Rotational diffusion coefficient of rod-like polymer with a slight flexibility in semidilute and concentrated solutions

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summary
        A confined stiff chain model is suggested for the prediction of the rotational diffusion coefficient of a rigid rodlike polymer with a slight flexibility above the region of dilute solution ($c \gg 1/L^3$). It shows a fairly good agreement with the experimental data of various polymers. Among them, PBLG and PBT with more rigidity are more consistent with the model when the log-jamming effect is considered. The predicted rotational diffusivity shows approximately the inverse seventh-power of length, which is less than 9 of Doi-Edwards tube model, but larger than the experimental value 5.7 of M-virus, while it shows the inverse power of concentration is a little larger than the value 2 of tube model except for the rodlike virus M-13.

Introduction
        The major part of polymers are flexible and take random coil structures. But certain polymers are not flexible and have a stiffness of chain and an anisotropic geometrical shape such as rigid rodlike structure. It has been known that they form anisotropic or liquid crystalline phase in a solution when the concentration becomes sufficiently high and simultaneously they orient toward a certain direction. The simplest type is a nematic in which the molecules have some order in a certain direction. According to Onsager (1), the solution of rigid polymers is isotropic below the concentration of $c_i = 4.253/dL^2$, the isotropic phase becomes unstable at the concentration of $c^* = 16/\pi dL^2$ and nematic above $c_n = 5.714/dL^2$. Here L and d are rod length and diameter respectively and c is the number of polymers in the unit volume.
        The main properties describing the dynamics of rodlike polymer are rotational diffusion coefficient (D_r), critical polymer concentration (c^*) at the onset of molecular ordering and orientational order parameter (S),etc. The most important one of these properties is the rotational diffusion coefficient, because the rheological properties such as viscosity have analogy with it. Therefore, we concentrate our efforts on the prediction of the rotational diffusion coefficient in a semidilute or a concentrated solution.
        It is certain that a rotational diffusion coefficient is influenced by various factors such as molecular weight (MW) or contour length (L), molecular weight distribution (MWD), the ratio of rod length to diameter (L/d), polymer concentration (c) and flexibility of main polymer chain, hydrodynamic interaction between polymer and solvent and intermolecular association. So far the flexibility of a polymer chain among those factors has been overlooked in the analysis of polymer dynamics. Hence we consider the effect of the flexibility and other basic factors such as

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molecular weight, L/d ratio and concentration.

In the present work we suggest "a confined stiff chain model" which describes the motion of a polymer chain with diameter d and contour length L trapped in a cylindrical tube of diameter D as shown in Fig.1 . It is assumed that this tube has a constant diameter and length under a given material and changes its position according to the confined chain motion. A new parameter λ , which we call the constraint release length or an effective diffusion length of a slightly flexible chain, is introduced to examine the flexibility effect on the rotational diffusion of a slightly flexible polymer. This effective diffusion length is assumed to be much shorter than the whole contour length L.
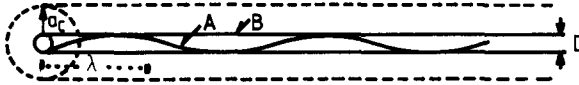

Fig.1. Confined stiff chain model
A : confined chain
B : longitudinal cylindrical tube
λ : constraint release length

Doi-Edwards tube model

Doi and Edwards postulate in a tube model that the test rod is released from its constraints by the diffusion through the whole tube length L (2,3,4) and that rotational diffusion is mainly attributed to the translational motion along the tube axis. They consider that this longitudinal motion is the dominant diffusion process and the diffusion length is little affected by the polymer concentration. The disengagement time for this process can be estimated as the time required for a rod to move a distance L along the axial direction. The final result for the rotational diffusion constant D_r is given by

$$D_r = D_{r0} \, / \, c^2 L^6 \cdot [\frac{4}{\pi} \int f(u;t)f(u';t)\sin(u,u')d^2u d^2u']^{-2} \qquad (1)$$

where D_{r0} is the unconstrained rotational diffusion coefficient (5,6) and written as

$$D_{r0} = \frac{3kT \cdot \ln(L/d)}{\pi \cdot \eta_s L^3} \qquad (2)$$

The confined stiff chain model

Experimental results such as viscoelasticity, the dynamic Kerr effect and dynamic light scattering appear to support the tube model for the motion of rodlike polymer (2,3). But a large discrepancy is reported on the magnitude of the main properties, particularly the rotational diffusion coefficient (7,8,9,10). Polymer chain flexibility is regarded as a crucial factor of this large discrepancy. Therefore, when the rods are no longer completely rigid, the chain flexibility should be taken into account for the motion of a molecular chain and its effect was confirmed by an electron micrograph pictures of M-13 virus (10). The flexibility effect was introduced to explain the motion of a stiff polymer by Odijk (11). Later a quantitative analysis of the flexibility effect was performed by Doi (12) who used Brownian motion governed by reptation only. But more advanced theoretical analysis is needed to improve the dynamic characteristics of rodlike polymer.

