Macromolecules **1991,** *24,* 193–196

Dynamics of Stiff-Chain Polymers in Isotropic Solution: Zero-Shear Viscosity of Rodlike Polymers

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Received February 6, 1990; Revised Manuscript Received April 30, 1990

ABSTRACT: An expression for zero-shear viscosity, η_0, of isotropic solutions of rodlike macromolecules from dilute through concentrated was derived from a general relation between η_0 and the rotational diffusion coefficient, D_r, for rodlike polymer solution. The necessary expression for D_r valid in the concentration range concerned was obtained by extending the recent Teraoka and Hayakawa's Green function formulation for D_r. Both D_r and η_0 were given as explicit functions of the length, the diameter, and the concentration of the rodlike macromolecule along with two universal constants. The validity of the viscosity expression obtained was demonstrated by comparison with experimental data of η_0 for aqueous solutions of rigid helical polysaccharides.

Introduction

Isotropic solutions of rodlike polymers are often classified into three concentration regimes: dilute, semidilute, and concentrated.[1] The crossover concentrations (the number densities) between the three regimes are given by $1/L^3$ and $1/(L^2d)$, where L and d are the length and the diameter of the rods, respectively. Thus, the semidilute solution is defined as a solution with the number density c' ranging in

$$1/L^3 \ll c' \ll 1/(L^2d)$$

Doi and Edwards[2,3] formulated the zero-shear viscosity, η_0, for semidilute solutions of rodlike polymers, using a tube model

$$\eta_0 = (k_BTL^6/10\beta D_{r0})c'^3 \tag{1}$$

where D_{r0} is the rotational diffusion coefficient at infinite dilution, β is a numerical constant, and k_BT has the usual meaning.

Actually, experimental data[4,5] for η_0 demonstrate that the concentration dependence of η_0 predicted by eq 1 holds only in a narrow concentration range. In the dilute regime, η_0 does not obey eq 1 but the Huggins equation,[6] which contains the first- and second-order terms in concentration, should be valid. This is partly because Doi and Edwards neglected the terms up to c'^2 using the tube model, which is irrelevant to the description of the rodlike polymer dynamics in the dilute regime. On the other hand, in the concentrated regime, experimental results for η_0 of rodlike polymer solutions show a much stronger concentration dependence than the third power predicted by eq 1.

Doi[2,7] modified the tube model theory, reducing the step length for the rotational diffusion by the thickness of the rod. His viscosity equation agreed fairly well with experimental results for a rigid polymer solution from the semidilute to the concentrated range.[2] However, it is not applied to dilute solutions, owing to the limitation of the tube model.

Recently, Teraoka and Hayakawa[8] treated the rotational diffusion process of rodlike polymer systems using a mean-field Green function formulation, which does not use the tube model. Their expression for the rotational diffusion coefficient, D_r, can be applicable to solutions from dilute to semidilute. Since for rodlike polymer solutions η_0 can be generally related to D_r (see eq 13), their D_r can give an equation of η_0, which holds in the corresponding concentration range. However, this viscosity equation does not agree with the experiment in the concentrated regime, because it is identical with eq 1 at high concentration.

In this paper, we first extend the Teraoka–Hayakawa theory for D_r to the concentrated regime, considering that the longitudinal diffusion of rods are hindered by surrounding rods; this hindrance effect is called a jamming effect. This extension needs a formulation of the longitudinal diffusion coefficient, $D_\parallel$, subjected to the jamming effect. We obtained an expression for $D_\parallel$ by the same formulation procedure as that used in the Teraoka–Hayakawa theory. The extended expression of D_r is used to obtain a viscosity equation, which can be applied to isotropic solutions from *dilute* to *concentrated.* Finally, the viscosity equation obtained is tested by experimental data of η_0 for two rigid helical polysaccharides, schizophyllan,[5] and xanthan.[9]

Rotational Diffusion Coefficient

Teraoka–Hayakawa Theory. Teraoka and Hayakawa[8] regarded the rotational diffusion process of a test rod entangled with other rods as the Brownian motion of a point on a spherical surface with the diameter L (L is the length of the test rod), which is perturbed by arc-shaped barriers, i.e., projections of hindering rods onto the spherical surface. At first, they evaluated the first-order perturbation term of the Green function for the test rod and obtained

$$D_r = D_{r0} - \frac{4}{3\sqrt{\pi}}\frac{f_c}{t-t'}\langle b\rangle(\tau D_{r0})^{3/2} \tag{2}$$

where f_c is the number of barriers per unit solid angle appearing in the time interval $t - t'$, $\langle b\rangle$ is the average central angle subtended by the barrier, and τ is the mean lifetime of the barrier. This equation considers only one collision between the test rod and some hindering rod and holds only for a sufficiently dilute solution.

