*Theory on the Light Scattering of High Polymer Solutions Considering the Anisotropy of Segments**

By Masayuki NAKAGAKI

(Received November 21, 1960)

To discuss the physico-chemical properties of high polymer solutions, the so-called pearl necklace model is often used. In the theory of light scattering, too, the segments are usually assumed to be small spheres which scatter light according to Rayleigh's theory, and the interference between scatterd light from these Rayleigh spheres is considered[1,2]. In some cases, however, the segments of high polymer are not spherical but optically anisotropic.

In the present paper, the angular distribution of the intensity of light scattered by the high polymer solution is calculated theoretically, taking the anisotropy of the segments into account, and the theory is applied for the analysis of the Zimm plot.

Theoretical

Scattering at Infinite Dilution.—In the studies of light scattering of high polymer solutions, the Zimm plot method is often used. Curves on the Zimm plot are usually formulated by the following equation for the polymers of spherical segments and for infinite dilution ($c \to 0$):

---

* Presented at the 9th Annual Meeting of the Society of Polymer Science, Osaka, May, 1960.

[1] B. H. Zimm, R. S. Stein and P. Doty, *Polymer Bull.*, **1**, 90 (1945).

[2] P. Debye, *J. Phys. & Colloid Chem.*, **51**, 18 (1947).

$$Kc/R_u(\theta)=1/MP_1(\theta) \tag{1}$$

where K is the well-known constant, c is the concentration, M is the molecular weight, and $P_1(\theta)$ is the intramolecular (intersegmental) interference factor given by[1,2]

$$P_1(\theta)=(2/\sigma^2)\,[\exp(-\sigma)-(1-\sigma)] \tag{2}$$

In this equation,

$$\sigma=(8\pi^2/3)\,(\overline{R^2}/\lambda^2)\sin^2(\theta/2) \tag{3}$$

where $\overline{R^2}$ is the mean square end-to-end distance, λ is the wavelength of light in the medium, and θ is the scattering angle. The wavelength in the medium λ is related to the the wavelength in vacuum λ_0 by the equation,

$$\lambda=\lambda_0/\mu_1 \tag{4}$$

where μ_1 is the refractive index of the medium.

The quantity $R_u(\theta)$ is defined by

$$R_u(\theta)=\frac{J_u(\theta)/I_0}{1+\cos^2\theta} \tag{5}$$

where $J_u(\theta)$ is the intensity of scattered light per unit solid angle at the scattering angle θ when unpolarized incident light is used, and I_0 is the intensity of incident light (per unit area). The factor $(1+\cos^2\theta)$ in Eq. 5 expresses the angular dependency of the scattered light from a Rayleigh sphere or a spherical segment, and because of this factor, the quantity $R_u(\theta)$ is called reduced scattering intensity. It is, however, obvious that the angular dependency of scattered intensity can not be reduced by the factor $(1+\cos^2\theta)$ if the segments are not spherical. In the latter case, another factor $P_u(\theta)$ must be introduced, and Eq. 1 must be rewritten to

$$Kc/R_u(\theta)=1/M^*P_1(\theta)P_u(\theta) \tag{6}$$

where M^* is the apparent molecular weight of the high polymer, and

$$P_u(\theta)=\frac{2}{1+\cos^2\theta}\cdot\frac{\langle i_u(\theta)\rangle}{\langle i_u(0)\rangle} \tag{7}$$

The quantity $\langle i_u(\theta)\rangle$ is defined by the equation:

$$J_u{}'(\theta)/I_0=(\lambda^2/4\pi^2)\langle i_u(\theta)\rangle \tag{8}$$

where $J_u{}'(\theta)$ is the intensity of light scattered by one segment.

