*Theory on the Small Angle Scattering of Light to Determine the Shape, Size and Orientation of High Polymer Molecules in Flow**

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As for the small angle scattering of light by high polymer moleculces in a solution at rest, the Zimm plot, that is a double extrapolation method devised by Zimm[1], has been used widely. On the other hand, a theory regarding the deformation of high polymer molecules in flow and on the light scattering by the deformed molecules has been developed by Peterlin, Heller and Nakagaki[2]. On the basis of this theory, it will be shown in the present paper that the Zimm plot can be used for the quantitative determination of the shape, size and orientation of high polymer molecules in flow, and that the photographic pattern of the small angle scattering can be used to determine the orientation of the molecules in flow.

Initial Slope of the Zimm Plot

The equation of light scattering derived by Debye[3] on the basis of fluctuation theory, and generalized by Zimm[4] is,

$$Kc/R_u(\vec{s}) = 1/MP(\vec{s}) + 2A_2c \tag{1}$$

where K is a constant, $R_u(\vec{s})$ is reduced scattering intensity, $P(\vec{s})$ is interference factor, and c, M and A_2 are concentration, molecular weight and the second virial coefficient of the polymer. The constant K is given by

$$K = (2\pi^2\mu_1{}^2/N_0\lambda_0{}^4)(\mathrm{d}\mu_{12}/\mathrm{d}c)^2 \tag{2}$$

where μ_1 is the refractive index of solvent, N_0 is the Avogadro number, λ_0 is wavelength of light in vacuo and μ_{12} is refractive index of solution. The reduced scattering intensity $R_u(\vec{s})$ is

$$R_u(\vec{s}) = (I_u(\vec{s})/I_0)/(1+\cos^2\theta) \tag{3}$$

where I_0 is the intensity of the unpolarized incident light, $I_u(s)$ is the intensity of light scattered in the direction designated by $\vec{s}$, and θ is the scattering angle. The scattering vector $\vec{s}$ is given by

$$\vec{s} = \vec{s'} - \vec{s_0} \tag{4}$$

where $\vec{s_0}$ and $\vec{s'}$ are unit vectors in the direction of the incident beam and scattered beam, respectively; and its absolute value, s, is

$$s = |\vec{s}| = 2\sin(\theta/2) \tag{5}$$

Here the scattering angle θ is the angle between $\vec{s_0}$ and $\vec{s'}$.

In the so called Zimm plot, (Kc/R_u) is taken as ordinate and $\sin^2(\theta/2)+kc$ is taken as abscissa, where k is a constant chosen arbitrarily. Therefore, the curve on the Zimm plot for the values extraporated to infinitely dilute concentration gives

$$[Kc/R_u(\vec{s})]_0 = 1/MP(\vec{s}) \tag{6}$$

as a function of σ defined by

$$\sigma = \sin^2(\theta/2) \tag{6a}$$

On the other hand, the theoretical expression for the interference factor of streaming polymer molecules derived by Peterlin, Heller and Nakagaki[2] is,

$$P(\vec{s}) = 2\int_0^1 (1-u)\exp[-X(u+\zeta u^2)]\,\mathrm{d}u \tag{7}$$

where

$$X = (8\pi^2/3\lambda^2)R^2\sin^2(\theta/2)\cdot\xi \tag{8}$$

and

$$\zeta = (2/3)\beta^2 \tag{9}$$

Here λ is the wavelength of light in the medium, R is the root-mean-square of the end-to-end distance of the polymer molecule at rest, and

$$\xi = \{1 + [\beta^2 + \beta(1+\beta^2)^{1/2}\cos 2\phi] \times\cos^2(\theta/2)\}/(1+2\beta^2/3) \tag{10}$$

Here β is a quantity proportional to the velocity gradient q defined by

$$\beta = (\pi a/6kT)\eta ZR^2q = (M/N_0kT)[\eta]\eta q \tag{11}$$

where a is the hydrodynamic radius of segments, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity, Z is the number of segments in a molecule, M is the molecular weight and $[\eta]$ is the intrinsic viscosity. The angle ϕ is concerned with the direction of observation as defined in Ref. 2 and will be described later (See Fig. 2).

