

Light Scattering from Dilute Solutions of Flexible Chain Polymers Consisting of Optically Anisotropic Segments

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Received March 10, 1964

A general theory of Rayleigh scattering is developed for dilute solutions of polymer molecules consisting of optically anisotropic segments. Simple expressions for the four components (V_v , V_h , H_v , and H_h) of reduced scattered intensity, as a function of angle and concentration, are obtained, and the behavior of the depolarization ratios is discussed. The results are used to investigate the effect of optical anisotropy on the determination of molecular weight, of second virial coefficient, and of mean square radius of gyration, and a useful procedure to estimate the optical anisotropy parameter δ from the conventional light scattering data is described. To illustrate the use of the theory, an analysis is made of the light scattering measurements of solutions of isoionic polyampholyte obtained by Erhlich and Doty. The anomalous light scattering data (negative gyration radius) are shown to be cast quantitatively in the present theory. More thorough comparison of theory and experiment is made with the use of light scattering results of atactic and isotactic polystyrene. The optical anisotropy of isotactic polystyrene is shown to be sixty times as large as that of atactic polystyrene, and its origin is briefly discussed in connection with stereoregularity.

I. INTRODUCTION

In the theory of light scattering, we assume that a thread-like molecule consists of a linear sequence of small identical particles which behave as independent dipolar scatterers. We call this particle the optical segment. If the segment is isotropic, the light scattered at 90° with reference to the direction of incident light is completely vertically plane polarized. Polymer molecules consisting of optically anisotropic segments, however, exhibit some depolarization effect when the incident light is either vertically polarized or unpolarized. The ratio of the horizontal component to the vertical component of the scattered light, known as the depolarization ratio, characterizes the optical anisotropy of the molecule.

The depolarization effect in the case of polymer solutions has been treated so far in a manner analogous to that in the case of small molecules. The well known Cabannes' factor has been used by several investigators to correct the effect of optical anisotropy on molecular weight determination.^{2,3,4} But this type of correction is usually of minor importance in the case of solutions of conventional polymers. The depolarization ratio has also been investigated, both theoretically and experimentally, with intention to obtain informations about such characteristics of polymer chain in solution as vari-

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ation of the molecular shape or size with molecular weight, solvent and concentration.⁵⁻¹²⁾ But, because of the present lack of the molecular theories of the depolarization ratio, it seems unlikely that an unambiguous picture of the molecular characteristics can be obtained from the depolarization ratio alone. Such pictures should be obtained directly by the analysis of the angular variation of the scattered light intensities. In addition, some concepts prevailing in this field appears to be inappropriate in view of the modern theories of polymer physics. For example, the dependence of the depolarization ratio on solvent and concentration is assumed to reflect directly the change in the size of optical segment.^{11,12)} But, this may be an oversimplification, and the segment size will rather be a constant characteristic of polymer species in view of the present-day understanding of the conformational properties of polymer chains.

As is well known, a merit of the depolarization measurement is in the fact that it can furnish information about the optical qualities of each single segment. With the appearance of isotactic polymers which show exceptionally large optical anisotropy in some cases,^{13,14)} the knowledge of optical properties of segment is becoming indispensable, and the anisotropy of the optical segment will play an important role in characterization of the local stereoregularity as well as the effective bond length does in characterization of the chain flexibility.¹⁵⁾ Hence, it may be important to place the depolarization measurement on the firm theoretical basis. In addition, it should be pointed out that in the determination of molecular weight,¹⁶⁾ of second virial coefficient, and of mean square radius of gyration, it will be necessary to take the effects of optical anisotropy into account. For the latter two quantities the anisotropy effect has hitherto not been investigated.

The physical chemical characteristics of the horizontal component of the light scattered at 90° have already been discussed by several authors,¹⁷⁻²¹⁾ though not very generally. The following work describes briefly the general theoretical derivation of some equations connected with the phenomenon of light scattered from solutions of flexible chain molecules consisting of optically anisotropic segments.²²⁾ The equations are applied to discuss the depolarization ratios and the effect of optical anisotropy on the determination of molecular weight, mean square radius of gyration, and second virial coefficient. It will be shown that the radius of gyration is considerably affected by the anisotropy of optical segments even in the case of conventional synthetic polymers, if molecular weight and or the radius of gyration is small. It will be also shown that the anomalous light scattering behavior (negative apparent radius of gyration) exhibited by synthetic polymeric ampholyte²³⁾ and by gelatin²⁴⁾ can be explained if optical anisotropy of the chain element is taken into account.²⁵⁾

Finally, the importance of the measurement of optical anisotropy in the study of stereoregularity will be shown for isotactic polystyrene, and the relation between the optical anisotropy parameter and the chain conformation will be briefly discussed.

II. THEORY

We consider a volume element V which contains N polymer molecules of n segments each, and introduce a cartesian coordinate system fixed in space as follows: x axis in the vertical direction, y axis in the horizontal plane perpendicular to the incident beam, z axis in the direction of incident beam, and its origin in the center of the volume element. The electric field E associated with incident parallel beam of wave length λ_0 in vacuum is :

$$E = E_0 \exp(i\omega t) \quad (1)$$

where E_0 is the amplitude and ω the angular velocity. The intensity of plane polarized incident beam is $E_0^2/4\pi$. The excess intensity of light scattered from the solution (over that of the solvent alone) is observed at the position r on the y - z plane. The analyzer is set at and orthogonal to r , and a unit vector M represents its direction. The position of each molecule is close enough to the origin of the coordinate in comparison with r ($=|r|$). Each segment (optical) has three different principal polarizabilities a_1 , a_2 , and a_3 along the principal axes x' , y' , and z' of the segment and scatters light according to the Rayleigh theorem. We assume free and independent orientation of each segment, and express the orientation of the segment in the coordinate system (x, y, z) at a given instant by the Euler angles (θ, φ, ψ) . The two coordinate systems are connected with each other by the transformation matrix T as :

