

농축 용액에서 막대형 고분자의 회전 확산계수

박 오 옥
한국과학기술원 화학공학과
(1986년 6월 13일 접수)

Rotational Diffusivity of Rod-Like Macromolecule in Concentrated Solution

O Ok Park

Dept. of Chem. Eng., Korea Advanced Institute of Science and Technology, Seoul 131, Korea
(Received June 13, 1986)

Abstract : Rotational diffusivity of rod-like macromolecules in concentrated solutions is severely affected by the entanglement of those molecules. The kinetic theory to describe this effect is recaptured to include the side wall effect of the test rod argument of Doi, which turned out to be very important in case of strong extensional flow. The initial relaxation time τ_1 of the Kerr effect depends on the concentration ρ and the molecular weight M such that $\tau_1 \propto \rho M^5$ instead of $\rho^2 M^7$ given by Doi, which is good for the relaxation time for the final stage.

INTRODUCTION

The importance of the entanglement effect on the concentrated polymer solutions has been well studied by Doi et. al. for both flexible¹ and rigid² system. As far as the rigid macromolecule is concerned, the translational motion along the rod axis is almost free and translational motion perpendicular to its axis is almost hindered so that the rotational diffusion governs the whole dynamics of the system. During the consideration of the rotational diffusion in Doi's elegant paper², there was an important factor neglected from the beginning so that it seems to appear some unusual nonexponential relaxation phenomenon predicted in the case of perfectly aligned macromolecules. This kind of perfect alignment can be achieved by either hydro-

dynamically or electrically. Here I am going to reconsider the problem from the beginning to correct this discrepancy for the further researches on the concentration effect of the rigid macromolecule solution under shear and electric field. The coupling effect on the rheological properties of the concentrated rigid polymer solution is under study in this laboratory, now.

The Kinetic Equations

In concentrated regime ($1/L^3 \ll C \ll 1/dL^2$), the kinetic equation describing the Brownian motion of each rod can be given by²

$$\frac{\partial F}{\partial t} = L_r[F] + L_u[F] \quad (1)$$

$$L_r[F] = D_{t0} \left(\underline{u} \cdot \frac{\partial}{\partial \underline{r}} \right)^2 F \quad (2)$$

$$L u(F) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(D_r \sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \varphi} \left(D_r \frac{\partial F}{\partial \varphi} \right) \quad (3)$$

Here \underline{r} denotes the position vector of the center of the mass and \underline{u} stands for the unit vector parallel to the rod axis. D_{t0} is the translational diffusivity of the rod at dilute regime and D_r is the rotational diffusivity of the rod at concentrated regime given above. The distribution function $F(\underline{r}, \underline{u}; t)$ would be normalized as

$$\int d\underline{r} \int d\underline{u} F(\underline{r}, \underline{u}; t) = 1 \quad (4)$$

If we are interested in the orientational distribution function $f(\underline{u}; t)$ defined by

$$f(\underline{u}; t) = \int d\underline{r} F(\underline{r}, \underline{u}; t) \quad (5)$$

then the translational term given by equation (2) can be neglected in the unbounded solution.

According to the test rod argument by Doi the dimensionless rotational diffusivity D_r/D_{r0} is given by

$$D_r/D_{r0} \doteq [a_c/L]^2 \quad (6)$$

Details can be found in reference² and here D_{r0} is the rotational diffusivity in dilute regime and L is the length of the rigid rod macromolecule and a_c is the radius of an imagined cylinder enveloping the test rod such that if we construct $N(a)$ equation for the number of rods crossing that cylinder, then a_c can be obtained from the equation

$$N(a_c) = 1 \quad (7)$$

For convenience, let us define two dimensionless parameters as

$$\epsilon_1 = d/L \quad (8)$$

$$\epsilon_2 = 1/cL^3 \quad (9)$$

$$a^* = a_c/L \quad (10)$$

Here d is the diameter of rigid rod and c is the number density of rod. And in the given concentration regime of Doi, it is clear that

$$\epsilon_1 \ll \epsilon_2 \ll 1 \quad (11)$$

$N(a^*)$ Equation

If we consider the side wall of the previously mentioned cylinder, the following equation for $N(a^*)$ can be easily obtained from the geometrical argument.

$$N(a^*, u; \{f\}) = \frac{2a^*}{\epsilon_2} \int du' f(u'; t) \sin(u u') + \frac{2\pi(a^*)^2}{\epsilon_2} \int du' f(u'; t) \cos(u u') \quad (12)$$

Here $(u u')$ is the angle between \underline{u} and \underline{u}' . The first term of left side of equation (12) is the term considered by Doi and the second one is due to the side wall effect which was neglected previously. Now it is obvious that if the first term is dominant a^* would be $O(\epsilon_2)$ and then D_r/D_{r0} be $O(\epsilon_2^2)$ as given by Doi, because the integrals in equation (12) are all $O(1)$. If the second term is dominant, a^* would be $O(\epsilon_2^{1/2})$, and then D_r/D_{r0} be $O(\epsilon_2)$.