Scattering from an Anisotropic Segment.—A segment or a particle may have two kinds of optical anisotropy: the one is "intrinsic" anisotropy and the other is "form" anisotropy. The intrinsic anisotropy occurs when the dispersed phase (that is the material composing the particle) itself has optical anisotropy because of, e. g., the orientation of valence bonds in the phase. In this case, the "excess" polarizability[3] of the dispersed phase can be expressed by an ellipsoid (a tensor in a more mathematical terminology) or a spheroid. For the sake of simplicity, a spheroid of the excess polarizability with principal axes $(\alpha_a, \alpha_b, \alpha_b)$ will be considered here. Then, the optical anisotropy is expressed by the ratio p_α,

$$p_\alpha=(\alpha_b/\alpha_a) \tag{9}$$

The form anisotropy, on the other hand, is the optical anisotropy due to the anisometry. In other words it is due to the anisotropic shape of the particle made of isotropic phase. If the shape of the particle is assumed to be a spheroid (it may of course be an ellipsoid in more general cases) and its semi-axes are (a, b, b), the anisometry is expressed by the axial ratio:

$$p=a/b \tag{10}$$

If the particle is sufficiently small compared to the wavelength of light, it may be assumed that one dipole is induced in a particle and the oscillation of the dipole radiates the scattered light. In this case, too, a spheroid of excess polarizability can be considered for each spheroidal particle, although the axial ratio of the polarizability spheroid p_α is not necessarily equal to the axial ratio p of the particle. Therefore, it can be expected that both kinds of anisotropy give the same type of expression for the angular dependency of the scattered light intensity.

The intensity of scattered light can easily be calculated for a particle having a spheroid of excess polarizability $(\alpha_a, \alpha_b, \alpha_b)$ by assuming that the electric vector of the scattered light is parallel and proportional to the induced dipole, the proportionality constant being set at k. On the other hand, the intensity of scattered light by an anisometric particle has already been calculated by Rayleigh[4] and Gans[5], if the particle is sufficiently small compared to the wavelength of light. These two theories give equations of the same form as expected above:

$$\left.\begin{aligned}
i_{//\to//}&=\Big[A\cos\theta+B\Big(\sin^2\Theta\cos^2\varphi\cos\theta\\
&\qquad+\frac{1}{2}\sin 2\Theta\cos\varphi\sin\theta\Big)\Big]^2\\
i_{//\to\perp}&=\Big[\frac{1}{2}B\sin^2\Theta\sin 2\varphi\Big]^2\\
i_{\perp\to//}&=\Big[\frac{1}{2}B(\sin^2\Theta\sin 2\varphi\cos\theta\\
&\qquad+\sin 2\Theta\sin\varphi\sin\theta)\Big]^2\\
i_{\perp\to\perp}&=[A+B\sin^2\Theta\sin^2\varphi]^2
\end{aligned}\right\} \tag{11}$$

---

[3] It is the difference between the polarizabilities of particle and medium as already used, for example, by A. Peterlin, W. Heller and M. Nakagaki [*J. Chem. Phys.*, **28**, 470 (1958).].

[4] L. Rayleigh, *Phil. Mag.*, **44**, 28 (1897).

[5] R. Gans, *Ann. Phys.*, (4), **37**, 881 (1912), **62**, 331 (1920).

where θ is the scattering angle and (Θ, φ) are the spherical coordinates of the direction of the symmetry axis of the spheroid (α_a-axis or a-axis). The suffixes $i_{//\to\perp}$ and so forth mean that the incident light is oscillating parallel to the observation plane and the component of scattered light oscillating prependicularly to the observation plane is observed and so forth. The constants A and B are, in the case where the spheroid of excess polarizability is considered

$$\left.\begin{aligned} A &= k\alpha_b \\ B &= k(\alpha_a - \alpha_b) \end{aligned}\right\} \quad (12)$$

and in the case of anisometric particle

$$\left.\begin{aligned} A &= p^2\alpha^3(m^2-1)/[3+(m^2-1)(3/4\pi)P'] \\ B &= p^2\alpha^3(m^2-1)/[3+(m^2-1)(3/4\pi)P] - A \end{aligned}\right\} \quad (13)$$

