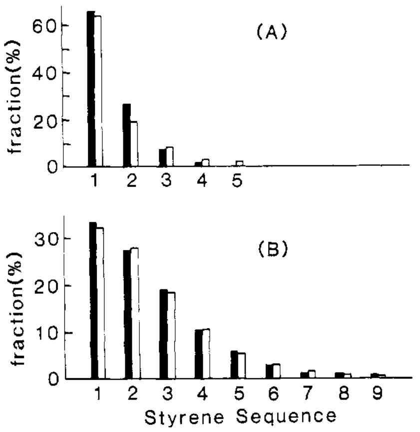
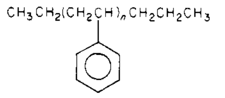


Figure 5. Sequence distribution of styrene units in the copolymer sample at 75.6% conversion (A) and the copolymer initiated with benzoyl peroxide (styrene, 42.6%; 1,2, 11.2%; 1.4, 46.2%) (B).

Table I
Extinction Coefficients for Styrene Oligomers

n	E_{254},[a] (mol/L)/cm)	E/n
1	242	242
2	570	285
3	811	270
4	975	244
5	1391	278
6	1471	245
	av	261

[a] Extinction coefficient at 254 nm for styrene oligomers:



$CH_3CH_2(CH_2CH(C_6H_5))_nCH_2CH_2CH_3$

copolymers initiated with n-butyllithium using the integrated equation of Mayo and Lewis.[6] The values of r_{St} = 0.16 and r_{Bd} = 13 are consistent with those of Spirin et al.[5] showing r_{St} = 0.1 and r_{Bd} = 12.5 for the copolymerization in toluene with ethyllithium. Monomer reactivity ratios of r_{St} = 0.94 and r_{Bd} = 1.2 were determined for the copolymers initiated with benzoyl peroxide using the Fineman–Ross equation. The sequence distribution of the styrene unit calculated from the copolymerization parameters was compared with that determined by the ozonolysis–GPC measurement as shown in Figure 5. Here, both 1,4-(St)$_n$-1,4 and 1,4-1,2-(St)$_n$-1,4 sequences are counted as the (St)$_n$ sequence. The observed sequence distribution for the radical copolymer at low conversion showed fairly good agreement with that calculated from monomer reactivity ratios. On the other hand, a small difference was observed between the observed and calculated distributions for the copolymer initiated with n-butyllithium and terminated at 75.6% conversion. This may be due to the error inherent in the determination of monomer reactivity ratios by the integrated equation; good agreement is obtained by the assumption of r_{Bd} = 13 and r_{St} = 0.18. These facts demonstrate the validity of our ozonolysis–GPC method to characterize the sequence distribution of styrene units in SBR.

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Registry No. Butadiene–styrene copolymer, 9003-55-8.

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Some Remarks on the Transport Theory for Wormlike Cylinder Models

Hiromi Yamakawa

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
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ABSTRACT: It is pointed out that whenever the Yamakawa–Fujii transport theory for wormlike cylinders fails to consistently explain experimental data, the diameter of the cylinder estimated from the intrinsic viscosity is definitely smaller than that from the sedimentation coefficient. Examination of various possible sources of this disagreement leads to the conclusion that the most probable one is the replacement of a rough surface of a real macromolecular chain by the smooth cylinder surface. Then the breakdown of the stick boundary condition that may occur on the rough surface has no significant effect on the result.

Introduction

During the past decade, there have been a number of experimental investigations of steady-state transport coefficients of stiff-chain macromolecules in dilute solution. Most of them have aimed to determine the model parameters by the use of the theoretical expressions that we derived by an application of the Oseen–Burgers (OB) procedure of classical hydrodynamics to wormlike (or helical wormlike) cylinder models.[1-4] On the whole, it appears that there is rather good agreement between theory and experiment, considering the approximations used in the theoretical derivation. However, disagreement beyond experimental uncertainty has been observed for several cases.[5-7] Then, in the language of experimentalists, the diameter of the cylinder estimated from, for instance, the sedimentation coefficient is inconsistent with that from the intrinsic viscosity; the diameter estimated from crystallographic data agrees with the former for some cases and with the latter for others. As a result of reexamination of these results, we have found that the diameter from the

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intrinsic viscosity is definitely smaller than that from the sedimentation coefficient whenever the inconsistency exists, there being no clear trend of disagreement for other model parameters. This makes us recognize a need to reexamine the theory itself.

