in Svedbergs) −2.9 against M. The full curve of Figure 3 represents the theoretical values for λ^{-1} = 1300 Å and d = 26 Å. Note that these values of λ^{-1} and d are very close to those obtained previously[1a] for linear DNA. A similar analysis has been made by the use of the equation (without excluded volume) of Gray et al.[7] and the best values are λ^{-1} = 1300 ± 100 Å and d = 18 ± 3 Å. Thus, both theories lead to the same value of λ^{-1}, though the theory (without excluded volume) of Gray et al. gives a smaller value of d than does our theory. A similar situation has been already observed in comparison of the Hearst–Stockmayer theory with our theory for linear wormlike chains.[1a]

Next, we estimate M_L, λ^{-1}, and d, based on an analysis of intrinsic viscosities and sedimentation coefficients, as in the previous paper.[1b] The details are omitted. The values of the molecular parameters thus estimated are M_L = 205 ± 10 daltons/Å, λ^{-1} = 1250 ± 100 Å, and d = 25 ± 4 Å. These values are to be compared with the previous estimates,[1b] M_L = 195 daltons/Å, λ^{-1} = 1130 Å, and d = 25 Å for linear DNA. The agreement is rather good. The plots corresponding to this analysis are shown in Figure 4. In the figure, the data for s are the same as those in Figure 3 and the data for $[\eta]$ are those of Opschoor et al.[21] and Dawson and Harpst.[24] The curves of Figure 4 represent the theoretical values for M_L = 205 daltons/Å, λ^{-1} = 1250 Å, and d = 25 Å.

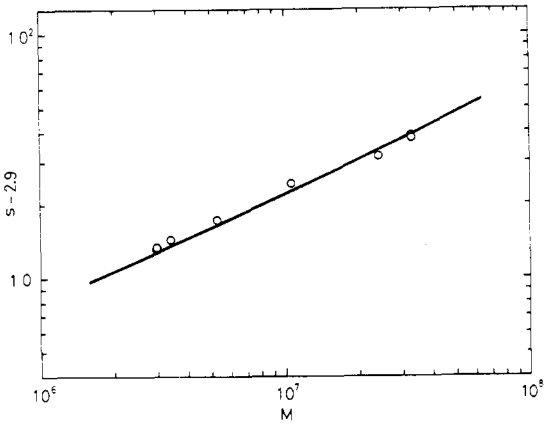

Figure 3. Double-logarithmic plots of s (sedimentation coefficient in Svedbergs) −2.9 against the molecular weight M for circular DNA.[19–26] The curve represents the theoretical values calculated with λ^{-1} = 1300 Å and d = 26 Å.

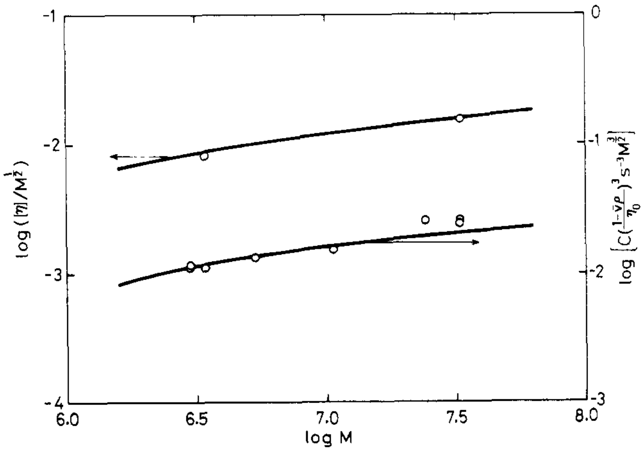

Figure 4. Combination of the data for $[\eta]$ (in dl/g) and s for circular DNA,[19–26] where $C = 1.0374 \times 10^{-13}$, $(1 - \bar{v}\rho)$ is the buoyancy factor, and η_0 is expressed in poises. The curves represent the theoretical values calculated with M_L = 205 daltons/Å, λ^{-1} = 1250 Å, and d = 25 Å.

IV. Discussion

In the present paper, we have improved, to some extent, the evaluation of the mean reciprocal distance by Gray et al. The analysis of the data for DNA shows that this improvement is of little significance in the parameter ranges corresponding to DNA. Our more reasonable estimate of d for DNA seems to result from the adequacy of the cylinder model and the Oseen–Burgers procedure. However, we believe that our transport theory for ring as well as linear wormlike chains is more rigorous and valid also for any other stiff chains. The discussion of the application itself of the Oseen–Burgers procedure to cylinder models need not be repeated.