It is supposed that a stiff chain of contour length L and diameter d

is trapped in a very long cylindrical tube of diameter D. This diameter is artificial but determined later. We think the diffusion process requires two steps of motion; after a test chain (rod) diffuses out of the tube by the constraint release length of λ, it rotates its direction by an amount of (a_c/L). The radius of a tube a_c called a jump frequency length may be a function of polymer concentration and the distribution of molecular ordering.

First, the estimation of radius a_c is a very important problem to be answered with absolute certainty. Doi estimated its value by calculating of the distance between the test rod and its nearest neighboring rod (2). He gave total number of rods $(N(a_c))$ penetrating the cylindrical rigid tube as

$$N(a_c) = 1/2 \cdot \pi c a_c L^2 \rho_f(f) \tag{3}$$

where $\rho_f(f)$ is the effect of tube dilation by which the average diameter of the tube becomes larger as the polymers orient in the same direction (13):

$$\rho_f(f) = \frac{4}{\pi} \int f(u;t)f(u';t)\sin(u,u')d^2u d^2u' \tag{4}$$

For an isotropic orientational distribution ρ_f becomes unity.

It has been argued that neighboring rods near the center of a test chain have not hindrance effect on the motion of the chain while those at both ends impede the movement of the chain in radial direction. Therefore, all neighboring rods do not contribute equally to the hindrance effect. Hence, we assume that the portion 2λ of contour length L is related to the calculation of effective number of neighboring rods. This number can be written by

$$N_e(a_c) = N(a_c)\frac{2\lambda}{L} = \pi c a_c L \lambda \rho_f(f) \tag{5}$$

The number 2 indicates the effect of both ends. It is also assumed that L is much larger than λ. The length a_c can be estimated from eq.(5) by setting $N_e(a_c)$ unity:

$$a_c = 1/(\pi c \lambda L \rho_f) \tag{6}$$

Next, the constraint release length λ is important for the calculation of rotational diffusivity. Keller et al. (8) supposed that a test chain was released completely when it diffused $\lambda = L/16$ (effective constraint length) along its own length. This effective constraint release length concept is useful, but it is difficult to be justified why the length is L/16. Jain and Cohen (14) made another suggestion that the constraint might be removed by a translation of a rod through only a fraction of its length. Thus they set $\lambda = \varepsilon L$, and obtained $0.15 < \varepsilon < 0.3$ from viscosity data.

In the present work we infer the constraint release length from the chain fluctuation and tube diameter. According to eq.(6) a_c is inversely dependent on concentration and gradually reducing as concentration is increasing. But above the onset concentration of nematic phase (c_n) it hardly changes its value because of tube dilation effect. Because the radius a_c approaches to a fixed value of a_s as a concentration increases we make a_c equal to D/2. In this nematic phase it is supposed that a slightly flexible chain (weakly bending chain) is confined in a tube with a diameter D which orients in a director n, the average direction of the nematic

polymers, i.e. a restriction is imposing a certain degree of orientational order on every chain owing to the nematic ordering. Therefore, λ should be estimated within the tube diameter D. This indicates that λ is affected mainly by the molecular property rather than the concentration, because the entire system is not influenced by a nematic field but inside the cylindrical tube the nematic potential prevent the chain fluctuation and keep the constant constraint release length as if a hypothetical tensile force is necessary to keep from longitudinal shrinkage (19). So λ can be written as:

$$\lambda = 2a_s / < \sin(\cos^{-1}u \cdot n) > = 2a_s / < \sin\theta > \tag{7}$$

where θ is an angle between director vector and polymer chain (11).