Here

$$\alpha = 2\pi a/\lambda \quad (14)$$

and

$$m = \mu_2/\mu_1 \quad (15)$$

where μ_2 and μ_1 are refractive indices of the particle and the medium, respectively. As shown by Gans[5])

$$P+2P' = 4\pi \quad (16)$$

For a prolate spheroid ($p \leqslant 1$),

$$P = 4\pi[(1-e^2)/e^2] \times \{(1/2e)\ln[(1+e)/(1-e)]-1\} \quad (17)$$

where e is the eccentricity given by

$$e = \sqrt{1-p^2} \quad (18)$$

and for an oblate spheroid ($p \geqslant 1$),

$$P = (4\pi/\varepsilon^2)[1-(\sqrt{1-\varepsilon^2}/\varepsilon^2)\sin^{-1}\varepsilon] \quad (19)$$

where ε is the eccentricity given by

$$\varepsilon = \sqrt{1-1/p^2} \quad (20)$$

Optical Anisotropy of Anisometrical Segments.—As already stated, a spheroid of excess polarizability can be considered for each spheroidal particle (segment in the present paper) if the size of the spheroid is small compared to the wavelength of light used, but the axial ratio of these spheroids, p_α and p, are not necessarily equal. Now, on the basis of Eq. 12,

$$p_\alpha = 1/(B/A+1) \quad (21)$$

and according to Eq. 13,

$$p_\alpha = [1+(m^2-1)(P/4\pi)]/[1+(m^2-1)(P'/4\pi)] \quad (22)$$

For spherical particles ($p=1$), the relation $P=P'=4\pi/3$ is obtained from Eq. 17 and also from Eq. 19, which gives

$$p_\alpha = 1 \qquad \text{for } p=1 \quad (23)$$

In this case, and only in this case, $p_\alpha = p$. On the other hand, if the particle is an infinitesimally thin rod ($p=0$), the relations $P=0$ and $P'=2\pi$ are obtained from Eqs. 16 and 17, which give

$$p_\alpha = 2/(m^2+1) \qquad \text{for } p=0 \quad (24)$$

while if the particle is an infinitesimally thin disk ($p=\infty$), the relations $P=4\pi$ and $P'=0$ are obtained from Eqs. 16 and 19, which give

$$p_\alpha = m^2 \qquad \text{for } p=\infty \quad (25)$$

Referring to these extreme cases, it can be concluded that the value of p and p_α are not equal for anisometric particles. Moreover, the value of p_α must be in the range,

$$2/(m^2+1) < p_\alpha < m^2 \quad (26)$$

for anisometrical particles and, if the value of p_α is out of this range, particles must have the intrinsic anisotropy.

Scattering from Randomly Oriented Segments.—If the orientation of segments in a flexible high polymer molecule is assumed to be completely random, the value of $\langle i \rangle$ can be calculated by averaging Eq. 11 over all ranges of Θ and φ. The results are:

$$\left.\begin{aligned} \langle i_{//\to//}\rangle &= (1/15)B^2 + [A^2+(2/3)AB \\ &\qquad + (2/15)B^2]\cos^2\theta \\ \langle i_{//\to\perp}\rangle &= \langle i_{\perp\to//}\rangle = (1/15)B^2 \\ \langle i_{\perp\to\perp}\rangle &= A^2+(2/3)AB+(1/5)B^2 \end{aligned}\right\} \quad (27)$$

Therefore, the quantity $\langle i_u(\theta)\rangle$ for unpolarized light:

$$\langle i_u(\theta)\rangle = (1/2)\langle i_{//\to//} + i_{//\to\perp} + i_{\perp\to//} + i_{\perp\to\perp}\rangle \quad (28)$$

can be expressed as follows:

$$\langle i_u(\theta)\rangle = (1/2)\{[A^2+(2/3)AB+(2/5)B^2 + [A^2+(2/3)AB+(2/15)B^2]\cos^2\theta\} \quad (28a)$$

This gives the following value of $P_u(\theta)$ of Eq. 7.

$$\left.\begin{aligned} P_u(\theta) &= 1 + Q_u(1-\cos^2\theta)/(1+\cos^2\theta) \\ Q_u &= (2/15)(B/A)^2/[1+(2/3)(B/A) \\ &\qquad + (4/15)(B/A)^2] \end{aligned}\right\} \quad (29)$$

The value of $P_u(\theta)$ reduces to unity for spherical segments, because $B=0$ and $Q_u=0$ if $p=1$.