Appendix

First we derive the solution for $[\eta]_0$ in the very long rigid ring limit, preaveraging the Oseen tensor. We attempt to obtain the solution for the integral eq 30 with $K = K^{(0)}$ and $g = g^{(0)}$ given by eq 23 and 36, respectively. We expand the solution $\psi(\xi,y)$ in a Fourier series,

$$\psi(\xi,y) = \frac{1}{2}a_0(y) + \sum_{n=1}^{\infty} [a_n(y)\cos n\pi\xi + b_n(y)\sin n\pi\xi] \tag{A1}$$

Substituting eq A1 into eq 30 with

$$t = (\pi/2)(x - \xi) \tag{A2}$$

we have

$$\int_{\pi(x-1)/2}^{\pi(x+1)/2} K^{(0)}(t)\left[\frac{1}{2}a_0 + \sum_{n=1}^{\infty}(a_n \cos n\pi x + b_n \sin n\pi x) \times \cos 2nt + \sum_{n=1}^{\infty}(a_n \sin n\pi x - b_n \cos n\pi x)\sin 2nt\right]\mathrm{d}t = \frac{L^2}{8\pi}\cos \pi|x-y| \quad \text{(A3)}$$

It is clear that $a_n = b_n = 0$ for $n \geq 2$, since only $\cos \pi x$ and $\sin \pi x$ are contained on the right of eq A3. Carrying out the integrations in eq A3 and comparing the coefficients of $\cos \pi x$ and $\sin \pi x$ on both sides, we evaluate a_0, a_1, and b_1 in the asymptotic limit $L/d \rightarrow \infty$. Thus we obtain the asymptotic solution for $\psi(\xi,y)$,

$$\psi(\xi,y) = \frac{L^2 \cos \pi(y-\xi)}{16\pi[\ln (L/d) + \ln (8/\pi) - 2]} \quad \text{(A4)}$$

so that $[\eta]_0$ is found to be

$$[\eta]_0 = \frac{N_A L^3}{8\pi M}\,\frac{1}{\ln (L/d) + \ln (8/\pi) - 2} \quad \text{(A5)}$$

Next, we evaluate the same limit of the intrinsic viscosity without preaveraging the Oseen tensor. Suppose that the unperturbed velocity field is $\mathbf{v}_0 = (\kappa y,0,0)$ with κ the constant velocity gradient, and that the molecular center of mass is fixed at the origin of a Cartesian coordinate systm $(\mathbf{e}_x,\mathbf{e}_y,\mathbf{e}_z)$. Then eq 14 becomes

$$\int_{-L/2}^{L/2} \langle \mathbf{T}(-\mathbf{R}+\mathbf{a})\rangle_{\mathbf{a}} \cdot \mathbf{f}(y)\mathrm{d}y = -\frac{1}{2}\kappa(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot \mathbf{S}(x) \quad \text{(A6)}$$

where $\mathbf{S}(x)$ is the distance from the center of mass to the contour point x, S being the radius of the ring. Now $[\eta]_0$ may be expressed as

$$[\eta]_0 = -\frac{N_A}{M\eta_0\kappa}\int_{-L/2}^{L/2}\langle[\mathbf{f}(s)\cdot\mathbf{e}_x][\mathbf{S}(s)\cdot\mathbf{e}_y]\rangle \mathrm{d}s \quad \text{(A7)}$$

where $\langle\ \rangle$ designates the average over all possible orientations. We choose a cylindrical coordinate system $(\mathbf{e}_r,\mathbf{e}_\theta,\mathbf{e}_{z'})$ attached to the rigid ring, where the z' axis passes through the center of the ring perpendicularly to its plane. We then have

$$\langle \mathbf{T}(-\mathbf{R}+\mathbf{a})\rangle_{\mathbf{a}} = \frac{1}{8\eta_0 L\delta^{1/2}}[\mathbf{I} + \langle K_{rr}\rangle\mathbf{e}_r\mathbf{e}_r + \langle K_{r\theta}\rangle \times (\mathbf{e}_r\mathbf{e}_\theta + \mathbf{e}_\theta\mathbf{e}_r) + \langle K_{\theta\theta}\rangle\mathbf{e}_\theta\mathbf{e}_\theta + \langle K_{z'z'}\rangle\mathbf{e}_{z'}\mathbf{e}_{z'}] \quad \text{(A8)}$$

where

$$\begin{aligned}\langle K_{rr}\rangle &= \frac{1}{\delta}\left(\sin^2\gamma + \frac{\pi^2 d^2}{8L^2}\right)\\ \langle K_{r\theta}\rangle &= -\frac{1}{\delta}\sin^3\gamma\cos\gamma\\ \langle K_{\theta\theta}\rangle &= \frac{1}{\delta}(\sin^2\gamma - \sin^4\gamma)\\ \langle K_{z'z'}\rangle &= \frac{1}{\delta}\frac{\pi^2 d^2}{8L^2}\end{aligned} \quad \text{(A9)}$$

with

$$\begin{aligned}\delta &= \sin^2\gamma + \frac{\pi^2 d^2}{4L^2}\\ \gamma &= \pi(y-x)/L\end{aligned} \quad \text{(A10)}$$