There seems to be at least four points to be reexamined: (1) the OB procedure itself, (2) the preaveraging of the Oseen hydrodynamic interaction tensor, (3) effects of the roughness of real molecular surfaces, and (4) validity of the stick boundary condition. In the following, these are discussed in order.

Oseen–Burgers Procedure

As has often been claimed, the OB procedure may be expected to give correct results for long enough cylinders. While the exact analytical solution of the linearized Navier–Stokes equation has not been obtained for any cylinder, the exact expressions for the translational and rotatory diffusion coefficients and intrinsic viscosity are well-known for spheroids (ellipsoids of revolution).[8–11] It is therefore worthwhile to compare them with the corresponding OB solutions. Consider a prolate spheroid of major axis L and minor axis d, the former being coincident with its rotation axis. We have already formulated the mean translational diffusion coefficient D_t (or the reduced sedimentation coefficient $\bar{s}$), the rotatory diffusion coefficient $D_{r,1}$ about the minor (transverse) axis, and the intrinsic viscosity $[\eta]$ for this spheroid (generally for spheroid cylinders) following the OB procedure with the nonpreaveraged Oseen tensor.[3] The complete analytical solutions for them are difficult to find, but the asymptotic solutions can easily be obtained for $L/d \equiv p \gg 1$ by a Legendre polynomial expansion method.[2] The results are written as

$$\begin{aligned} \bar{s} &= 3\pi\eta_0 L D_t / k_B T = \ln p + \gamma_s(p) \\ D_{r,1} &= (3k_B T/\pi\eta_0 L^3)[\ln p + \gamma_r(p)] \qquad (1) \\ [\eta] &= (2\pi N_A L^3/45M)[\ln p + \gamma_\eta(p)]^{-1} \end{aligned}$$

with

$$\begin{aligned} \gamma_s(\infty) &= \ln 2 \\ \gamma_r(\infty) &= \ln 2 - \tfrac{1}{2} \qquad \text{(spheroids)} \qquad (2) \\ \gamma_\eta(\infty) &= \ln 2 - \tfrac{3}{4} \end{aligned}$$

where η_0 is the solvent viscosity, k_B the Boltzmann constant, T the absolute temperature, N_A the Avogadro number, and M the molecular weight. Now it can be shown that these asymptotic results agree with those from the corresponding exact hydrodynamic solutions quoted above. This indicates that the OB procedure is certainly valid for $p \gg 1$. However, as p becomes smaller than ca. 50, the difference between the two solutions is appreciable, as has previously been shown numerically.[3]

If we evaluate similarly the transport coefficients above for long straight cylinders of length L and diameter d following the OB procedure with the nonpreaveraged Oseen tensor, we obtain formally the same forms as eq 1 but with

$$\begin{aligned} \gamma_s(\infty) &= 2\ln 2 - 1 \\ \gamma_r(\infty) &= 2\ln 2 - \tfrac{11}{6} \qquad \text{(cylinders)} \qquad (3) \\ \gamma_\eta(\infty) &= 2\ln 2 - \tfrac{25}{12} \end{aligned}$$

Note that the second and third of eq. 3 have been obtained previously[1] and that the first happens to be consistent with the result for $\bar{s}$ derived previously[2] by the OB procedure with the preaveraged Oseen tensor and with the Kirkwood–Riseman approximation[12] to the solution of the OB integral equation. We believe that eq 3 give the hydrodynamically correct asymptotic solutions for cylinders, considering the results above for spheroids. In this connection, we note that $\gamma_s(\infty)$ and $\gamma_r(\infty)$ in eq 3 are somewhat different from those obtained by Tirado and García de la Torre[13,14] for a cylinder as the continuous limit of a stack of rings, each composed of touched beads. The difference may be regarded as arising from the uncertainties associated with the extrapolation and also from the fact that in the continuous limit their linear equation (eq 15 of ref 13) becomes formally the same integral equation as ours (eq 32 of ref 3), but their kernel is the modified Oseen tensor, instead of the Oseen tensor. The kernel should be the Green's function of the linearized Navier–Stokes equation (for a continuous body), i.e., the Oseen tensor.