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[1] B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[2] A. Peterlin, W. Heller and M. Nakagaki, ibid., **28**, 470 (1958).

[3] P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).

[4] B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).

The value of $[Kc/R_u(0)]_0$, that is the height of the ordinate at which the Zimm plot for infinite dilution intersects and the value of the initial slope of this Zimm plot are obtained by expanding $[Kc/R_u(\vec{s})]_0$ of Eq. 6 as a power series of σ of Eq. 6a. These values are:

$$[Kc/R_u(0)]_0 = 1/M \tag{12}$$

and

$$\begin{aligned}(\text{Initial slope}) &= [Kc/R_u(0)]_0 \times (8\pi^2 R^2/9\lambda^2) \\ &\times [1+\beta^2+\beta(1+\beta^2)^{1/2}\cos 2\phi] \\ &\times (1+\beta^2/3)/(1+2\beta^2/3)\end{aligned} \tag{13}$$

If a parameter g defined by

$$g = (9\lambda^2/8\pi^2)\ (\text{Initial slope})/[Kc/R_u(0)]_0 \tag{14}$$

is used, the value is

$$\begin{aligned}g = R^2 &[1+\beta^2+\beta(1+\beta^2)^{1/2}\cos 2\phi] \\ &\times (1+\beta^2/3)/(1+2\beta^2/3)\end{aligned} \tag{15}$$

Thus, the value of the ordinate at which the Zimm plot intersects is constant irrespective of whether the solution is streaming or not. From this value, the molecular weight may be determined on the basis of Eq. 12. On the other hand, the value of g depends on the velocity gradient or β. The value of g in the case of the solution at rest, designated by g_0, is obtained from Eq. 15 with $\beta=0$. The value is

$$g_0 = R^2 \tag{16}$$

Therefore, it is equal to the mean square end-to-end distance. The value of g for streaming solution depends on the direction of observation or ϕ as well as the velocity gradient or β.

At first, the observation plane is fixed and the variation of g with velocity gradient (or β) is considered. Since the angle ϕ is also a function of β, angle ω is used instead (see Fig. 2). The angle ω is the angle between the direction of flow and the plane of observation, and is related to ϕ by the equation:

$$\omega = \phi + 90° - \chi \tag{17}$$

where χ is the extinction angle varying with β according to

$$\beta = -\cot 2\chi \tag{18}$$

Then, Eq. 15 is rewritten to

$$\begin{aligned}g/g_0 = &(1+\beta^2+\beta\sin 2\omega+\beta^2\cos 2\omega) \\ &\times (1+\beta^2/3)/(1+2\beta^2/3)\end{aligned} \tag{19}$$

The variation of g/g_0 due to β for several values of ω are shown in Fig. 1 with solid curves. Then, at a constant value of β, the maximum and minimum value of g/g_0 are calculated. The results are:

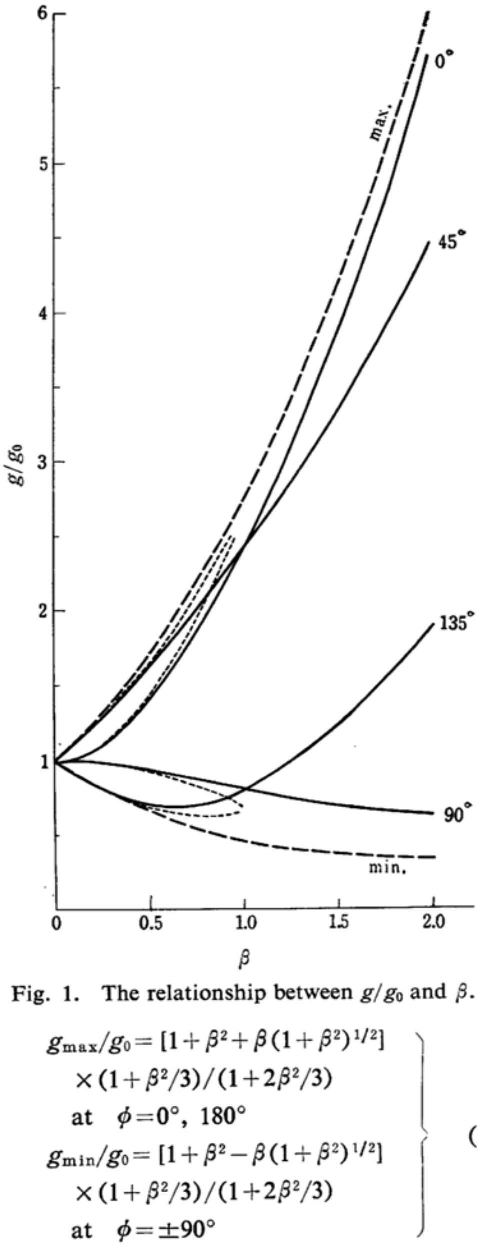

Fig. 1. The relationship between g/g_0 and β.

$$\left.\begin{aligned} g_{\max}/g_0 &= [1+\beta^2+\beta(1+\beta^2)^{1/2}] \\ &\times (1+\beta^2/3)/(1+2\beta^2/3) \\ &\text{at}\quad \phi = 0°,\ 180° \\ g_{\min}/g_0 &= [1+\beta^2-\beta(1+\beta^2)^{1/2}] \\ &\times (1+\beta^2/3)/(1+2\beta^2/3) \\ &\text{at}\quad \phi = \pm 90° \end{aligned}\right\} \tag{20}$$

These values are shown in Fig. 1 with broken lines.

It may be instructive to estimate here the order of magnitude of β. If $[\eta]=100$, $\eta=1$ c.p.s., $M=3\times10^5$ and $q=1\times10^4\ \text{sec}^{-1}$, the value of β calculated by Eq. 11 is 0.12. Therefore, the usual value of β seems to be smaller than unity. If $\beta \ll 1$, Eq. 19 is reduced to

$$g/g_0 \fallingdotseq 1+\beta\sin 2\omega+\beta^2(2/3+\cos 2\omega) \tag{21}$$

The error committed by this approximate equation is less than 5% as far as $\beta \lesssim 0.7$. The values calculated by this equation are shown in Fig. 1 with dotted curves.

As already mentioned, the quantity β is proportional to the velocity gradient q. When a concentric cylinder apparatus is used, β is, therefore, proportional to the rate of rotation $\Omega(\mathrm{sec}^{-1})$, that is

$$\beta = k_1 q = k_2 \Omega \tag{22}$$

with

$$k_2 = k_1(2\pi\rho/d) \tag{23}$$

where ρ is the radius of the rotating cylinder, d is the width of the gap of the concentric cylinder, and the value of k_1 is readily obtained from Eq. 11. Thus, there are three methods to determine the value of k_2 (or k_1). The first is to calculate the value of k_1 by Eq. 11. The second is to measure the extinction angle χ by a streaming double refraction measurement in order to obtain the value of β on the basis of Eq. 18. The values of β for various values of q or Ω will give the value of k_1 or k_2 by Eq. 22. The third and the most direct method for the present experiment is to use the equation derived from Eq. 21, that is:

$$(g/g_0 - 1)/\Omega = A + B\Omega \tag{24}$$

where

$$\left.\begin{aligned} A &= k_2 \sin 2\omega \\ B &= k_2{}^2(2/3 + \cos 2\omega) \end{aligned}\right\} \tag{25}$$

From the value of A or B determined experimentally, the value of k_2 will be obtained.