Let us take a few simple examples using variables θ and φ for \underline{u} . First of all at equilibrium, first term in (12) is dominant so that $a^* = (2/\pi) \epsilon_2$ and $D_r/D_{r0} = (4/\pi^2) \epsilon_2^2$ with $f(\theta, \varphi) = 1/4\pi$. Next for a strong shear flow $f(\theta, \varphi)$ can be assumed by $\frac{1}{2\pi} \delta(\theta)$ and then D_r/D_{r0} does not depend on the orientation of the test rod so that

$$N(a^*) = \frac{4a^*}{\pi \epsilon_2} + \frac{2(a^*)^2}{\epsilon_2} = 1 \quad (13)$$

If the first term is dominant, a^* is of $O(\epsilon_2)$ and then the second term becomes $O(\epsilon_2)$ so that it can be neglected for the first approximation.

$$a^* = \frac{\pi \epsilon_2}{4} [1 + O(\epsilon_2)] \quad (14)$$

$$\frac{D_r}{D_{r0}} = \left(\frac{\pi \epsilon_2}{4} \right)^2 [1 + O(\epsilon_2)] \quad (15)$$

Finally, let us consider the strong extensional flow considered by M. Doi when he dealt with the relaxation of the Kerr effect. In this case, it is obvious that $f(\theta, \varphi)$ can be assumed $\delta(\theta)\delta(\varphi)$ for the extreme situation. Then the first term in (12) becomes zero so that from the second term a^* would be $[\epsilon_2/2\pi]^{1/2}$. Now it is clear that the entanglement effect on the rotational diffusivity of the rigid rod is less severe in the case of extensional flow than shear flow. The consequence of this fact shall be discussed in for the relaxation of the Kerr effect in the next section.

Relaxation of the Kerr Effect

As the simplest application of the theory, Doi considered the relaxation of the Kerr effect and I am going to just reconsider it. As a static electric field is applied to the solution of rod-like macromolecules, the rods will be aligned in the direction of external field due to the permanent dipole or anisotropy of the polarizability of the macromolecules. Then the electric field is off at $t=0$, the orientation of the rods will be relaxed to the equilibrium state. This relaxation is detected by the birefringence, which is proportional to

$$K(t) = \langle P_2(\cos \theta) \rangle \doteq \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (17)$$

where P_2 is a Legendre polynomial. As mentioned by M. Doi, the relaxation time for the dilute system would be $(1/6D_r)$, but the case of the concentrated system is different because the diffusivity depends on the orientational distribution of rods. At the final stage close to equilibrium, the relaxation time would be related to the rotational diffusivity of the concentrated system given before so that

$$K(t) = \exp(-6D_r t) \quad (18)$$

and the relaxation time would be $\tau_F = 1/(6D_r)$ and proportional to $c^2 L^3$ or $\rho^2 M^3$ where ρ is the density of the polymer solution and M is the molecular weight. Consider the case of the early stage close to the perfect alignment. The

kinetic equation can be simplified into

$$\frac{\partial f}{\partial t} = \frac{1}{\theta} \frac{\partial}{\partial \theta} \left(D_r \theta^2 \frac{\partial f}{\partial \theta} \right) \quad (19)$$

and if we assume $f(\theta; t)$ has a gaussian form, then $f(\theta; t)$ can be obtained by the self-consistency analysis of M. Doi,

$$f(\theta; t) = \frac{1}{2\pi g(t)} \exp\left[-\frac{\theta^2}{2g(t)}\right] \quad (20)$$

The equation for $g(t)$ is

$$\begin{aligned} \frac{dg}{dt} &= -2\pi \int_0^\infty d\theta \left(D_r \theta^2 \frac{\partial f}{\partial \theta} \right) \\ &= D_r \int_0^\infty d\theta \left[\frac{\theta^3}{g^2} \exp\left(-\frac{\theta^2}{2g}\right) \right] \end{aligned} \quad (21)$$

Then

$$\frac{dg}{dt} = 2D_r = \frac{\epsilon_2}{\pi} D_{r0} \quad (22)$$

And if we use the result of the previous section for the diffusivity, the last equality in (22) holds so that

$$g(t) = \frac{\epsilon_2}{\pi} D_{r0} t + g(0) \quad (23)$$

and

$$\frac{K(t)}{K(t=0)} = \exp\left[-\frac{3\epsilon_2 D_{r0} t}{2\pi}\right] \quad (24)$$

Therefore the relaxation time for the early stage is

$$\tau_1 = \frac{2\pi}{3D_{r0}\epsilon_2} \propto cL^6 \propto \rho M^3 \quad (25)$$

CONCLUSION

It is clear now that there is still exponential decay from the beginning but much faster than the final stage relaxation. The molecular weight dependence of the relaxation time would be useful to be checked by the future experimental work for the validity of the theory. In fact, experimental works are under consideration in this laboratory. And it is also interesting to see the

response of the concentrated rod-like macromolecule solution in the electrohydrodynamic field, because the restricted rotational diffusivity affects both electric and hydrodynamic responses.

ACKNOWLEDGEMENTS

Author is indebted to Dr. G.G.Fuller at Stanford University for the idea. Partial support

from KOSEF is also gratefully acknowledged.

REFERENCES

1. M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. II*, **74**, 1789(1978).
2. M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. II*, **74**, 560(1978).