For spheroid cylinders,[3] we have previously obtained the numerical solutions from the integral equations equivalent to the linearized Navier–Stokes equation (with the stick boundary condition) for small p and constructed interpolation formulas for the transport coefficients on the basis of those and also the OB (numerical) solutions without the preaveraging for large p. From the point of view of classical hydrodynamics, these formulas may therefore be regarded as valid for spheroid cylinders of arbitrary size, apart from the question of whether real rigid rodlike molecules may be or may not be well represented by such bodies. [Recall that our results for $\bar{s}$ and $D_{r,1}$ are appreciably different from those of Broersma[15] at finite p, although our and his $\gamma_s(\infty)$ and $\gamma_r(\infty)$ are in good agreement with each other.] On the other hand, the expressions for $\bar{s}$ and $[\eta]$ for wormlike (or helical wormlike) cylinders have been derived following the OB procedure with the preaveraged Oseen tensor.[2,4] However, it is known that they extrapolate well to spheroid cylinders.[4] Thus they may also be considered good approximations for typical stiff chains near the rod limit in the same sense as above.

Preaveraging Approximation

As the chain flexibility or the length L (for semiflexible chains) is increased, our equations for wormlike (or helical wormlike) cylinders become inaccurate because of the use of the preaveraged Oseen tensor. Recall that they reduce to the corresponding Kirkwood–Riseman equations[12] in the coil limit. This is the most serious defect in our theory. The effects of this preaveraging have already been, to some extent, examined for flexible (Gaussian) chains,[16–20] but the problem has not completely been solved as yet. At present, we can say only that our equations may be expected to be rather accurate near the rod limit, as mentioned above. However, the effects can be, to some extent, examined also for weakly bending rods, and the results will be reported in another paper.[21]

Smooth vs. Rough Surfaces

The surfaces of real macromolecular chains are more or less rough, and thus there arises the question of whether they may be or may not be represented by cylinder models having smooth surfaces, although our hydrodynamic treatments are orthodox, especially for spheroid cylinders. The roughness of surfaces is also closely related to the boundary conditions discussed in the next section. In this section, we carry out model calculations to examine its effects, still assuming the stick boundary condition in a flow of a continuous solvent medium. Then it is convenient and illustrative to compare a spherocylinder of length L and diameter d as a special case of the spheroid cylinder with a linear array of touched spherical beads of total length L, each having diameter d', as depicted in Figure 1.

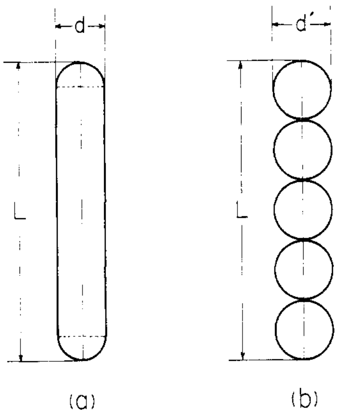

Figure 1. Models for rigid rodlike molecules to examine the effects of surface roughness: (a) spherocylinder and (b) linear array of touched spherical beads.

We may calculate $\bar{s}$, $D_{r,1}$, and $[\eta]$ for the spherocylinder from eq 116, 120, and 127 of ref 3 (with $\epsilon = 1$), respectively. For the bead model, we should also carry out similar calculations by numerically solving hydrodynamic integral equations. However, this is possible only when the number of beads is very small. Therefore, we adopt conveniently the numerical results obtained by Nakajima and Wada[22] for their model I (the same as the present bead model) from conventional calculations with the modified Oseen tensor. We note that although the use of the modified Oseen tensor is not necessarily at the same level of approximation for translation ($\bar{s}$) and rotation ($D_{r,1}$ and $[\eta]$),[23] it is much better than the use of the original Oseen tensor for discrete models. Then, in order to compare the two models, we must introduce a shift factor f_d to relate d' to d:

$$d = f_d d' \tag{4}$$

This factor may be determined in such a way that the values of $\bar{s}$, $D_{r,1}$, or $[\eta]$ for the two models agree with each other, as the case may be.