A Method for Measurement of the Semi-Major and Minor Axes of Flexible High Polymer Molecules

The extension of high polymer molecules in solution is expressed by the probability distribution of end-to-end distance, that is the probability ψ per unit volume to find one end of the high polymer molecule in a volume element when the other end is fixed at the origin. In the case of freely flexible high polymer molecules, it is well known that the function ψ is Gaussian:

$$\left.\begin{aligned} \psi &= (\mu/\pi)^{3/2} \exp(-\mu r^2) \\ \mu &= 3/2R^2 \end{aligned}\right\} \tag{26}$$

where r is the distance to the volume element from the origin and R is the root mean square end-to-end distance. On the other hand, it is often assumed that the distribution of segments around the center of gravity of the molecule is also Gaussian. The probability W to find a segment in a unit volume of a volume element is then:

$$\left.\begin{aligned} W &= Z(\mu^*/\pi)^{3/2} \exp(-\mu^* r^2) \\ \mu^* &= 6\,\mu \end{aligned}\right\} \tag{27}$$

where Z is the number of segments in one molecule, and r in this case is the distance between the volume element and the center of gravity. The relation between μ^* and μ shown in Eq. 27 is based on the fact established by Debye[5] that the root mean square distance S of a segment from the center of gravity of the molecule is

$$S = R/\sqrt{6} \tag{28}$$

On the other hand, Debye and Bueche[6] concluded from the study of intrinsic viscosity that the radius R_s of a high polymer molecule considered as a sphere should be

$$R_s = \sqrt{5/18}\,R \tag{29}$$

Now, by assuming that the distribution of segments is homogeneous in a sphere of radius R_s the root mean square distance of a segment from the center of gravity of the molecule is readily calculated and the result is

$$S = \sqrt{3/5}\,R_s \tag{30}$$

This result together with Eq. 29 yields a relation exactly the same as that of Eq. 28, the latter being obtained originally on the basis of the Gaussian distribution formulated in Eq. 27.

On the basis of these facts, one may say that the shape of a high polymer molecule in a solution at rest is a sphere with the radius of R_s. Then the value of W at the surface of the sphere (W_s) relative to the value of W at the center of gravity of the molecule (W_0) is,

$$W_s/W_0 = \exp(-5/2) = 0.082 \tag{31}$$

Therefore, to assume a high polymer molecule as a sphere of radius R_s corresponds to the assumption that the surface of the molecule is defined by the points at which $W_s/W_0 = 0.082$ in the Gaussian distribution.

Now, considering high polymer molecules in a streaming solution, Peterlin, Heller and

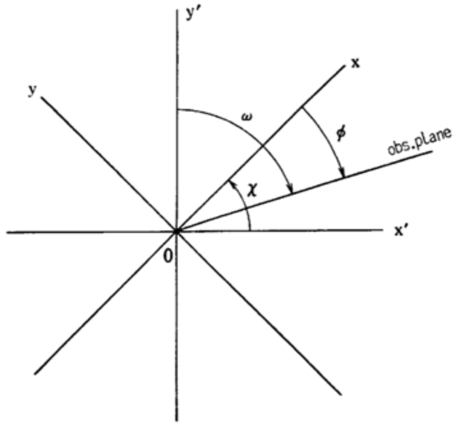

Fig. 2. The coordinate system and angles used.

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[5] P. Debye, ibid., 14, 636 (1946).

[6] P. Debye and A. M. Bueche, ibid., 16, 573 (1948).