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = T \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2)$$

with

$$T = \begin{pmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{pmatrix} \quad (3)$$

$$l_{11} = \cos \varphi \cos \theta \cos \psi - \sin \varphi \sin \psi$$

$$l_{12} = \sin \varphi \cos \theta \cos \psi + \cos \varphi \sin \psi$$

$$l_{13} = -\sin \theta \cos \psi$$

$$l_{21} = -\cos \varphi \cos \theta \sin \psi - \sin \varphi \cos \psi$$

$$l_{22} = -\sin \varphi \cos \theta \sin \psi + \cos \varphi \cos \psi$$

$$l_{23} = \sin \theta \sin \psi$$

$$l_{31} = \cos \varphi \sin \theta, \quad l_{32} = \sin \varphi \sin \theta$$

$$l_{33} = \cos \theta$$

Now, according to the electromagnetic theory, the electric field associated with the light scattered from the j th element of i th polymer molecule is given by the formula :

$$\begin{aligned} E_{ij}^0 &= -\omega^2 [r \cdot P_{ij}(q)] / c^2 r^3 \\ &= -\omega^2 \{ (r \cdot P_{ij}(q) r - r^2 P_{ij}(q)) \} / c^2 r^3, \end{aligned} \quad (4)$$

where c is the velocity of light in vacuum. $P_{ij}(q)$, the induced electric dipole moment expressed in the (x, y, z) coordinate system, is given by the formula :

$$\begin{aligned} P(q) &= T^{-1} \alpha(q') T E(q) \\ &= P_0(q) \exp(i\omega t), \end{aligned} \quad (5)$$

where

$$\alpha(q') = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix} \quad (6)$$

In order to compound all the wavelets scattered from different segments, phase relations among them should be considered. Then, the total electric field E_N , and the scattered light intensity I observed through the analyzer is given by the formula :

$$E_N = (\omega^2/c^2 r) \sum_{i=1}^N \sum_{j=1}^N P_{ij}(q) \exp\{2\pi i(\mathbf{S} \cdot \mathbf{r}_{ij})/\lambda\} \quad (7)$$

$$I = (1/4\pi) \langle (\mathbf{E}_N \cdot \mathbf{M}) (\mathbf{E}_N^* \cdot \mathbf{M}) \rangle_{Av} \quad (8)$$

In these equations, \mathbf{S} is the vector difference between unit vectors in the directions of the incident and scattered rays and its magnitude is $2 \sin(\theta/2)$, λ is the wave length of light in solution, \mathbf{r}_{ij} is the position vector of the ij th segment, E_N^* is the conjugate complex of E_N . The averaging should be performed over the orientation of segment, the orientation of polymer molecule, and its position.

i) Four Components of Scattered Light

When the analyzer is set in the vertical direction, we obtain the expression for the intensity of the light scattered by the solution from Eq. (8) with Eq. (5) and Eq. (7) as :

$$\begin{aligned} I &= (\omega^4/4\pi r^2 c^4) [nN \langle P_{0x}^2 \rangle_{Av} - \langle P_{0z} \rangle_{Av}^2 \\ &\quad + \langle P_{0x} \rangle_{Av}^2 \langle \sum_{i,i'} \sum_{j,j'} \exp(2\pi i \mathbf{S}(\mathbf{r}_{ij} - \mathbf{r}_{i'j'})/\lambda) \rangle_{Av} \end{aligned} \quad (9)$$

and in the case that the analyzer is set horizontally, we obtain :

$$\begin{aligned} I &= (\omega^4 \cos^2 \theta / 4\pi r^2 \cdot c^4) [nN \langle P_{0y}^2 \rangle_{Av} - \langle P_{0y} \rangle_{Av}^2 \\ &\quad + \langle P_{0y} \rangle_{Av}^2 \langle \sum_{i,i'} \sum_{j,j'} \exp(2\pi i \mathbf{S}(\mathbf{r}_{ij} - \mathbf{r}_{i'j'})/\lambda) \rangle_{Av} \\ &\quad (\omega^4 \sin^2 \theta / 4\pi r^2 \cdot c^4) [nN \langle P_{0z}^2 \rangle_{Av} - \langle P_{0z} \rangle_{Av}^2 \\ &\quad + \langle P_{0z} \rangle_{Av}^2 \langle \sum_{i,i'} \sum_{j,j'} \exp(2\pi i \mathbf{S} \mathbf{r}_{ij} - \mathbf{r}_{i'j'})/\lambda \rangle_{Av} \end{aligned} \quad (10)$$

Various average values of P_0 over the orientation of the segment, appearing in Eq. (9) and Eq. (10) are given by the following equations :²⁰⁾

$$\langle P_{0x} \rangle_{Av}^2 = A^2 E_{0x}^2, \quad \langle P_{0y} \rangle_{Av}^2 = A^2 E_{0y}^2, \quad \langle P_{0z} \rangle_{Av}^2 = 0 \quad (11)$$

$$\begin{aligned} \langle P_{0x}^2 \rangle_{Av} &= (A^2 + 2B^2/3) E_{0x}^2 + (B^2/2) E_{0y}^2 \\ \langle P_{0y}^2 \rangle_{Av} &= (B^2/2) E_{0x}^2 + (A^2 + (2B^2/3)) E_{0y}^2, \end{aligned} \quad (12)$$

$$\langle P_{0z}^2 \rangle_{Av} = (B^2/2) (E_{0x}^2 + E_{0y}^2)$$

where A is the average polarizability and B is a parameter of optical anisotropy which vanishes for the isotropic segment. They are expressed by

$$\begin{aligned} A &= (a_1 + a_2 + a_3)/3 \\ B^2 &= \{(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2\}/15 \end{aligned} \quad (13)$$

The last term in Eq. (9) may be divided into two parts^{27,28,29)}, the intramolecular and intermolecular contribution as follows :³⁰⁾

$$\begin{aligned} &\langle \sum_{i,i'} \sum_{j,j'} \exp(2\pi i S(\mathbf{r}_{ij} - \mathbf{r}_{i'j'})/\lambda) \rangle_{Av} \\ &= Nn^2 P(\theta) - (n^2 N^2/V)(2A_2 \cdot M^2/N_A) \cdot Q(\theta) \end{aligned} \quad (14)$$

where A_2 is the second virial coefficient between two polymer molecules, M the molecular weight of polymer, N_A the Avogadro number, $Q(\theta)$ the intermolecular correlation function. $P(\theta)$ is the well known particle scattering factor which is expressed in terms of mean square radius of gyration $\langle S^2 \rangle$ as :

$$P(\theta) = 1 - (4/3)(2\pi/\lambda)^2 \langle S^2 \rangle \sin^2(\theta/2) + \dots \quad (15)$$

Both $P(\theta)$ and $O(\theta)$ is unity at θ is zero.