In order to consider a multiple perturbation (i.e., multiple collisions between the test rod and hindering rods), Teraoka and Hayakawa derived a recurrence formula for D_r, which yields

$$\frac{D_r}{D_{r0}} = \left[1 + \frac{2}{3\sqrt{\pi}}\frac{f_c}{t-t'}\langle b\rangle\tau^{3/2}D_{r0}^{1/2}\right]^{-2} \tag{3}$$

This equation is applicable to a wide concentration range.

It should be noted that, in the above formulation of D_r, the free rotational diffusion of the test rod between collisions with barriers at finite concentration is assumed

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to occur just as in dilute solution. In other words, the *intra*molecular hydrodynamic interaction present in dilute solution persists at finite concentration, but the *inter*molecular hydrodynamic interaction (i.e., the hydrodynamic screening effect) is neglected. We adopt this assumption in our theory described below, following the previous authors.[1-3,8,10] The following reasons for this assumption may be in order. First, we quote the effective medium argument of Muthukumar and Edwards,[11] which shows that the hydrodynamic screening effect is much weaker in rodlike polymer solutions than in flexible polymer solutions where the screening effect is known to be remarkable at high concentration.[12] Second, since this effect should decrease with decreasing polymer concentration, it is expected to be marginal at lower concentrations. This may be the case with rodlike polymers where the upper bound of the concentrated isotropic regime is relatively low because of the appearance of a liquid-crystal phase.[13]

The appearance and the disappearance of the barrier on the spherical surface are caused predominantly by the longitudinal diffusion of the hindering rods or the test rod. This is the case, even in dilute solutions, because $D_{\parallel 0}$ is twice as large as $D_{\perp 0}$,[14] where $D_{\parallel 0}$ and $D_{\perp 0}$ are the longitudinal and the transverse diffusion coefficients at infinite dilution, respectively. Therefore, τ can be identified with the time that the rod takes to diffuse longitudinally a distance of the order of L. Teraoka and Hayakawa assumed that the rod diffuses in the longitudinal direction with $D_{\parallel 0}$, namely as in dilute solution, and used the relation

$$\tau \propto L^2/D_{\parallel 0} \tag{4}$$

From this relation, together with the additional two relations $f_c \propto L^3c'(t - t')/\tau$ and $D_{r0} = 6D_{\parallel 0}/L^2$,[14] eq 3 is transformed to

$$D_r/D_{r0} = (1 + \beta^{-1/2}L^3c')^{-2} \tag{5}$$

where β is a numerical constant. This equation agrees with the expression of D_r derived from the tube model theory[2,3] at the high concentration limit.

Modification. Because any rodlike polymer has a finite thickness, the longitudinal diffusion of the rod in concentrated solutions also must be hindered by surrounding rods. This hindrance makes τ longer than that estimated using eq 4. To take this effect into account, we replace $D_{\parallel 0}$ in eq 4 with the longitudinal diffusion coefficient $D_\parallel$ of the rod at a finite concentration; i.e.

$$\tau \propto L^2/D_\parallel \tag{6}$$

This relation yields

$$D_r/D_{r0} = [1 + \beta^{-1/2}L^3c'(D_{\parallel 0}/D_\parallel)^{1/2}]^{-2} \tag{7}$$

To complete the formulation of D_r, we need the expression of $D_\parallel$. Prior to Teraoka and Hayakawa's formulations of D_r, Edwards and Evans[10] applied the mean-field Green function method to formulate $D_\parallel$ for a test rod that diffuses along a one-dimensional path and is hindered by other rods on the test-rod path. Considering only the first-order perturbation, they obtained

$$D_\parallel = D_{\parallel 0} - \frac{8}{3\sqrt{\pi}}\frac{f'_c}{t - t'}(\tau D_{\parallel 0})^{3/2} \tag{8}$$

where f'_c is the number of barriers (hindering rods) per unit length of the test-rod path appearing in time interval $t - t'$ and τ is the mean lifetime of the barrier.

Applying a recurrence formula similar to that used for the derivation from eq 2 to eq 3, we can take into account the multiple perturbation and extend Edwards and Evans' theory (eq 8) to a wide concentration range, with the result

$$\frac{D_\parallel}{D_{\parallel 0}} = \left[1 + \frac{4}{3\sqrt{\pi}}\frac{f'_c}{t - t'}\tau^{3/2}D_{\parallel 0}{}^{1/2}\right]^{-2} \tag{9}$$

From eq 6 and the relation $f'_c \propto Ldc'(t - t')/\tau$ (d is the diameter of the rod), eq 9 can be rewritten as

$$D_\parallel/D_{\parallel 0} = [1 + \alpha^{-1}L^2dc'(D_{\parallel 0}/D_\parallel)^{1/2}]^{-2} \tag{10}$$

or

$$D_\parallel/D_{\parallel 0} = (1 - \alpha^{-1}L^2dc')^2 \tag{11}$$

with a numerical constant α.