Some algebraic manipulation after substitution of eq A8 into eq A6 leads to

$$[\eta]_0 = \frac{N_A L^3}{8\pi M}\left(\frac{1}{15}\right)\int_{-1}^{1}\mathrm{d}x\{-4\psi_{r1}(x)\cos^2\pi x + 10\psi_{r2}(x) \times \sin^2\pi x + [5\psi_{r3}(x) + 2\psi_{\theta 1}(x) + 5\psi_{\theta 2}(x)]\sin 2\pi x + 5\psi_{\theta 3}(x) \times \cos 2\pi x - 2\psi_{z'1}(x)\cos\pi x - 10\psi_{z'2}(x)\sin\pi x\} \quad \text{(A11)}$$

where ψ_{ri}, $\psi_{\theta i}$, and $\psi_{z'j}$ are the solutions for the integral equations,

$$\begin{aligned}\int_{-1}^{1}[K_1(x,y)\psi_{ri}(y) + K_2(x,y)\psi_{\theta i}(y)]\mathrm{d}y &= f_i(x)\\ \int_{-1}^{1}[K_2(x,y)\psi_{ri}(y) + K_3(x,y)\psi_{\theta i}(y)]\mathrm{d}y &= g_i(x)\\ \int_{-1}^{1}K_4(x,y)\psi_{z'j}(y)\mathrm{d}y &= h_j(x)\end{aligned} \quad \text{(A12)}$$

The kernels K_i are given by

$$\begin{aligned}K_1(x,y) &= \delta^{-1/2}(1 + \langle K_{rr}\rangle)\\ K_2(x,y) &= \delta^{-1/2}\langle K_{r\theta}\rangle\\ K_3(x,y) &= \delta^{-1/2}(1 + \langle K_{\theta\theta}\rangle)\\ K_4(x,y) &= \delta^{-1/2}(1 + \langle K_{z'z'}\rangle)\end{aligned} \quad \text{(A13)}$$

and f_i, g_i, and h_j are given by

$$\begin{aligned}f_1(x) &= \frac{2}{\pi}\left(-\cos 2\pi x + \frac{1}{4}\right)\\ f_2(x) &= \frac{2}{\pi}\left(-\cos 2\pi x + \frac{1}{2}\right)\\ f_3(x) = g_1(x) = g_2(x) &= \frac{2}{\pi}\sin 2\pi x\\ g_3(x) &= \frac{2}{\pi}\cos 2\pi x\\ h_1(x) &= -\frac{2}{\pi}\cos\pi x\\ h_2(x) &= -\frac{2}{\pi}\sin\pi x\end{aligned} \quad \text{(A14)}$$

We substitute the Fourier expansions of $\psi_{ri}(y)$, $\psi_{\theta i}(y)$, and $\psi_{z'j}(y)$ into the integral eq A12 to evaluate the Fourier coefficients. Thus the solution for $[\eta]_0$ is found to be

$$[\eta]_0 = \frac{N_A L^3}{8\pi M}\left(\frac{17}{15}\right)\frac{1}{\ln (L/d) + \ln (8/\pi) - (144/85)} \quad \text{(A15)}$$

in the case of the nonaveraged Oseen tensor.

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Upper and Lower Critical Solution Temperatures in Polystyrene Solutions. IV. Role of Configurational Heat Capacity