Finally, the use of Eq. (11), Eq. (12), Eq. (14), and Eq. (15) in Eq. (9) gives the expressions for the V_v component (vertical component of the scattered light intensity when incident light is vertically polarized) and for the V_h component (vertical component when incident light is horizontally polarized) of the reduced scattered intensity $R(\theta) (= I(\theta)r^2/I_0 \cdot V)$ as :

$$R_{Vv}(\theta) = KcM\{P(\theta) - 2A_2MQ(\theta)c + 4\delta\} \quad (16)$$

$$R_{Vh}(\theta) = KcM \cdot 3\delta \quad (17)$$

Similarly, we obtain the expressions for H_v and H_h components as :

$$R_{Hv}(\theta) = KcM \cdot 3\delta \quad (18)$$

$$R_{Hh}(\theta) = KcM\{(P(\theta) - 2A_2MQ(\theta)c + \delta) \cos^2 \theta + 3\delta\} \quad (19)$$

Hence the sum of vertical and horizontal components of the reduced scattered intensity, when the natural incident light is used, reads :

$$\begin{aligned} R_{Vh}(\theta) &= (KcM/2)\{P(\theta) - 2A_2MQ(\theta)c + 13\delta \\ &+ (P(\theta) - 2A_2MQ(\theta)c + \delta) \cos^2 \theta\} \end{aligned} \quad (20)$$

In deriving these equations, the following relations are used :

$$\omega/c = 2\pi/\lambda = 2\pi n_0/\lambda_0 \quad (21)$$

$$A = (c/2\pi n_0)(V/nN)(dn/dc), \quad (22)$$

and K and δ are given by :

$$K = (4\pi^2 n_0^2/\lambda_0^4 N_A)(dn/dc)^2, \quad \delta = (B/A)^2/6n \quad (23)$$

In the above equations, λ_0 is the wave length of light in vacuum, n_0 and n are the refractive indices of solvent and solution, respectively, c the concentration expressed in weight per unit volume, and δ a measure of optical anisotropy of the segment which vanishes if the segment is isotropic. It may be noted that the additional scattered intensity having its origin in

the optical anisotropy is proportional to the solute concentration, molecular weight of segment, and the intrinsic anisotropy. It does not depend on polymer molecular weight, nor on the intra and intermolecular destructive interference. These results are the natural consequence of the assumption of the free and independent orientation of each segment, which may be appropriate if the size of the segment is taken to include a number of monomeric units, and this is probably the case.

ii) **Effect of Optical Anisotropy on the Determination of Molecular Weight, Size, and Second Virial Coefficient**

In the usual method of Zimm plot, the second virial coefficient is estimated from the slope of the plot, reciprocal intensity function extrapolated to $\theta=0$ vs. c , and the mean square radius of gyration is estimated from the slope of the plot, reciprocal intensity function extrapolated to $c=0$ vs. $\sin^2(\theta/2)$. The intercepts on the ordinate axis in the both plots are equal, giving $(1/M)$. Here we examine the effect of optical anisotropy on A_2 , $\langle S^2 \rangle$, and M estimated from the Zimm plot of R_{vv} and R_{vu} . Rewriting Eq. (16) we have :

$$\lim_{\theta \rightarrow 0} Kc/R_{vv}(\theta) = 1/\{M(1+4\delta)\} + 2A_2C/(1+4\delta)^2 - \dots \quad (24)$$

$$\lim_{c \rightarrow 0} Kc/R_{vv}(\theta) = [1/\{M(1+4\delta)\}][1 + (4/3) \times (2\pi/\lambda)^2 \langle S^2 \rangle \sin^2(\theta/2)/(1+4\delta) - \dots] \quad (25)$$

Hence the apparent quantities read :

$$M_{app} = M(1+4\delta), \quad A_{2app} = A_2/(1+4\delta)^2, \quad \langle S^2 \rangle_{app} = \langle S^2 \rangle / (1+4\delta) \quad (26)$$

When we use R_{vu} , the conventional reciprocal intensity function may be written from Eq. (20) as Eq. (27) and Eq. (28), and Eq. (29) expresses the apparent quantities.

$$\lim_{\theta \rightarrow 0} Kc(1 + \cos^2 \theta)/2R_{vu}(\theta) = 1/[M(1+7\delta)] + 2A_2c/(1+7\delta)^2 - \dots \quad (27)$$

$$\lim_{c \rightarrow 0} Kc(1 + \cos^2 \theta)/2R_{vu}(\theta) = \{1/[M(1+7\delta)]\}[1 + (4/3)(2\pi/\lambda)^2 \times \{\langle S^2 \rangle / (1+7\delta) - (3/4)(\lambda/2\pi)^2(12\delta/(1+7\delta))\} \sin^2(\theta/2) - \dots] \quad (28)$$

$$M_{app} = M(1+7\delta), \quad A_{2app} = A_2/(1+7\delta)^2, \quad \langle S^2 \rangle_{app} = \langle S^2 \rangle / (1+7\delta) - (3/4)(\lambda/2\pi)^2(12\delta/(1+7\delta)) \quad (29)$$