Substituting this equation in eq 7, we obtain the final equation

$$\frac{D_r}{D_{r0}} = \left(1 + \beta^{-1/2}\frac{L^3c'}{1 - \alpha^{-1}L^2dc'}\right)^{-2} \tag{12}$$

which is valid for isotropic solutions from dilute to concentrated.

Zero-Shear Viscosity

Doi[15] formulated the Kirkwood general theory[16] for the polymer dynamics in the form of a variational principle. From the application of his formulation to rodlike polymer solutions from dilute through concentrated, a general relation between η_0 and D_r can be derived as[17]

$$\eta_0 = \eta_s + \frac{c'k_BT}{30D_{r0}} + \frac{c'k_BT}{10D_r} \tag{13}$$

where η_s is the solvent viscosity. The second term on the right-hand side comes from the viscous stress, which arises from the energy dissipation by the friction between the rodlike molecule and the solvent. On the other hand, the third term corresponds to the elastic stress, which is produced by the orientational entropy loss of rods. It is noted that this relation is valid for any concentration regimes, if the screening effect of the hydrodynamic interaction can be neglected.

Substituting eq 12 into eq 13, we have

$$\eta_{sp}/c = [\eta]\left[\frac{1}{4} + \frac{3}{4}\left(1 + \frac{B_0c'}{1 - A_0c'}\right)^2\right] \tag{14}$$

with

$$B_0 = \beta^{-1/2}L^3 \tag{15}$$

$$A_0 = \alpha^{-1}L^2d \tag{16}$$

Here, η_{sp} is the specific viscosity $[\equiv(\eta_0 - \eta_s)/\eta_s]$, and c and $[\eta]$ are the mass concentration and the intrinsic viscosity of the polymer, respectively; we have used Kirkwood–Auer's relation[18]

$$[\eta] = (2N_A/15M\eta_s)(k_BT/D_{r0}) \tag{17}$$

where N_A is the Avogadro's number and M is the molecular weight of the polymer.

By modifying the tube model theory, Doi[2,7] derived a viscosity equation that has the same form as eq 14 in the high concentration limit. However, this agreement seems to be rather accidental, because he did not consider the jamming effect on the longitudinal diffusion, and his $(1 - A_0c')^2$ factor was introduced from a different argument.

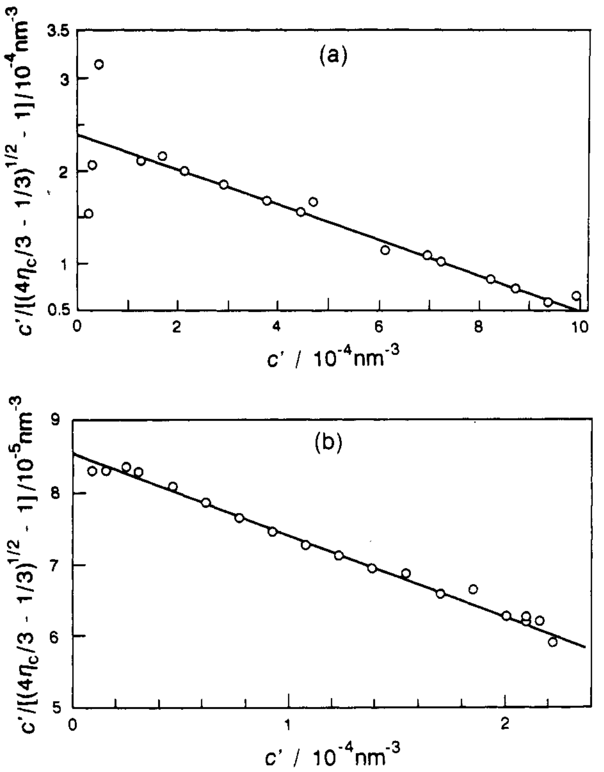

Figure 1. Plots of $c'/[(4\eta_c/3 - 1/3)^{1/2} - 1]$ vs c': (a) aqueous schizophyllan ($M = 1.28 \times 10^5$; $N = 0.15$; $[\eta] = 64$ cm^3 g^{-1}; $c_i' = 1.0 \times 10^{-3}$ nm^{-3} [22]); (b) xanthan in 0.1 M NaCl ($M = 1.85 \times 10^5$; $N = 0.40$; $[\eta] = 127.5$ cm^3 g^{-1}; $c_i' = 2.4 \times 10^{-4}$ nm^{-3} [23]). N = Kuhn's statistical segment number; c_i' = the phase boundary concentration (number density) between the isotropic phase and the isotropic–liquid crystal biphasic regions.