In an actual high polymer molecule, the mutual orientation of segments in a molecule might not be completely random, and this might require us to recalculate $P_1(\theta)$ of Eq. 6, but it is not easy to know the mutual orientation of segments in a polymer molecule. However, one may, at first, average the intensity of light scattered from each segment over all possible orientations of the segment, and then consider the interference of these scattered beams, because the segments are originally defined as dynamically independent units. In this method of approximation, one can use Eq. 6 together with Eq. 29 for $P_u(\theta)$ and Eq. 2 for $P_1(\theta)$. Of course, the extension of the high polymer chain might be different according to whether the segments are isotropic or anisotropic. This affects the value of $P_1(\theta)$. This effect, however, had already been taken care of by $\overline{R^2}$ in Eq. 3.

Apparent Molecular Weight.—In the case of $\theta=0$, Eq. 6 reduces to

$$Kc/R_u(0)=1/M^* \tag{30}$$

but the apparent molecular weight M^* thus obtained does not coincide with the true molecular weight M except when the segments are spherical.

Debye's theory[6] of light scattering based upon the fluctuation theory is originally derived for the turbidity τ, but not for the reduced scattering intensity $R_u(\theta)$. Therefore,

$$Hc/\tau=1/M \tag{31}$$

is always correct for infinitely dilute solutions irrespective of whether the particles (segments in the present paper) are spherical or not, but Eq. 30 is not always correct because the relation used in order to convert τ to $R_u(\theta)$:

$$R_u(\theta)/\tau=3/16\pi \qquad \text{for } p=1 \tag{32}$$

is correct only for spherical particles. Therefore, the relation

$$K=(3/16\pi)H \tag{33}$$

must not be used for anisometric particles to obtain the correct values of the molecular weight, or, if the Eq. 33 is still used for anisometric particles, the apparent molecular weight M^* thus obtained must be reduced to the true molecular weight M, by using a correction factor to be obtained from the true relationship between $R_u(\theta)$ and τ.

The reduced scattering intensity $R_u(\theta)$ is given by

$$R_u(\theta)=(\lambda^2N/4\pi^2)\,[\langle i_u(\theta)\rangle/(1+\cos^2\theta)]\,P_1(\theta) \tag{34}$$

where N is the number of segments per unit volume, while the turbidity τ is given by

$$\tau=(\lambda^2N/2\pi)\int_0^{\pi}\langle i_u(\theta)\rangle\sin\theta\,\mathrm{d}\theta \tag{35}$$

By using Eq. 28a,

$$\tau=(2\lambda^2N/3\pi)\,[A^2+(2/3)AB+(1/3)B^2] \tag{35a}$$

is obtained. Then referring to Eq. 29 and to the equation:

$$R_u(\theta)/\tau=(3/16\pi)P_1(\theta)P_u(\theta)M^*/M \tag{36}$$

the relation:

$$M/M^*=1+(1/15)(B/A)^2/[1+(2/3)(B/A)+(4/15)(B/A)^2] \tag{37}$$

is obtained, keeping the relation between K and H as it is in Eq. 33.

Comparison with Experimental Data

Serious anomalies in the Zimm plots have been found by Ehrlich and Doty[7] for aqueous solutions of copolymers of methacrylic acid and 2-dimethylaminoethyl methacrylate. Their data for isoionic P-7 (a fractionated sample) in 0.10 M sodium chloride and in distilled water are read off from their figures and plotted in Figs. 1 and 2 for the values extrapolated to the infinite dilution. They also stated in their paper that the molecular weight of the sample P-7 obtained from light scattering measurement by the dissymmetry method was 270000 and that the square root of the mean

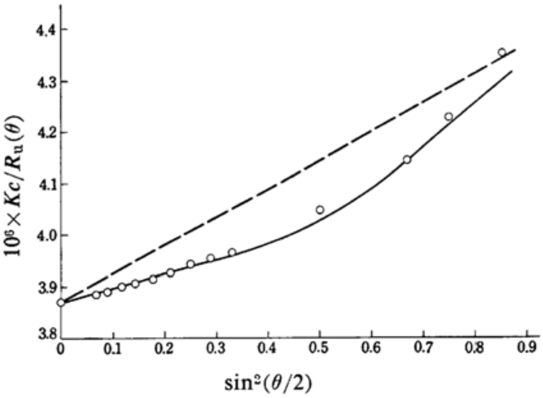

Fig. 1. Isoionic P-7 in 0.10 M sodium chloride.