Since δ is positive definite, Eq. (26) and Eq. (29) show that M_{app} is greater, while A_{2app} and $\langle S^2 \rangle_{app}$ are smaller than the true values. The extents of error involved in these quantities are estimated, for illustration, using the following numerical values which may be appropriate for atactic polymer solutions.

$$\lambda_0 = 4360 \text{ \AA}, \quad n_0 = 1.5, \quad \delta = 0.004, \quad \langle S^2 \rangle^{1/2} = 360 \text{ \AA}$$

Substitution of these values in Eq. (24) gives :

$$M_{app} = 1.03M, \quad \langle S^2 \rangle_{app} = 0.91 \langle S^2 \rangle, \quad A_{2app} = 0.95A_2 \quad (30)$$

It may be noted that the effect of optical anisotropy on the apparent mean

square radius of gyration is too large to be neglected even in the case of ordinary polymer solutions, and the magnitude of error is greater for molecules of smaller size and or large optical anisotropy. In the extreme case of large optical anisotropy, or small molecular size, which has been encountered in isotactic polystyrene and synthetic polyampholyte, respectively, the envelope of the plot of the reciprocal intensity function at infinite dilution vs. $\sin^2(\theta/2)$ becomes concave upward as referred to later and we obtain vanishing apparent mean square radii of gyration or even negative values. In these cases, corrections of optical anisotropy should also be applied to molecular weight and second virial coefficient.

According to the procedure hitherto in use, the scattered intensity is divided by a Cabannes' factor before the molecular weight is calculated. When vertically polarized incident light is used, the factor is $(3+3\rho_v)/(3-4\rho_v)$, where ρ_v is the depolarization ratio with vertically polarized incident light. If the incident light is unpolarized, the factor becomes $(6+6\rho_u)/(6-7\rho_u)$, with ρ_u the corresponding depolarization factor. The depolarization is extrapolated to infinite dilution. Equations from Eq. (16) through Eq. (19) give for these factors the expressions :

$$\begin{aligned} (3+3\rho_v)/(3-4\rho_v) &= (1+7\delta) \\ &\times (1+(2/3)(2\pi/\lambda)^2 \langle S^2 \rangle \cdot 7\delta/(1+7\delta)) \end{aligned} \quad (31)$$

$$\begin{aligned} (6+6\rho_u)/(6-7\rho_u) &= (1+13\delta) \\ &\times (1+(2/3)(2\pi/\lambda)^2 \langle S^2 \rangle \cdot 13\delta/(1+13\delta)) \end{aligned} \quad (32)$$

Hence the use of the Cabannes' factor may result in the overcorrection of the anisotropy effect as long as we measure the depolarization at $\theta=\pi/2$. The procedure in which we can completely be free from the anisotropy effect may be simply to measure both $R_{v_v}(\theta)$ and $R_{v_h}(\theta)$ and to subtract $4/3 R_{v_h}(\theta)$ from the former. The analogous but different procedure may be deduced from the results obtained in the previous section, depending upon the experimental conditions of polarization of incident and scattered light.

iii) Depolarization Ratios and their Dependence on Chain Size and second Virial Coefficient

The character of the depolarization of the light scattered transversely by a system of rigid particles depends both on the size and the optical anisotropy of the particle³¹. Small isotropic particles exhibit completely vertically polarized scattered light, while small anisotropic particles show some depolarization. A rigid spherical particle, the size of which is comparable to the wave length of light, also exhibit some depolarization due to quadrupole radiation, although the particle may not be anisotropic as a whole³¹. Homogeneous but nonspherical particles exhibit form anisotropy and the shape of the particle can be determined by using a specific depolarization ratio³². On the analogy of the studies on depolarization of light scattered at 90° by rigid particles, many investigations of depolarization have been performed heretofore on the flexible polymer solutions in order to get information about

the size and shape of the molecule. The situation, however, differs significantly. As already stated, a flexible polymer molecule should be treated not as a spherical particle as a whole, but as an assembly of small particles which are the centers of linear dipolar oscillation. From this point of view, the optical anisotropy obtained for the flexible polymer molecule is not of the whole molecule but of a segment, and provides information about the local structure of the polymer chain.

Using Eq. (16), Eq. (17), and Eq. (18), we obtain for the three depolarization ratios, ρ_v , ρ_h , and ρ_u as :

$$\begin{aligned}\rho_v &\equiv R_{Hv}(\pi/2)/R_{Vv}(\pi/2) \\ &= 3\delta/\{P(\pi/2) - 2A_2MQ(\pi/2)c + 4\delta\}\end{aligned}\quad (33)$$

$$\rho_h \equiv R_{Vh}(\pi/2)/R_{Hh}(\pi/2) = 1 \quad (34)$$

$$\begin{aligned}\rho_u &\equiv \{R_{Hh}(\pi/2) + R_{Hv}(\pi/2)\}/\{R_{Vh}(\pi/2) + R_{Vv}(\pi/2)\} \\ &\equiv (1 + (1/\rho_h))/(1 + (1/\rho_v))\end{aligned}\quad (35)$$

The equivalence of the second and the third term of Eq. (35)³³⁾ states the reciprocity theorem³⁴⁾, that is $H_v = V_h$. Then, ρ_u is a quantity derivable from ρ_v and ρ_h , and is not considered here. Eq. (33) shows that the plot of ρ_v vs. solute concentration gives a straight line, its intercept and slope being $3\delta/\{P(\pi/2) + 4\delta\}$ and $6A_2MQ(\pi/2)\delta/(P(\pi/2) + 4\delta)^2$, respectively.

Since the second virial coefficient increases and the particle scattering factor decreases as the solvent becomes better, both the intercept and the slope are larger for the better solvent systems.