Furthermore, no consistent means are available to extend the tube model into the dilute regime. Matheson[19] added the first- and second-order terms in c' to Doi's equation truncated at the c'^3 term and obtained a viscosity equation similar to eq 14 up to the c'^2 term. However, this is nothing but an interpolation equation between the Huggins equation[6] and Doi's equation without invoking any new theoretical ground.

Test with Experimental Data

Equation 14 can be rewritten in the form

$$c'/\left[\left(\frac{4}{3}\eta_c - \frac{1}{3}\right)^{1/2} - 1\right] = \frac{1}{B_0}(1 - A_0 c') \qquad (18)$$

where η_c is a reduced viscosity defined by

$$\eta_c = (\eta_{sp}/c)/[\eta] \qquad (19)$$

Therefore, our viscosity equation predicts that the plot of the left-hand side in eq 18 against c' should be linear. Figure 1 shows such plots for aqueous solutions of two helical polysaccharides, schizophyllan,[5] and xanthan.[9] Here, to calculate η_c, $[\eta]$ was estimated from the Huggins and Mead–Fuoss[20] plots constructed by dilute-solution data of η_0. Both panels a and b demonstrate the linearity of the plots over a wide concentration range from dilute up to the vicinity of the isotropic–liquid crystal phase boundary. Further, the intercept of each plot gives the Huggins constant, which agrees with that obtained from the corresponding Huggins plot within an error of ±5%.[21] Similar linear plots were obtained for other samples of schizophyllan and xanthan with Kuhn's statistical segment number, N, smaller than 0.6. It should be noted that the Teraoka–Hayakawa theory (eq 5) combined with eq 13 gives the viscosity equation, which is identical with eq 18 with $A_0 = 0$, and it cannot explain the negative slope of the straight line shown in Figure 1.

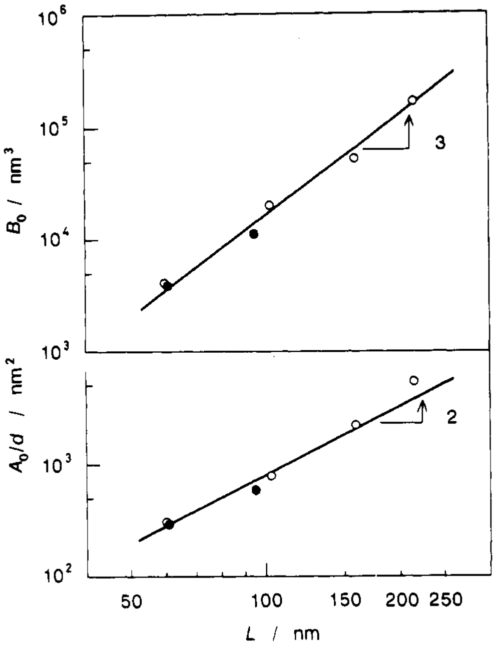

Figure 2. Double-logarithmic plots of B_0 and A_0/d vs L: (○) schizophyllan; (●) xanthan.

Values of B_0 and A_0 for $N < 0.6$ were evaluated from straight lines fitting the data points as shown in Figure 1. Figure 2 shows double-logarithmic plots of B_0 and A_0/d against L,[24] where the values of d used are 2.6 nm for schizophyllan[25] and 2.2 nm for xanthan,[26] which have been determined by hydrodynamic studies on dilute solutions. Irrespective of the polymer species studied, the data points for B_0 and A_0/d follow closely the indicated straight lines. The slopes of the straight lines for B_0 and A_0/d are 3 and 2, respectively, which agree with eqs 15 and 16. The values of β and α were estimated to be $(4.4 \pm 1.0) \times 10^3$ and 13 ± 2, respectively, from the straight lines indicated in Figure 2. Teraoka et al.[27] estimated β to be 1.35×10^3 from a detailed calculation of D_r using a tube model. Our experimental β is the same order but about 3 times as large as Teraoka et al.'s. The fact that the data for both schizophyllan and xanthan are described by a single pair of parameters, β and α, suggests that these values are universal in agreement with our basic assumptions. Viscosity data for samples with N larger than 0.6 did not obey eq 14 or eq 18,[5,9,28] which manifests itself the finite stiffness of the polymers studied. This problem will be pursued in detail in the forthcoming paper.[29]

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Registry No. Schizophyllan, 9050-67-3; xanthan, 11138-66-2.