S. Konno, S. Saeki, N. Kuwahara,* M. Nakata, and M. Kaneko

Department of Polymer Science, Hokkaido University, Sapporo, Japan.
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ABSTRACT: Temperature dependence of the polymer–solvent interaction parameter χ_1 has been estimated by use of the critical χ_1 values $\chi_{1,c}$ and the upper and lower critical solution temperatures in solutions of polystyrene ($M_w \times 10^{-4} = 0.22$–$345$) in methyl acetate, *sec*-butyl acetate, *tert*-butyl acetate, ethyl formate, ethyl *n*-butyrate, diethyl malonate, and *trans*-decalin. The critical solution temperatures are characterized by the T_c^{-1} dependence of $(\chi_{1,c} - 0.5)$ for the ucst and of $-(\chi_{1,c} - 0.5)$ for the lcst in the diethyl malonate and *sec*-butyl acetate solutions, for the ucst in the *trans*-decalin solution and for the lcst in the ethyl *n*-butyrate solution, while the $T_c^{-4/3}$ dependence of $(\chi_{1,c} - 0.5)$ for the ucst and the T_c^{-2} dependence of $-(\chi_{1,c} - 0.5)$ for the lcst in the *tert*-butyl acetate and methyl acetate solutions. Temperature dependence of the $(\chi_{1,c} - 0.5)$ in the polystyrene–ethyl formate system exhibiting the hour glass phase diagram is approximately expressed by a parabolic-like curve with a minimum. Temperature dependence of the polymer chain dimension estimated by the limiting viscosity number in the polystyrene–*tert*-butyl acetate system over the temperature range including the Θ_u (23°C) and Θ_l (84°C) indicates the continuous change with a maximum value at 55°C, which is consistent with the behavior of temperature dependence of the χ_1. An application of the method derived by Eichinger for the evaluation of the heat capacity term in the dilute polymer solution to the polystyrene–*tert*-butyl acetate system leads to a parabolic-like function of temperature with a minimum at 52°C for the reduced excess chemical potential at infinite dilution $-B(T)$ or $\chi_1 - 0.5$. Temperature dependence of the unperturbed mean-square end-to-end distance of polystyrene in *tert*-butyl acetate, which is determined from viscosity measurements at the Θ_u and the Θ_l, is $\mathrm{d} \ln \langle r_0^2 \rangle/\mathrm{d}T \times 10^3 = 0.34 \pm 0.07\ \mathrm{deg}^{-1}$ for $M_w \times 10^{-4} = 345$ and $0.07 \pm 0.07\ \mathrm{deg}^{-1}$ for $M_w \times 10^{-4} = 67$.

Evaluation of the polymer–solvent interaction parameter such as the χ_1 parameter or the second virial coefficient A_2, of the first derivative of χ_1 or A_2 on temperature (the excess partial molar entropy and enthalpy), and of the second derivative of χ_1 or A_2 on temperature (the excess partial molar heat capacity) over a wide range of temperature including the Θ_u and Θ_l, where the Θ_u and Θ_l are respectively the Flory or Θ temperatures for the upper critical solution temperature (ucst) and lower critical solution temperature (lcst), is of great interest to examine the thermodynamic properties of the polymer solution. The contribution to χ_1 originating from differences of the characteristics of pure components such as the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient should be taken into account in addition to the enthalpic contribution of the contact interaction between the polymer segment and solvent molecule. Introduction of "the equation of state of the liquid" in the thermodynamic theory of the polymer solution by Patterson[1–7] and by Flory,[8–12] which is based on the Prigogine theory of corresponding state,[13,14] has led to the semiquantitative prediction of the lcst[15–25] and the other properties such as the excess volume of mixing,[26–28] pressure dependence of the ucst and lcst,[29–31] and concentration dependence of χ.[12,16,26–28,32] The increase of χ_1 with an increase of temperature is characterized by the configurational heat capacity or equation of state term. The division of the χ_1 parameter into the contact interaction term of a decreasing function of temperature and the configurational heat capacity term of an increasing function of temperature is of great importance in understanding of fundamental aspects of the polymer–solvent interaction over the temperature range of Θ_u–Θ_l.[23] Investigation of temperature dependence of the polymer chain dimension in the dilute polymer solution over Θ_u–Θ_l is also of great importance in obtaining useful information on the excluded volume effect in the dilute polymer solution.

In this work we have determined the ucst and lcst in the solutions of polystyrene in *sec*- and *tert*-butyl acetate, methyl acetate, ethyl ester (ethyl formate, ethyl *n*-butyrate), and diethyl malonate and the ucst for the polystyrene–*trans*-decalin system. We also determined the limiting viscosity number in the polystyrene–*tert*-butyl acetate over the temperature range including the Θ_u and Θ_l.

Experimental Section

The polystyrene samples were obtained from the Pressure Chemical Co. The samples are characterized by $M_w/M_n < 1.10$ for $M_w \times 10^{-4} = 0.22$ and 0.4, $M_w/M_n < 1.06$ for $M_w \times 10^{-4} = 1.0$ and 2.04. Characterizations for the other samples of $M_w \times 10^{-4} = 3.7$–270 have been described elsewhere.[21] A sample designated by 14b-1 for measurements of the limiting viscosity number was obtained from the solution fractionation described in detail elsewhere[21] and is characterized by $M_w \times 10^{-4} = 345$, $M_w/M_n < 1.10$. Solvents were reagent grade and were further purified before use. *tert*-Butyl acetate (500 g) refluxed for 2 hr over about 15 g of acetic anhydride was dried over anhydrous potassium carbonate and fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with stainless-steel helices. Ethyl formate was treated with phosphorus pentoxide and *sec*-butyl acetate, ethyl *n*-butyrate, diethyl malonate, and *trans*-decalin were dried over anhydrous potassium carbonate. The dried solvents were fractionally distilled by the same column. Purification of methyl acetate has been described in detail elsewhere.[23]