Doty long ago predicted the same behavior of ρ_v for the flexible polymer solutions by means of qualitative examination of the phenomenon⁷⁾, although the reasoning to the conclusion is quite different. The essential point of his treatment may be stated as ; the segment will be shortened or somewhat curled in poor solvent media and this tendency will become more pronounced as the concentration increases. But as long as the polymer molecule is molecularly dispersed in a stable state in solution, the mean end to end distance will be about $1/M^{1/2}$ of the stretched chain length and the linear expansion factor dose not exceed three or four in the extremely good solvent. This consideration may therefore avoid the possibility that the segment will be altered in average configuration in poor solvents, and in fact there is no experimental indication that the effective bond length changes with solvent power. It should be pointed out, however, that the magnitude of δ may possibly be affected by the surrounding medium in electromagnetic sense, although the effect is not clear yet.

Next we turn to the discussion about ρ_h . Generally speaking, ρ_h will be unity irrespective of segmental anisotropy and shape if the terms corresponding to the higher electric and magnetic multipoles can be ignored. But with increasing size and form anisotropy of the segment, this assumption will become unwarrantable. Since the both quantities R_{Vh}/c and R_{Hh}/c depend only on the optical qualities of the single segment as shown in the

preceding section, the knowledge of ρ_h for small rigid particles might directly be applied for flexible polymer molecule. According to Gans and Neugebauer^{32,35}, ρ_h should be expressed as a function of the length of rodlike particles and as a function of the diameter of disklike particles. Furthermore, the numerical value of ρ_h is less than unity for the disklike particles but is greater than unity for the rodlike particles. Hence the measurement of ρ_h may supply some information about the shape of the segment.

III. COMPARISON WITH EXPERIMENTAL DATA AND DISCUSSION

i) Synthetic Polyampholyte and Gelatin in Aqueous Solutions

More than ten years ago, Ehrlich and Doty²³ investigated the solution behavior (light scattering and viscosity) of a polymeric ampholyte, a copolymer of 2-dimethylaminoethyl methacrylate and methacrylic acid, which is soluble in water over the entire pH range of interest. They observed that in the absence of added screening electrolyte, the light scattering behavior of the isoionic polyampholyte was anomalous in that the reciprocal scattering envelopes, including the best extrapolation to zero concentration, showed a negative limiting slope followed by an upward curvature. With increasing the added electrolyte concentration the anomaly disappeared, and they estimated the radius of gyration in 0.1 M NaCl. It may be noted, however, on closer examination of the light scattering data in 0.1 M NaCl, that the envelopes still show upward curvature which may be anomalous, too. The effects of very small changes of pH on both sides of the isoionic point in the absence of added salt were more remarkable and reciprocal reduced intensities decreased monotonically with the angle of observation. Ehrlich and Doty ascribed these anomalous behaviors to the striking indication of pronounced local ordering of the solute molecules which persisted even at the lowest concentrations at which measurements were performed. But if this molecular cluster is stable against the concentration change, the dimension of the cluster ought to be obtained by the light scattering method, and if it is not, the reduced viscosity plot may likewise be anomalous. Moreover, even if the clustering is transient and independent of concentration, the intermolecular interference effect will not be so large as to give negative limiting slope. Therefore, the explanation for the anomaly may have to be sought for in other factors.

In 1961, Nakagaki first considered the effect of optical anisotropy and showed that even negative limiting slope might be obtained due to the effect of segmental anisotropy²⁵. But the anisotropy effect was not considered properly. Here we analyze the data again by using the present theory in order to estimate real quantities of molecular weight, mean square radius of gyration, and the second virial coefficient. Rearrangement of Eq. (20) together with the assumption, $Q(\theta) = P^2(\theta)$ ²⁷, gives for the reciprocal scattered intensity function, $Z(\theta)$, the expressions:

$$1/Z(\theta) = M(1 - 2A_2Mc) \{1 - k \sin^2(\theta/2)(1 - 4A_2Mc) / (1 - 2A_2Mc)\}$$

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$$\begin{aligned}
 & +\delta(13+\cos^2\theta)/(1-2A_2Mc)(1+\cos^2\theta) \\
 & =M(1-2A_2Mc)-Mk(1-4A_2Mc)\sin^2(\theta/2) \\
 & +M\delta(13+\cos^2\theta)/(1+\cos^2\theta), \tag{36}
 \end{aligned}$$

$$1/Z(\theta)-1/Z(\pi-\theta)=Mk(1-4A_2Mc)\{1-2\sin^2(\theta/2)\}, \tag{37}$$

where $k=(4/3)(2\pi/\lambda)^2\langle S^2\rangle$. Therefore, we can estimate the quantity, $Mk(1-4A_2Mc)$, from the slope of the plot, $1/Z(\theta)-1/Z(\pi-\theta)$ vs. $(1-2\sin^2(\theta/2))$. Substituting this quantity into Eq. (36) and plotting $(1/Z(\theta))+Mk(1-4A_2Mc)\times\sin^2(\theta/2)$ against $(13+\cos^2\theta)/(1+\cos^2\theta)$, we obtain both $M(1-2A_2Mc)$ and $M\delta$ from the intercept and the slope of the plot, respectively. If the segment is isotropic, the latter plot will give a flat straight line. Finally, if the experimental data of $Z(\theta)$ at various solute concentration or molecular weight are available, all quantities, M , A_2 , δ , and k may be derived.

The experimental data of Ehrlich and Doty for isoionic P-7 (a fractionat-

Table 1. The anisotropy effect on light scattering results for isoionic polyampholyte in water and in 0.10M NaCl.