In Figure 2 are shown the values of the factors $\ln p + \gamma(p)$ in eq 1 as functions of $p = L/d$ for the spherocylinder by the full curves and for the bead model by the points with

$$\begin{aligned} f_d &= 0.891 \quad \text{for } \bar{s} \\ &= 0.741 \quad \text{for } D_{r,1} \\ &= 0.724 \quad \text{for } [\eta] \end{aligned} \tag{5}$$

Here we have not included the values of $[\eta]$ for the bead model for $L/d' \lesssim 10$, since rotation about the rod axis has not been considered—it is in fact impossible for this bead model—despite the fact that its contribution to $[\eta]$ is not negligible for small p. It is then seen that with the above f_d independent of p in the range displayed, there is good agreement between the values for the two models. We have $f_d = 0.826$ for $\bar{s}$ if we use the asymptotic analytical expression for the bead model whether the Oseen tensor is original or modified.[24] Therefore, f_d may depend on p over its wide range.

It is interesting to see that the values of f_d above for different transport coefficients are different. In the case of the spheroid and the corresponding bead model, García de la Torre and Bloomfield[25] have shown that the values of these coefficients for the two models agree with each other except at small p if f_d is commonly determined to make the volumes of the two models equal. (Their f_d also depends on p.) In the present case, if f_d is determined from this equal-volume criterion, it turns out that it decreases monotonically from 1 to 0.816 as p is increased from 1 to ∞. This is not consistent with the results in eq 5.

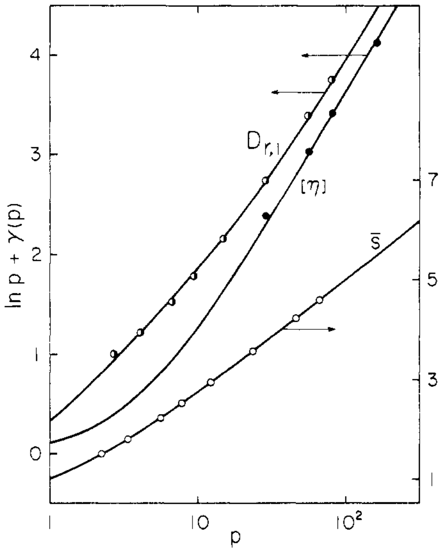

Figure 2. Factors $\ln p + \gamma(p)$ in eq 1 plotted against $p = L/d$. The full curves and the points represent the values for the spherocylinder and the bead model, respectively (see text).

Now we have from eq 4 and 5

$$\begin{aligned} d(\text{from } D_{r,1}) &= 0.832 d(\text{from } \bar{s}) \\ d(\text{from } [\eta]) &= 0.813 d(\text{from } \bar{s}) \end{aligned} \tag{6}$$

The implication is that if our equations for cylinder models are applied to real chains having rough molecular surfaces, the diameter d of the cylinder estimated from $D_{r,1}$ is smaller than that from $\bar{s}$, and the diameter from $[\eta]$ is even smaller. We believe that this prediction regarding the direction of disagreement is correct, although the values above for the numerical coefficients in eq 6 are not necessarily correct for the present bead model and also although they may depend on the shape of the rough surface. It is pertinent to note that our prediction is consistent with, for instance, the results obtained by Itou et al.[7] from $\bar{s}$, $D_{r,1}$, and $[\eta]$ for α-helical polypeptides.

Finally, we note that qualitatively the present conclusion remains unchanged if we adopt the data obtained by Nakajima and Wada[22] for the same bead model with the original Oseen tensor. Then we have $f_d = 0.891$ for $\bar{s}$, 0.861 for $D_{r,1}$, and 0.813 for $[\eta]$ instead of eq 5, and 0.966 and 0.912 for the numerical coefficients in the first and second of eq 6, respectively. Further, we note that the error[25] contained in their formulation of $[\eta]$ has no effect at all on their numerical results for the present bead model.