To calculate the value of λ we need the angle θ and α. These values can be obtained by using the equilibrium distribution function $f(u)$ determined through minimization of the Helmholtz free energy (1). The calculation procedure can be seen in many literatures (15,16,17,18). Because a nonlinear integral equation appeared in the minimization of the Helmholtz free energy equation with respect to the orientational distribution function, Onsager chose a trial function as

$$f(u) = \frac{\alpha \cosh(\alpha \cos\theta)}{4\pi \sinh\alpha} \tag{8}$$

where the parameter α can be determined at the minimum condition of the Helmholtz free energy. The results at the concentration c_n were given as follows (1).

$$\alpha = 18.64, \quad \cap_f = 0.497$$

In fact λ is a little dependent on concentration but we use a fixed value of λ for the calculation of rotational diffusivity.

rotational diffusion constant

A trapped chain can move freely in a cylindrical tube without meeting any other constraint, but it changes its position by reptational diffusing process. After the chain escapes from the original cylindrical rigid tube and rotates, it is confined again in newly formed tube. Hence the chain changes its direction by an amount of (a_c/L) during the disengagement time (T_λ). The successive releases of constraints with a jump frequency $(1/T_\lambda)$ yield a diffusion of the chain. The parallel component of diffusion (D_t) will be disturbed by the presence of other rods. This disturbance is called a log-jamming effect and depends on the concentration. Edwards and Evans (20) took into consideration of this disturbance in the high concentration ($c \doteq dL^2$). The Edwards and Evans model gives as (20)

$$D_t = D_{t0}(1-b(cdL^2)^{3/2}) \tag{9}$$

where b is a numerical constant. But $b(cdL^2)^{3/2}$ should not exceed a unity even in the high concentration. Because of this reason eq.(9) is modified as follows:

$$D_t = D_{t0}(1 - (c/c^{**})^{3/2}) \tag{10}$$

The disengagement time (T_λ) required for the translational motion of a trapped chain to an extent of λ can be estimated by

$$T_\lambda = \lambda^2 / D_t = \frac{2\lambda^2}{3 [1-(c/c^{**})^{3/2})D_{r0}L^2]} \tag{11}$$
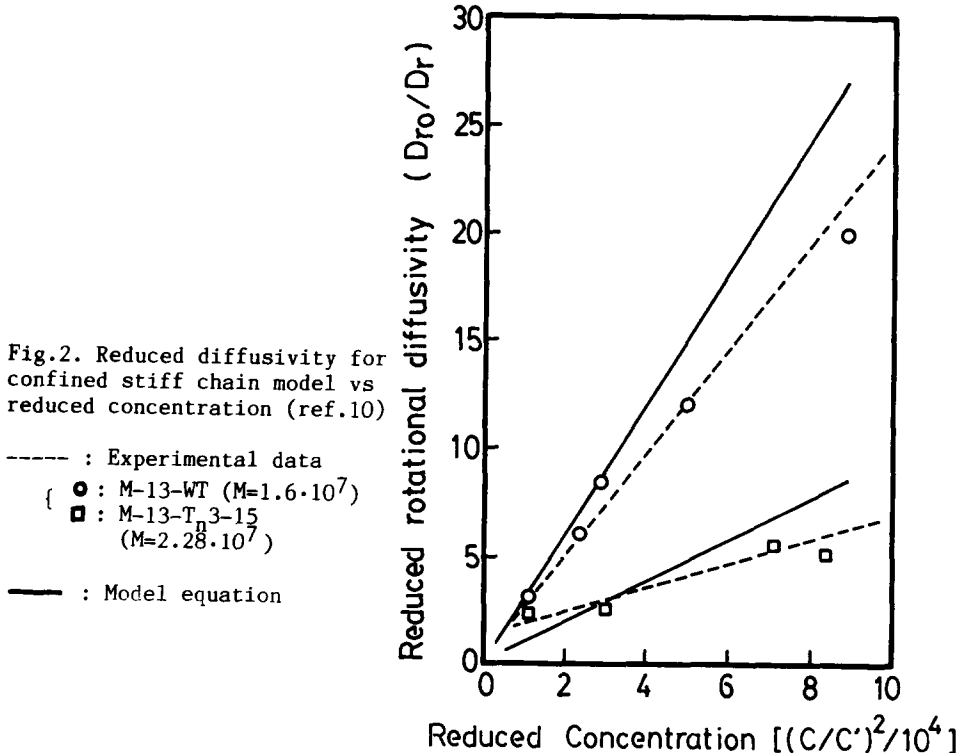
$$D_{t0} = 3/2 \, D_{r0}L^2$$

Thus the rotational diffusion constant D_r can be estimated by a jump frequency and the mean square displacement $(a_c/L)^2$. Therefore, the rotational diffusion constant D_r is given by

$$D_r = (a_c / L)^2 / T_\lambda = \frac{3D_{r0} [1-(c/c^{**})^{3/2}]}{2\pi^2 c^2 \lambda^4 L^2 \rho^2} \tag{12}$$

Comparison with experiments

The diffusion coefficient predicted by the confined stiff chain model is compared with many experimental results observed by a depolarized dynamic light scattering (7), a flow birefringence in a four-roll mill (8) and an electric birefringence decay (10). Another experimental data (14) obtained from the viscosity data are also compared.