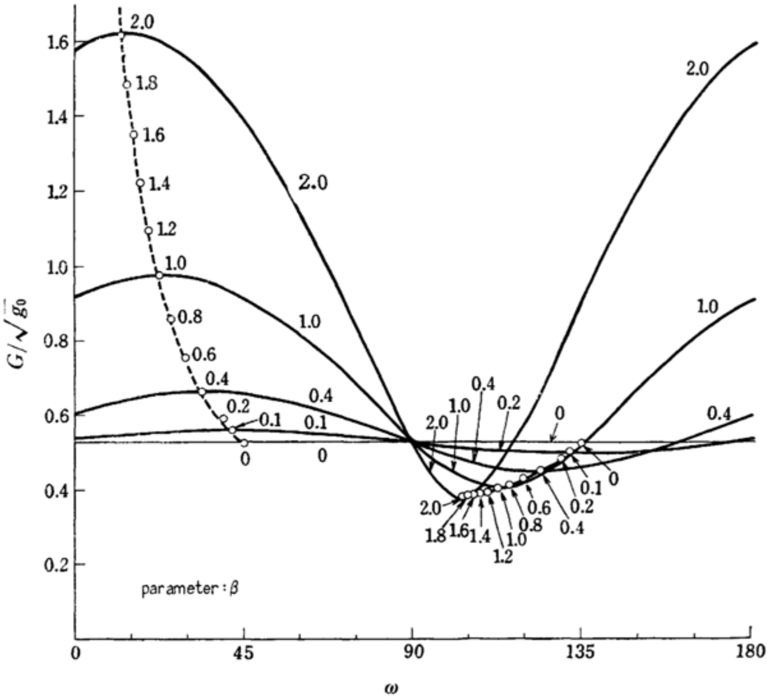

Fig. 3. The relationship between $G/\sqrt{g_0}$ and ω. Parameter: β.

Nakagaki[2] gave the probability distribution of end-to-end distance by the equation:

$$\psi=\frac{1}{abc}\left(\frac{\mu}{\pi}\right)^{3/2}\times\exp\{-\mu[(x/a)^2+(y/b)^2+(z/c)^2]\} \quad (32)$$

where

$$\left.\begin{aligned} a^2&=\sqrt{1+\beta^2}(\sqrt{1+\beta^2}+\beta)\\ b^2&=\sqrt{1+\beta^2}(\sqrt{1+\beta^2}-\beta)\\ c^2&=1 \end{aligned}\right\} \quad (33)$$

Here, the coordinate system x, y, z is that obtained by rotating the coordinate system x', y', z by the angle χ around the z-axis, as shown in Fig. 2, x' and y' being the direction of velocity gradient and velocity, respectively. Eq. 32 is reduced to the usual Gaussian distribution (Eq. 26) when $\beta=0$.

The distribution of segments around the center of gravity of the molecule may then be assumed to be

$$W=\frac{Z}{abc}\left(\frac{\mu^*}{\pi}\right)^{3/2}\times\exp\{-\mu^*[(x/a)^2+(y/b)^2+(z/c)^2]\} \quad (34)$$

with $\mu^*=6\,\mu$, in analogy to Eq. 27. By the assumption that the surface of the molecule is defined by the points at which $W_s/W_0=\exp(-5/2)$, the molecule should be an ellipsoid expressed by the equation:

$$\mu^*[(x/a)^2+(y/b)^2+(z/c)^2]=5/2 \quad (35)$$

the semi-axes of the ellipsoid R_a, R_b, and R_c being in the direction of the coordinate axes x, y and z, respectively, and the values being[7]

$$\left.\begin{aligned} R_a&=\sqrt{5/18}\;aR\\ R_b&=\sqrt{5/18}\;bR\\ R_c&=\sqrt{5/18}\;cR \end{aligned}\right\} \quad (36)$$

When $\beta=0$,

$$R_a=R_b=R_c=R_s \quad (37)$$

since $a=b=c=1$.