Salt conc.	0		0.1M NaCl	
	Corrected for optical anisotropy	Apparent values*	Corrected for optical anisotropy	Apparent values*
$M_{90}\times 10^{-5}$	2.52	2.58	2.52	2.58
$A_2\times 10^4$	-8.44	-4.9	3.41	3.2
k	0.0395	—	0.141	—
$\langle S^2\rangle^{1/2}(\text{\AA})$	89.4**	negative	169**	120
$\delta\times 10^3$	6.7	—	4.5	—

* Ehrlich and Doty.²

** n is assumed 1.334.

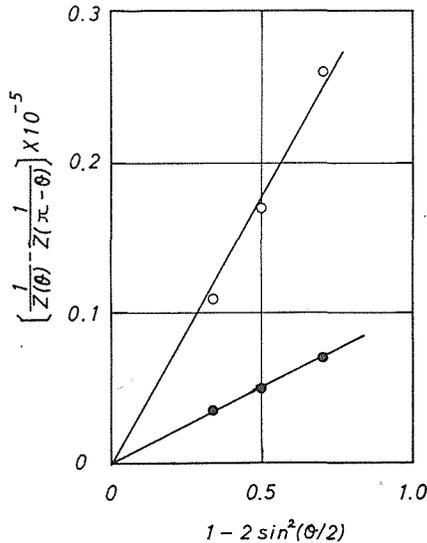


Fig. 1. Plots of $[1/Z(\theta)-1/Z(\pi-\theta)]$ at infinite dilution as a function of $[1-2\sin^2(\theta/2)]$ for isoionic polyampholyte (P-7) in the absence of added electrolyte (filled circles) and in 0.1M NaCl (open circles).

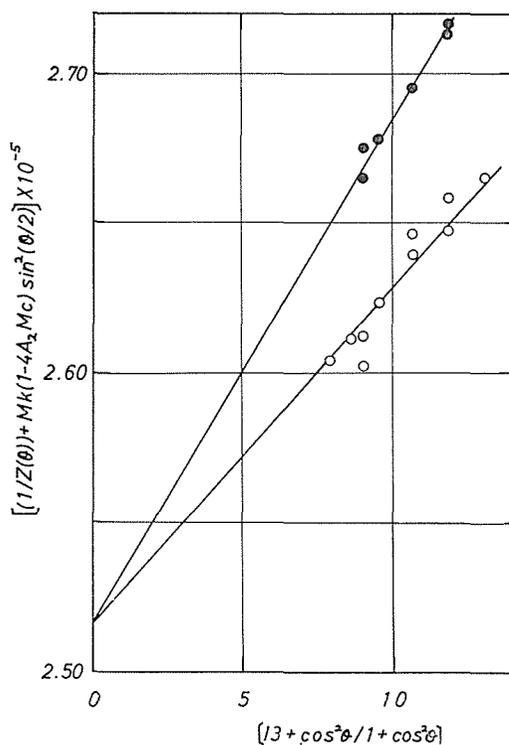


Fig. 2. Plots of $[1/Z(\theta) + Mk(1 - 4A_2Mc) \sin^2(\theta/2)] \times 10^{-5}$ at infinite dilution as a function of $(13 + \cos^2\theta)/(1 + \cos^2\theta)$ for isoionic polyampholyte (P-7) in the absence of added electrolyte (filled circles) and in 0.10M NaCl (open circles).

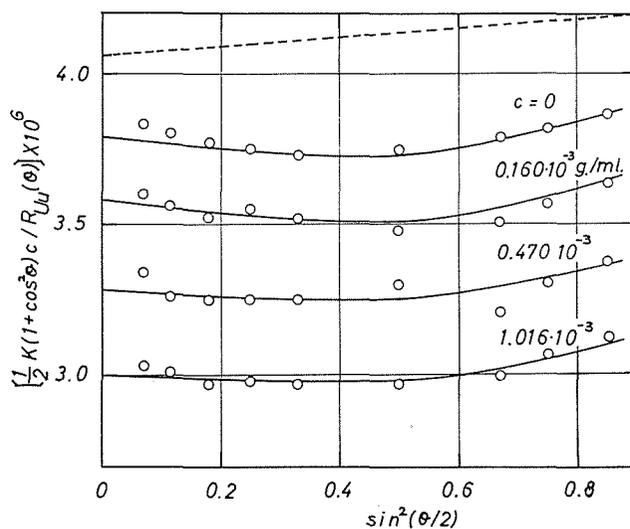


Fig. 3. A comparison of theoretical (solid lines: Eq. (20) with $M_w = 2.52 \times 10^5$, $A_2 = -8.44 \times 10^{-4}$, $k = 0.0395$, $\delta = 6.7 \times 10^{-3}$) and experimental (open circles) values of reciprocal reduced intensity for isoionic polyampholyte (P-7) in the absence of added electrolyte. The dotted straight line shows the reciprocal angular envelope at infinite dilution which is corrected for the effect of optical anisotropy.

ed sample) in the absence of added electrolyte and in 0.1 M NaCl are read off from the figures (Fig. 3 and Fig. 5, in the original paper) and analyzed following the above procedure. The results are shown in Fig. 1 and Fig. 2, and the derived quantities are collected in Table 1 together with those obtained without correction of anisotropy. The reduced scattered intensity function $Z(\theta)$ for isoionic P-7 in the absence of added salt are calculated with these numerical values, for illustration, and compared with experimental values in Fig. 3. It is apparent that the experimental data can quantitatively be cast in the present theory.

It should be stressed here that although the numerical value of δ is of the same order of magnitude as that of atactic vinyl polymers, optical anisotropy actually plays important role in this case because of the relatively small size of amphoteric polymer at isoionic pH. With the use of numerical values of radius of gyration, of second virial coefficient, and of optical anisotropy obtained in the present analysis of the experimental data of Ehrlich and Doty, some important aspects of solution properties of polymeric ampholyte have been brought to light. The detailed discussion about this will be published elsewhere.

The light scattering behavior of amphoteric polymer solution upon the addition of acid or base to aqueous isoionic solution is more anomalous in that the reduced intensity function decreases monotonically with the angle of observation. This behavior cannot be explained by the present theory, because Eq. (37) clearly shows that $Z(\pi-\theta)$ should in general be greater than $Z(\theta)$. In order to obtain the clear explanation of this discrepancy, further information about the angular variation of four components of scattered light is necessary and light scattering investigation on the same polymeric ampholyte is now proceeding in our laboratory.