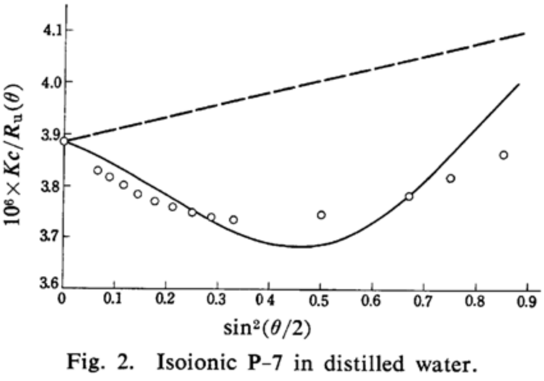

Fig. 2. Isoionic P-7 in distilled water.

---

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

[7] G. Ehrlich and P. Doty, *J. Am. Chem. Soc.*, **76**, 3764 (1954).

square end-to-end distance $\sqrt{\overline{R^2}}$ obtained from viscosity data on the basis of the Flory-Fox theory with the correction for polydispersity was 410 Å in 0.10 M sodium chloride and 270 Å in distilled water. The wavelength used was $\lambda_0=4360$ Å in vacuum, so that $\lambda=3254$ Å in water since $\mu_1=1.33986$ at 25°C. By using these values in Eqs. 2 and 3, the value of $P_1(\theta)$ can be calculated. If the segments are assumed to be spherical and $P_u(\theta)=1$, the value of $Kc/R_u(\theta)$ can be calculated from Eq. 6 by using the experimental values of $Kc/R_u(0)$, which is equal to $1/M^*$. The results of calculations are shown in Figs. 1 and 2 with broken lines. Experimental values shown by open circles are definitely lower than broken lines especially at about $\sin^2(\theta/2)=0.5$ or $\theta=90°$. If these discrepancies are due to the anisotropy of segments, the deviation of $P_u(\theta)$ from unity must be expressed by Eq. 29. Using the values of Q_u determined to obtain the best fit with the experimental plots and cited in Table I, solid curves in Figs. 1 and 2 are obtained.

TABLE I. CONSTANTS FOR ISOIONIC P-7

	In 0.10 M NaCl (Fig. 1)	In water (Fig. 2)
Q_u	0.0291	0.0870
B/A	0.565	1.190
p_α	0.639	0.457
ρ_2	3.26	5.93
M^*	258000	257000
M/M^*	1.0146	1.0448
M	262000	269000

In the case of 0.10 M sodium chloride as the solvent (Fig. 1), the initial slope of the Zimm plot is smaller than that of the broken curve, although its sign is still positive. In the case of distilled water as the solvent (Fig. 2), the initial slope is negative. The anomalous negative slope could not be expected from any theory presented so far. On the basis of the present aspect, however, the anomalous negative value can be explained by the great value of Q_u, the value being about three times greater for Fig. 2 than for Fig. 1. The value of B/A calculated from Eq. 29 is about twice as great for Fig. 2 as for Fig. 1. However, the axial ratio p_α of the spheroid of polarizability to give the anisotropy of segments is only 30% smaller for Fig. 2 than for Fig. 1. This demonstrates that only the small difference in the anisotropy of segments results in any very great difference in the initial slope of the Zimm plot.