In order to determine the values of R_a, R_b, and R_c experimentally, a quantity G defined by

$$G=\sqrt{(5/18)g(1+2\beta^2/3)/(1+\beta^2/3)} \quad (38)$$

is introduced. Here g is obtainable experimentally from the measurement of the initial slope by using Eq. 14, and β is obtainable experimentally by Eq. 22 as a quantity proportional to the rate of rotation Ω. Therefore, the quantity G is a measurable quantity. The theoretical expression for G may be obtained by using Eq. 15 and the result is:

$$G=\sqrt{5/18}\;R\sqrt{1+\beta^2+\beta\sqrt{1+\beta^2}\cos 2\phi} \quad (39)$$

Thus, G as a function of the direction of observation plane, ω, has one maximum and one

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[7] The quantity R is the root mean square end-to-end distance at rest. The value in flow is $\langle r^2\rangle=R^2(1+2\beta^2/3)$.

minimum in the range $\omega=0\sim180°$. The maximum of G occurs at $\phi=0$, that is, $\omega=90°-\chi$ or the direction of x-axis. The maximum value of G is

$$G_{\max}=R_a \quad \text{at} \quad \omega_{\max}=90°-\chi \tag{40}$$

On the other hand, the minimum value of G occurs at $\phi=90°$, that is the direction of y-axis, at which,

$$G_{\min}=R_b \quad \text{at} \quad \omega_{\min}=180°-\chi \tag{41}$$

The value of χ can be predetermined theoretically by Eq. 18. Thus, the major and minor semi-axes of the ellipsoidal molecule, R_a and R_b, are obtained experimentally from the values of $G_{\max}$ and $G_{\min}$, and the direction of the major and minor axes of the molecule coinside with $\omega_{\max}$ and $\omega_{\min}$. The value of R_c is equal to the value of G for $\beta=0$, that is the value for the solution at rest:

$$G_0=R_c \tag{42}$$

The values of $G/\sqrt{g_0}$ *are shown in Fig. 3,* where g_0 is the value of g for the solution at rest. $G_{\max}$ and $G_{\min}$ are shown by open circles. The numerical values of $G_{\max}/\sqrt{g_0}$ and $G_{\min}/\sqrt{g_0}$ are shown in Table I for perfectly flexible molecules.

TABLE I. THE MAXIMUM AND MINIMUM OF G FOR PERFECTLY FLEXIBLE HIGH POLYMER MOLECULE

β	$\omega_{\max}$	$G_{\max}/\sqrt{g_0}$	$\omega_{\min}$	$G_{\min}/\sqrt{g_0}$
0	45.00°	0.52705	135.00°	0.52705
0.1	42.14	0.55540	132.14	0.50263
0.2	39.34	0.58784	129.34	0.48190
0.4	34.10	0.66475	124.10	0.45007
0.6	29.52	0.75642	119.52	0.42827
0.8	25.67	0.86032	115.67	0.41349
1.0	22.50	0.97388	112.50	0.40339
1.2	19.91	1.0948	109.91	0.39185
1.4	17.77	1.2212	107.77	0.39134
1.6	16.01	1.3518	106.01	0.38769
1.8	14.53	1.4857	104.53	0.38500
2.0	13.28	1.6221	103.28	0.38290

Expectation from Photographic Study of Small Angle Scattering

The shape of the pattern to be obtained by photographing the small angle scattering from a streaming solution will be discussed here. Let the distance from the specimen (a streaming solution) to the photographic plate be D, and the coordinate of one point P on the plate be (x', y'). Here the origin of the coordinate system is placed on the point where the primary beam hit the plate, the x'-axis being parallel to the direction of the velocity gradient, $\vec{q}$, and the y'-axis being parallel to the direction of flow, $\vec{v}$, and the direction of the primary beam being perpendicular to the plate.

Since the small angle scattering only is considered here, $\theta\ll1$ or $r/D\ll1$. Therefore,

$$\left.\begin{aligned}\sin(\theta/2)&\fallingdotseq r/2D\\ \cos\theta&\fallingdotseq 1-r^2/2D^2\end{aligned}\right\} \tag{43}$$

The intensity I_u of light per unit solid angle scattered to the direction SP in Fig. 4 is