Stick vs. Slip Boundary Conditions

It is known that the stick boundary condition is valid for a macroscopic body, but the slip boundary condition works better on rough surfaces of real (small) molecules, especially for rotational motions.[26] Indeed, Zwanzig[27] has treated the rotation of a bumpy infinite cylinder about its axis to show how much smaller the rotatory friction coefficient with the slip boundary condition on the rough surface is than that with the stick boundary condition on the averaged smooth surface as the diameter is decreased relative to the scale of surface roughness. For our spheroid cylinder, such effects on $\bar{s}$ and $D_{r,1}$ may be regarded as small, since they are not concerned with the rotation about the longitudinal axis. The contribution of this rotation to $[\eta]$ relative to the rotation about the transverse axis may be roughly estimated to be of order $D_{r,1}/D_{r,3}$, where $D_{r,3}$ is the rotatory diffusion coefficient about the former axis. With the stick boundary condition, this ratio is of $\mathcal{O}$-

(p^{-2}).[1,15,28] Therefore, the former rotation makes a significant contribution to $[\eta]$ for $p \lesssim 10$. (The numerical solutions[3] show that the two contributions are of the same order of magnitude at $p = 2$.) Thus it follows that $[\eta]$ with the slip boundary condition may be appreciably smaller than that with the stick boundary condition only for $p \lesssim 10$, while the effects on it may be regarded as negligibly small for larger p.

Conclusion

We have examined various possible sources of the disagreement between the diameters estimated from different transport coefficients by the use of our equations for them for cylinder models. The most probable source seems to be the replacement of rough surfaces of real macromolecular chains by smooth surfaces; the trend of disagreement may be interpreted by this effect. The possible breakdown of the stick boundary condition on the rough surfaces is immaterial. Then there arises the question: Why is the diameter from crystallographic data close to that from $\bar{s}$ for some cases and to that from $[\eta]$ for others? Probably the answer is that it depends on the degree of solvation. As seen from eq 5, the diameter from crystallographic data may be closer to that from $\bar{s}$ or from $[\eta]$ as the degree of solvation is small or large. Of course, there are not few cases for which the good agreement between the diameters is found. A typical example is a triple helix of *Schizophyllum commune* polysaccharide.[29] The cylinder model is a good approximation to them.

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Chain Dimensions and Interaction Parameters in Neutron Scattering from Polymer Blends with a Labeled Component

Mark Warner

Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, U.K.

Julia S. Higgins* and Andrew J. Carter

Department of Chemical Engineering, Imperial College, London SW7 2BY, U.K.

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ABSTRACT: A short derivation is presented of the scattering laws for a two-component polymer blend in which one component contains some deuterated molecules. It is shown that the scattering can be separated into two terms, one arising from the single-chain contribution of the deuterated molecules and the other arising from concentration fluctuations within the blend. This second term contains the interaction parameter. The application of this scattering law in interpreting results from real systems is discussed and its use demonstrated on data from two low molecular weight polymer blends.

1. Introduction

It has recently become clear[1] that the best way of observing single-chain properties in small-angle neutron scattering from polymer blends is by deuterating a reasonably high fraction (c) of a component, labeled 1, rather than only small fractions and then letting $c \rightarrow 0$ in a Zimm analysis (the usual way[2] of seeing single-chain properties in a dense environment).

Another aspect of investigations of blends is the recognition by de Gennes[3] that the random phase approximation (RPA) can be applied in such dense systems of chains to calculate the response functions and thus the scattering cross sections.

We present here a short derivation of the general scattering law for a two-component blend (with a fraction c of the component 1 deuterated) which has been referred to in a series of papers by Summerfield and Akcasu[1] but not explicitly derived. We use this derivation as a vehicle for discussing what the apparent "single-particle" law actually means. This is all clarified (by a simple extension of the de Gennes results to the case where the monomer volumes v_1 and v_2 of the components are not the same)

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