Figure 2 shows that the reduced diffusivity, D_{r0}/D_r, versus square of reduced concentration, $(c/c')^2$, for two different M-13 virus particles M-13-WT (L=8920 Å; d=85 Å; molecular weight M=1.6·10⁷) and M-13-T 3-15 (L=15750 Å; d=85 Å; M=2.28·10⁷) in aqueous solution examined by Maguire et al (10). Here, c' is M/NL^3. (M is a molecular weight and N is a Avogadro's number). The data of two M-13 virus are fairly good agreement with the suggested model without consideration of log-jamming effect. It is very successful because we do not use any correction factor. The two slopes of the model equation are more or less

Fig.2. Reduced diffusivity for confined stiff chain model vs reduced concentration (ref.10)

----- : Experimental data
{ ● : M-13-WT (M=1.6·10⁷)
  ■ : M-13-T_n 3-15
      (M=2.28·10⁷)

── : Model equation

Reduced rotational diffusivity (D_{r0}/D_r)

Reduced Concentration $[(C/C')^2/10^4]$

larger than those of the data. This indicates that the inverse power of length (L) dependence of the rotational diffusivity is larger than 5.7 of experimental result. The rotational diffusion coefficient has an inverse fifth-power dependence as shown explicitly in the eq.(12), but because the constraint release length is also connected implicitly with length (L), actually it has an inverse seventh-power dependence which is consistent with the result of Zero and Pecora (7).

Zero and Pecora (7) obtained data of three different length PBLG polymer in dichloroethane by using the depolarized dynamic light scattering technique. For the molecular weights 150000, 170000 and 210000 they calculated the correction factor of 1070, 1170 and 1768 respectively in connection with Doi-Edwards equation i.e., $D_r = \beta\, kT\ln(L/d)/\eta_s\, L^9 c^2$. Figure 3 represents this correction equation and our model equation. The results are good for all data; the more concentration increases the more discrepancy reduces. According to the model equation, D_r reduces to zero at critical concentration (c^*) owing to log-jamming effect. In reality log-jamming effect term is a function of material and solvent, and has a saturated value above a certain concentration (limited to a constant value). This constant value should be determined from the experimental data. In many experimental observations (8,14,19) an inverse power concentration dependence of D_r is a little larger than the Doi-Edwards theoretical value of 2. This phenomena is caused by a log-jamming effect.
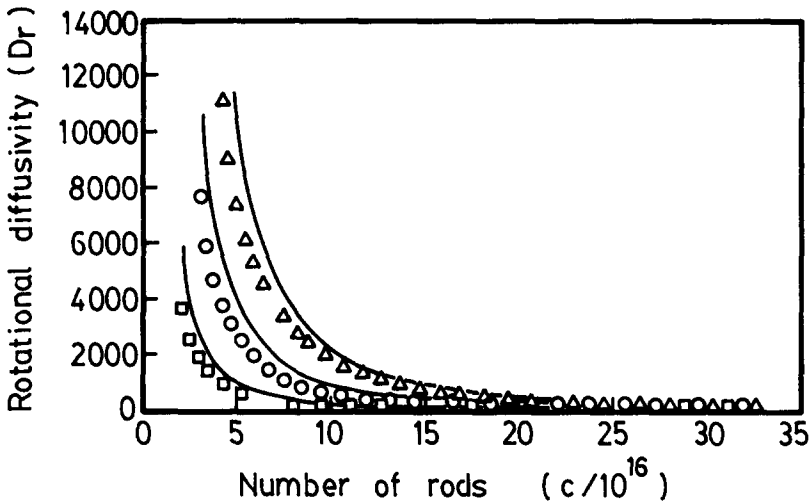

Fig.3. Rotational Diffusion Coefficient for PBLG in dichloethane (ref.7)
Model equation (eq.12) vs. three different molecular weight,
Rotational diffusivity decreases as molecular weight increases.