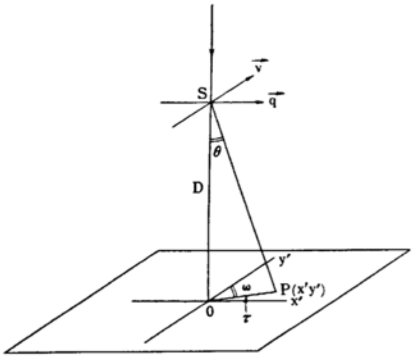

Fig. 4. Illustration of coordinate systems and angles.

$$I_u=I_0(1+\cos^2\theta)\,R_u \tag{44}$$

where I_0 is the intensity of the unpolarized incident light, and R_u is the reduced scattering intensity as defined by Eq. 3. Then, the intensity, I_u' of scattered light per unit area on the plate is

$$I_u'=I_u\cos\theta/(D^2+r^2) \tag{45}$$

Now, using Eq. 6 for sufficiently dilute solution, expanding the interference factor P in a power series of r/D and using Eq. 43,

$$\begin{aligned}I_u'=&(2I_0KcM/D^2)\,[1-(r^2/2D^2)\{4+E\\&\times(1+\beta^2+\beta\sqrt{1+\beta^2}\cos2\phi)\}]\end{aligned} \tag{46}$$

where

$$E=(4\pi^2R^2/9\lambda^2)(1+\beta^2/3)/(1+2\beta^2/3) \tag{47}$$

The contrast to be obtained on the photographic plate is probably not very great, although it will be the greater, the greater the value of R/λ is. Let us, however, expect that the contrast can be emphasized sufficiently by using adequate photographic technique. Here, the shape of the pattern obtained by connecting the points of equal blackness on the plate is discussed. Since I_u' is constant for these points, the value of h defined by

$$h=1-(D^2/2KcM)(I_u'/I_0) \tag{48}$$

is constant. Now changing the coordinate system from (x', y') to (x, y) shown in Fig. 2,

$$\begin{aligned}&x^2/\{2D^2h/[4+E(1+\beta^2+\beta\sqrt{1+\beta^2})\}\\&\quad+y^2/\{2D^2h/[4+E(1+\beta^2-\beta\sqrt{1+\beta^2})]\}=1\end{aligned} \tag{49}$$

is obtained from Eqs. 46 and 48. Therefore, the shape of the pattern to be obtained on the plate is an ellipse. The direction of the major axis of the ellipse is parallel to the direction of the minor axis of the molecule (y-direction) and the direction of the minor axis of the pattern is parallel to the direction of the major axis of the molecule (x-direction). Thus, the orientation of the flexible high polymer molecules in flow can be determined by photographing the small angle scattering of light.

Summary

Small angle scattering of light by streaming flexible high polymer molecules is studied theoretically. It is concluded that the position at which the Zimm plot for infinite dilution cuts the ordinate does not change with the velocity gradient and is equal to $1/M$. The initial slope of the Zimm plot, however, varies with the velocity gradient as well as the direction of the observation plane. The quantity g proportional to the initial slope varies with the rate of rotation Ω of a concentric cylinder apparatus according to the approximation equation:

$$(g/g_0-1)/\Omega = A+B\Omega$$

where g_0 is the value of g at $\beta=0$, and A and B are parameters depending upon the direction of observation.

Now, when a quantity G:

$$G=\sqrt{(5/18)\ g\ (1+2\beta^2/3)/(1+\beta^2/3)}$$

(where β is a quantity proportional to the velocity gradient, the proportionality constant being obtained from the value of A or B) is measured, the value of $G_{\max}$ is equal to the length of the semi-major axis of the molecule, the observation plane for this $G_{\max}$ being parallel to the direction of the major axis of the molecule, while the value of $G_{\min}$ is equal to the length of the semi-minor axis of the molecule, the observation plane for this value being parallel to the direction of the minor axis of the molecule.

The pattern to be obtained by photographing the small angle scattering from a streaming solution of high polymer is discussed. The pattern is expected to be an ellipse, the orientation of the pattern is expected to be rotated by exactly 90° from the orientation of the molecule.

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