Next we turn to the discussion about gelatin solutions. Since the gelatin molecule possesses both positively and negatively ionized groups, it may be expected that aqueous gelatin solutions show the similar anomalous light scattering behavior as exhibited by isoionic solutions of synthetic polyampholyte. In fact, Boedtker and Doty³⁶⁾ obtained a negative value for the radius of gyration on a sample of ossein gelatin at the isoelectric point in the absence of added electrolyte. The further analysis of the data is not attempted here, because the range of the angle of observation in their light scattering measurement was restricted below 60°. It should be pointed out, however, that the limiting slope of the constant concentration in Zimm plot increases drastically with concentration, attaining to positive values at the solute concentration greater than 0.06 g./100 ml.. This phenomena, characteristic for gelatin aqueous solution at the isoelectric point, 40°C, clearly shows large dependence of optical anisotropy on concentration.

Another important features of the solution properties of gelatin may be found in the fact that although gelatin molecules are molecularly dispersed in solution at the temperatures higher than 40°C, they form aggregated particles at the lower temperatures, the particle size depending on both tempera-

ture and solute concentration. At somewhat higher concentrations, gelation takes place³⁶⁾. Therefore, the gelatin solution may be suitable for the study of the change of optical qualities of the segment upon the formation of aggregated particles and upon the gelatin. From this point of view, it may be important to reinvestigate the light scattering behavior of gelatin solutions. The detailed experimental results will be published in the near future.

ii) Atactic and Isotactic Polystyrene³⁷⁾

In order to compare Eqs. (16), (17), (18), and (19) with experiment directly, the dependence of the reduced scattered intensity on concentration and the angle of observation was investigated for the four components, V_v , V_h , H_v , and H_h separately on a fraction of atactic polystyrene obtained by the thermal polymerization and fractional precipitation ($M_w=51.2 \times 10^4$).

The scattered intensity was measured in a modified Brice type light scattering photometer (Shimadzu Seisakusho Co., Kyoto) with polarizer and analyzer located in the proper positions. 436 m μ line of mercury arc was used as incident light and the scattered intensity was measured with a Type 1P21 multiplier photo-tube over the angular range from 30° to 135°. The temperature of the test liquid could be kept constant within 0.02°C. Purified monochlorobenzene was used as solvent and all the test liquids were filtered directly into a cylindrical cell through two sheets of cella filter of grade M in order to eliminate dust. The polarized light scattering results on pure liquids such as benzene and carbon tetrachloride coincide with theory quantitatively, which vouches for the accurate construction of the photometer.

Table 2. The angular variation of four components of the reduced scattered intensity for an atactic polystyrene sample in monochlorobenzene at 25.3°C; $c=0.443$ g./dl.

θ	$R_{V_v} \times 10^5$ (obs.)	$R_{V_h} \times 10^5$ (obs.)	$R_{H_v} \times 10^5$ (obs.)	$R_{H_h} \times 10^5$ (obs.)	$R_{H_h} \times 10^5$ (cal.)
30	27.5	0.20	0.19	21.2	20.7
40	26.7	0.27	0.23	16.6	15.7
55	25.4	0.36	0.49	8.83	8.30
70	24.7	0.53	0.53	3.50	3.07
90	23.4	0.70	0.67	0.17	0.20
110	22.6	1.00	0.90	3.11	2.82
130	21.7	1.35	1.23	9.85	9.10
140	21.2	1.42	1.44	13.7	12.5

A typical light scattering results on the atactic polystyrene are shown in Table 2. We begin with the discussion about the behavior of V_h and H_v components. They agree with each other over the angular range investigated in the present study, but they increase with angle. The limiting values at $\theta=0$ seem to coincide with H_h value at $\theta=\pi/2$. Therefore, some additional term which increases with angle may be involved in V_h and H_v components. Moreover this additional term seems to depend on concentration. As shown in Table 3, $R_{H_v}(\pi/2)$ decreases with concentration, while $R_{H_h}(\pi/2)$ is inde-

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Table 3. Concentration dependence of V_h and H_h components, and δ for polystyrene in monochlorobenzene at 25.3°C.

Atactic Polystyrene				Isotactic Polystyrene			
$c(\text{g./dl.})$	$R_{Hv}(\pi/2)/c \times 10^4$	$R_{Hh}(\pi/2)/c \times 10^4$	$\delta \times 10^3$	$c(\text{g./dl.})$	$R_{Hv}(\pi/2)/c \times 10^4$	$R_{Hh}(\pi/2)/c \times 10^4$	$\delta \times 10^3$
0.443	0.153	0.038	0.804	0.107	2.12	1.88	57.1
0.615	0.101	0.049	1.04	0.180	1.69	1.57	47.7
0.759	0.100	0.034	0.727	0.198	2.15	2.03	61.7
				0.228	1.89	1.80	55.5
				0.326	1.75	1.64	49.7
δ average = 0.86×10^{-3}				δ average = 54.4×10^{-3}			

pendent of concentration as Eq. (19) predicts. Hence the anisotropy parameter δ has been estimated from $R_{Hh}(\pi/2)$ and listed in Table 3.

The reduced intensity of H_h component can then be calculated from experimental values of R_{Vv} and δ . The results are also listed in Table 2. The agreement between the observed and the theoretical values seems satisfactory.

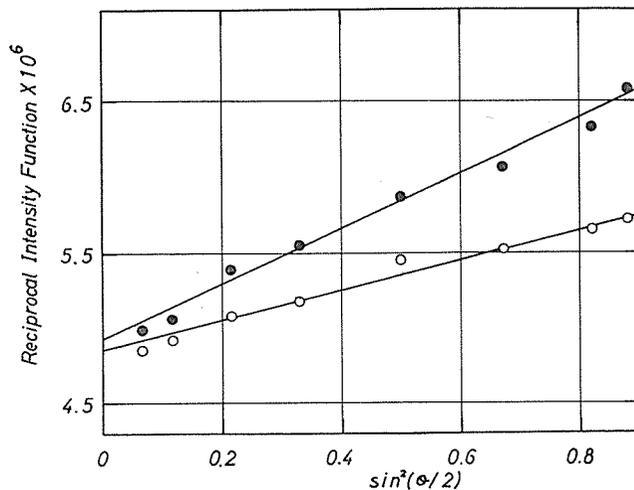


Fig. 4. Reciprocal reduced intensity plot for an atactic polystyrene sample ($M_w=51.2 \times 10^4$) in monochlorobenzene at 25.3°C; $c=0.442$ g/dl.. The closed circles represent $Kc/\{R_{Vv}-4/3R_{Hh}(\pi/2)\}$ and the open circles $K(1+\cos^2 \theta) c/2 R_{Uu}$.