    : Molecular weight 150,000
    : Molecular weight 170,000
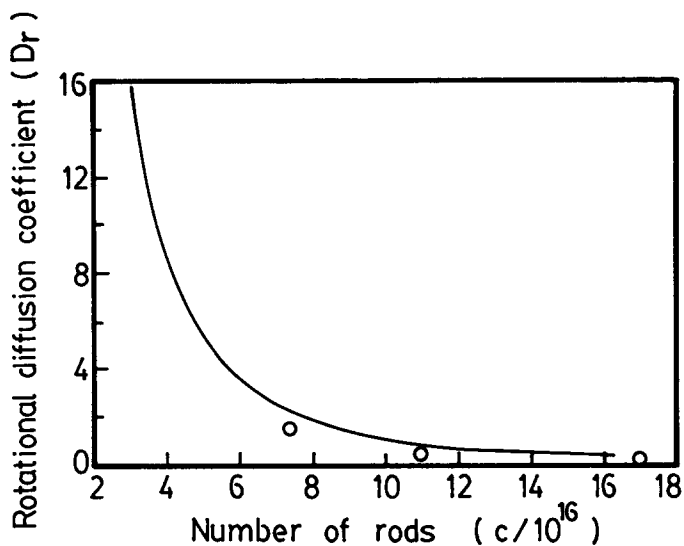   : Molecular weight 210,000
    : Model equation.

Fig.4. Rotational diffusion coefficient for PBLG in
m-cresol ; molecular weight 270,000 (ref.14).

o : Experimental data
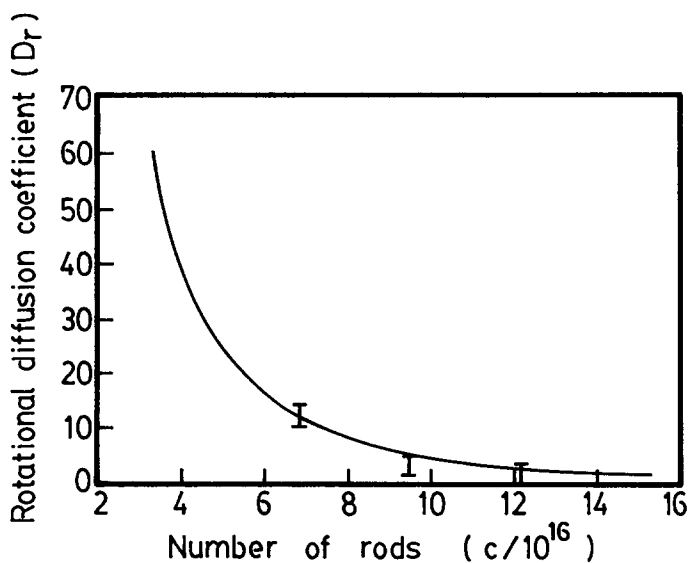— : model equation (eq.12)

Fig.5. Rotational diffusion coefficient for PBT in 97.5%
methanesulfonic acid + 2.5% chlorosulfonic acid ; mole-
cular weight 41,500 (ref.8).

I : experimental data
— : model equation (eq.12)

Figure 4 and 5 represent rotational diffusion coefficient versus concentration for the PBLG in m-cresol (14) and PBT in the solvent 97.5% methanesulfonic acid and 2.5% chlorosulfonic acid (8) respectively. These two polymer systems have fairly good agreement with data when the log-jamming effect is considered. The constant (c^{**}) in the log-jamming effect term in the eq.(10) is different according to the polymer. Because c^{**} is a concentration at which the viscosity has a maximum, its value may be around c^{*}. (for example, $32/\pi dL^{2}$ is for PBLG system (21) and $16/\pi dL^{2}$ for PBT (8) system respectively).

Conclusion

The suggested confined stiff chain model is compared with the various experimental data. According to Doi-Edwards tube model, concentration dependence of D_r is proportional to the inverse square of concentration (c^{-2}), but for some materials this dependence is more or less severe owing to log-jamming effect, and this effect should be considered as the polymer rigidity increases. λ dependent exponent value is -4 and its value is proportional to the square root of contour length ($\lambda \propto \sqrt{dL}$). Therefore, rotational diffusion coefficient has an inverse seventh-power dependence on the rod length. Inspite of this consistent result, we need a more advanced model in consideration of molecular weight distribution and exact critical concentration. As an additional remark, rod diameter is considered for the first time in the calculation of λ ($\lambda \propto \sqrt{dL}$), and the its effect should not be neglected in the advanced analysis of rigid rod motion in the concentrated solution.

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