The value of p_α for either case is smaller than unity. This means that the spheroid of the excess polarizability is prolate in both cases. To discuss whether this anisotropy is due to intrinsic anisotropy or anisometry, the value of the relative refractive index m must be known. On the basis of the mixture rule,

$$\mathrm{d}\mu_{12}/\mathrm{d}c=(m-1)\mu_1/\rho_2 \tag{38}$$

By using $\mathrm{d}\mu_{12}/\mathrm{d}c=0.188$ as reported by the original authors, the value of m is obtained if the value of the density of the polymer ρ_2 is known. If the value of ρ_2 is 1.4, the value of m is 1.20. These values seem to be reasonable. Then, according to Eq. 26,

$$0.82<p_\alpha<1.44 \qquad \text{for } m=1.20 \tag{39}$$

if the anisotropy is due to the anisometry. Since the values cited in Table I are smaller than the limiting value, the anisotropy in these cases must be intrinsic. Putting it the other way around, the value of ρ_2, which is necessary to explain the anisotropy as the form anisotropy, may be estimated according to Eq. 24 for infinitesimally thin rods. The values of ρ_2 must be greater than 3~6 as shown in Table I, which is too great for polymers. Therefore, the anisotropy seems to be intrinsic.

On the molecular weight of the polymer, the value of the apparent molecular weight M^* obtained from the value of $Kc/R_u(0)$ and cited in Table I is a little too small compared to the value $M=270000$ reported by the original authors. The correction factor M/M^* given by Eq. 37 is calculated and cited in Table I. The molecular weight corrected by this factor (M in Table I) is closer to 270000 than M^* is.

Thus the essential feature of the anomalous θ dependency of the Zimm plot of isoionic P-7 could be explained by assuming that the segments are anisotropic. However, the agreement between the experimental plots and the theoretical curves in Figs. 1 and 2 is not perfect yet. For the discrepancy, several reasons may be pointed out: Some errors might have been made in the double extrapolation in the Zimm-plot to obtain the value of $Kc/R_u(0)$; the estimation of $\overline{R}^2$ used to calculate $P_1(\theta)$ might not be correct; the effect of the molecular weight distribution was neglected; the mutual orientation of segments in a polymer chain is not completely random, but this effect was neglected. Some of these points, especially the last one, will be discussed in a later paper.

Proposal for the Direct Measurement of Q_u

If the value of Q_u can be measured directly, it will give a good criterion to see whether the phenomenon is actually due to the anisotropy of segments or not. This will be done by measuring the scattering ratio, S, that is the ratio of scattered intensities from parallelly and perpendicularly polarized incident beams.

$$S(\theta) = J_{/\!/}(\theta)/J_{\perp}(\theta) = \langle i_{/\!/}(\theta)\rangle / \langle i_{\perp}(\theta)\rangle \tag{40}$$

According to the relations:

$$\left.\begin{aligned} \langle i_{/\!/}\rangle &= \langle i_{/\!/\to/\!/} + i_{/\!/\to\perp}\rangle = (2/15)B^2 \\ &\quad + [A^2 + (2/3)AB + (2/15)B^2]\cos^2\theta \\ \langle i_{\perp}\rangle &= \langle i_{\perp\to/\!/} + i_{\perp\to\perp}\rangle = A^2 \\ &\quad + (2/3)AB + (4/15)B^2 \end{aligned}\right\} \tag{41}$$

the value of $S(\theta)$ theoretically obtained is

$$S(\theta) = Q_u + (1 - Q_u)\cos^2\theta \tag{42}$$

At $\theta = 90^\circ$,

$$S(90) = Q_u \tag{43}$$

Therefore, the scattering ratio at 90° is the value of Q_u.

Summary

The anomaly of the angular dependency of the reduced scattering intensity in the Zimm plot for infinitely dilute solution was discussed for the solutions of high polymer molecules having anisotropical segments, and the theoretical relationship between $Kc/R_u(\theta)$ and θ was derived. The equation had the same form for both intrinsic anisotropy and form anisotropy. In the latter case, the axial ratio of the spheroid of excess polarizability was concluded to be not equal to the axial ratio of the segment. Moreover, the correction factor for the molecular weight was derived.

Applying these theoretical equations to the experimental data by Ehrlich and Doty on the solution of copolymer of methacrylic acid and 2-dimethylaminoethyl methacrylate, it was shown that the anomalies of the Zimm plot could be explained by assuming that the segments have intrinsic anisotropy.

It was also suggested that the scattering ratio is a good criterion to see whether the anomaly is actually due to the anisotropy of segments or not.

Faculty of Pharmacy
Kyoto University
Sakyo-ku, Kyoto