We consider next about the particle scattering factor. Fig. 4 shows the reciprocal scattered intensity plot for U_u component and for the component $\{R_{Vv}-4/3R_{Hh}(\pi/2)\}$. The latter quantity may be taken as such that the anisotropy effect is properly corrected for. The difference in the slope of the two straight lines looks too large to be solely due to optical anisotropy. It will be clearly understood, however, that the above mentioned anomalous tendency of V_h and H_v components to increase with angle makes a large negative contribution to the angular variation of the reciprocal reduced intensity of U_u component. Hence we recommend to estimate the radius of

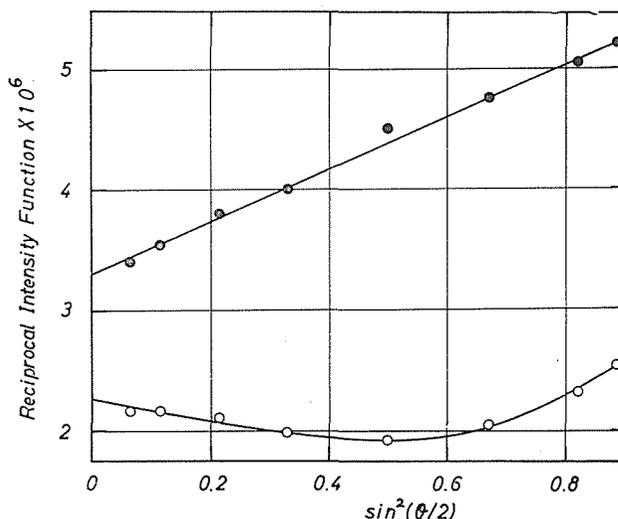


Fig. 5. Reciprocal reduced intensity plot for an isotactic polystyrene fraction ($M_w = 35.9 \times 10^4$) in monochlorobenzene at 25.3°C ; $c = 0.107$ g./dl. The closed circles represent $Kc/\{R_{Vv} - 4/3R_{Hh}(\pi/2)\}$ and the open circles $K(1 + \cos^2 \theta)c/2R_{Vu}$.

Table 4. The angular variation of four components of the reduced scattered intensity for an isotactic polystyrene fraction in monochlorobenzene at 25.3°C ; $c = 0.107$ g./dl.

θ	$R_{Vv} \times 10^6$ (obs.)	$R_{Vh} \times 10^6$ (obs.)	$R_{Hv} \times 10^6$ (obs.)	$R_{Hh} \times 10^6$ (obs.)	$R_{Hh} \times 10^6$ (cal.)
30	122.9	20.1	20.9	101	97.2
40	119.2	20.3	20.5	80.9	78.3
55	112.9	21.2	21.5	32.5	50.0
70	108.4	22.0	22.4	32.1	30.3
90	99.3	22.8	22.7	20.1	20.1
110	95.3	23.3	23.7	29.9	28.9
130	91.2	24.0	24.8	51.3	49.5
140	89.2	24.9	25.0	63.6	60.7

gyration from the latter plot.

In order to see the effect of stereoregularity on optical anisotropy, similar light scattering measurements were made on an isotactic polystyrene fraction ($M_w = 35.9 \times 10^4$), which was separated out from the bulk isotactic polystyrene by a specific fractionation procedure and its film shows large crystallizability. Some typical results are shown in Table 3, Table 4, and in Fig. 5. It may be understood that the light scattering behavior of isotactic polystyrene resembles that of atactic polystyrene in all respects except that the quantity $R_{Hv}(\pi/2)/c$ does not depend on concentration. It should be pointed out, however, that the numerical value of δ of isotactic polystyrene is about sixty times greater than that of atactic polystyrene. In such case, neither molecular weight nor radius of gyration and nor second virial coefficient can be obtained accurately unless the anisotropy effect is taken into account pro-

perly.

Lastly, we briefly discuss about the origin of large optical anisotropy of isotactic polystyrene. According to the calculation by Stein and Tobolsky³⁸⁾, the optical anisotropy of styrene monomer depends significantly upon the assumption which are made regarding the orientation of the benzene ring. The difference of principal polarizabilities along and perpendicular to the C-C bond is; (1) -4.9×10^{-22} (cm³) if all single bonds within the monomer is freely rotating; (2) -6.2×10^{-22} (cm³) if the benzene ring may rotate freely about the bond which connects the benzene ring to the chain; (3) -62.8×10^{-22} (cm³) if the benzene ring is oriented within the plane perpendicular to the axis of the chain. In addition, the corresponding value for an optical segment may in general be greater than that of a monomer unit owing to the restricted internal bond rotation. Hence the large increase in optical anisotropy of polystyrene with the increase in stereoregularity may be a natural consequence of the circumstance that the rotating motion of the benzene ring is restricted to a great extent by the steric hindrance between the successive benzene ring in the isotactic configuration. Therefore the measurement of the optical anisotropy will be a useful method for the determination of the local stereoregularity, because the method is based on an intrinsic property and is not affected by other factors except the solvent effect.

ACKNOWLEDGMENT

The authors are pleased to acknowledge stimulating discussions with Dr. Ryuzo Koyama and Professor Masayuki Nakagaki of our University.

This work was supported in part by a grant-in-aid of research from the Ministry of Education.

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