

A Convenient Method to Determine the Rayleigh Ratio with Uniform Polystyrene Oligomers

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ABSTRACT: The Rayleigh ratio of toluene at 25°C for a wavelength of 632.8 nm was determined by static light scattering measurement of a certified polystyrene reference material PS 2400 with exactly evaluated or certified mass-average molecular mass (M_w). At first, static light scattering measurements were carried out for PS 2400 in toluene with a literature value of the Rayleigh ratio of toluene. Then, corrections of degree of depolarization, density fluctuations, and molecular mass dependence of refractive index incre-

ment were applied to the observed M_w of PS 2400 to obtain apparent M_w . Finally, from the ratio between the apparent M_w and the certified M_w , the Rayleigh ratio of toluene was reevaluated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1953–1959, 2006

Key words: static light scattering; molecular mass distribution; refractive index; Rayleigh ratio

INTRODUCTION

The Rayleigh ratio is one of the most important quantities to determine the mass-average molecular mass (M_w) of polymers by static light scattering. For accurate determination of the ratio, accurate optical geometries are required. However, because of the difficulty in experimental determination of the ratio, most operators usually choose a value for the ratio from the literature. Recently, various kinds of laser light of different wavelengths are used as incident lights for light scattering photometers. Then, it is often difficult to find the Rayleigh ratio measured at the same wavelength. Furthermore, some literature values have large uncertainty. For example, the Rayleigh ratio of benzene at 25°C for the wavelength 546.1 nm has great uncertainty of about 8% among literatures.¹ However, it is often difficult to judge which literature value is the most correct one.

As a conventional method to determine the Rayleigh ratio, pure liquids, low molecular weight compounds, and polymers with known M_w can be used for static light scattering.^{2–4} However, they have advantages and disadvantages.² For example, pure liquids are inapplicable to instruments of low sensitivity and with substantial levels of stray light. On the other

hand, because of the molecular mass distribution, polymer generally gives great uncertainty in the Rayleigh ratio.

Compared to polymers and low molecular mass compounds, oligomers with precisely known molecular mass distribution and higher average molecular mass have advantages in determining the Rayleigh ratio. Although a molecular mass of oligomer can be absolutely determined by some methods, average molecular mass is determined only by light scattering, which must be calibrated by Rayleigh ratio. The experimental standard deviation or precision in light scattering experiments is generally expected to be around $\pm 5\%$ to 10%.^{5,6} Furthermore, even in these experiments, the systematic errors or biases in the Rayleigh ratio and refractive index increment dn/dc were not taken into account. On the other hand, since intensity of scattered light is proportional to the product of molecular mass and concentration, low molecular mass compounds provide much weaker light scattering intensity than oligomers at the same concentration.

Disadvantages of using oligomers originate from the difficulties in the corrections of optical anisotropy, density fluctuation, and molecular mass dependence of dn/dc . Even if the individual correction is small, they cannot be neglected and should be carefully evaluated for exact determination of the Rayleigh ratio. The difficulties in the correction of the optical anisotropy and density fluctuation can be overcome by very careful experiments, because one can apply the procedure in the literature.⁷ On the other hand, because it is almost impossible to obtain an oligomer with pre-

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cisely known molecular mass distribution, correction of molecular mass dependence of dn/dc has never been discussed.

In this study, we propose a convenient and exact method to determine the Rayleigh ratio from static light scattering measurements, using an accurately evaluated polystyrene oligomer with exactly known M_w . Corrections of degree of depolarization and density fluctuation were carried out. Additionally, we propose a new method to correct the molecular mass dependence of the refractive index increment. To confirm the validity of this method, the Rayleigh ratio of toluene at 25°C for 632.8 nm was determined. Toluene is known as a best standard solvent for light scattering, because the Rayleigh ratio is larger than cyclohexane and methanol and the toxicity is lower than benzene.

THEORY AND PROCEDURE

Our theoretical background is based on Einaga et al.'s study, where the second virial coefficient of simple molecules and oligomers in solution was determined.⁷ The procedure for the determination of the Rayleigh ratio is as follows: first, we obtain the Rayleigh ratio due to the isotropic scattering at vanishing scattering angle θ from the total light scattering intensity from a certified polystyrene reference material in solution. We then determine the component originating from concentration fluctuations (concentration scattering) by subtracting the component originating from density fluctuations (density scattering) at finite concentrations from the isotropic Rayleigh ratio. Finally, the Rayleigh ratio is determined from the ratio between the apparent M_w determined by static light scattering with some corrections and the certified M_w determined by supercritical fluids chromatography. A detailed theory for determining an exact Rayleigh ratio is described below.

Correction of degree of depolarization

For a system of independent small scatterers, a correction for degree of depolarization is represented as follows:

$$R_{Uv}^* = R_{\theta=0} \left(\frac{6}{6 - 7\rho_u} \right) \quad (1)$$

where R_{Uv}^* and $R_{\theta=0}$ are the reduced intensity of unpolarized scattered light for vertically polarized incident light and the isotropic Rayleigh ratio at angle $\theta = 0$. The asterisk indicates the scattering from anisotropic scatterers. ρ_u is the depolarization ratio as defined in the following relations:

TABLE I
Measured Molecular Mass of the Polystyrene Samples

Sample code	M_w	M_n
PS-300	455.1	387.2
PS-1000	1007	881.0
PS-2400	2415	2292
SRM 705a*	1.79×10^5	1.67×10^5

* Nominal value by NIST.

$$\rho_u = \frac{I_{Hu=x/2}}{I_{Vu=x/2}} = \frac{2\rho_v}{1 + \rho_v} \quad (2)$$

where $I_{Hu} = \pi/2$ and $I_{Vu} = \pi/2$ are horizontal to vertical component of the scattered intensity at $\theta = \pi/2$ for unpolarized incident light. The depolarization ratio ρ_v is estimated from the measurements of vertical ($I_{Hv} = \pi/2$) and horizontal ($I_{Vv} = \pi/2$) scattered intensity for vertically polarized incident light at $\theta = \pi/2$ for each solution.

$$\rho_v = \frac{I_{Hv=x/2}}{I_{Vv=x/2}} \quad (3)$$

Correction of density scattering

On the basis of the fluctuation theory,^{8,9} the isotropic Rayleigh ratio for the binary solution may be written in the form

$$R_{\theta=0} = R_d + \Delta R_{\theta=0} \quad (4)$$

with

$$R_d = \frac{4\pi^2 n^2 k_B T \left(\frac{\partial n}{\partial p} \right)_{T,m}^2}{\lambda^4 \kappa_T} \quad (5)$$

and

$$\Delta R_{\theta=0} = - \frac{4\pi^2 n^2 k_B T V_0 c \left(\frac{\partial n}{\partial c} \right)_{T,P}^2}{\lambda^4} / \left(\frac{\partial \mu_0}{\partial c} \right)_{T,P} \quad (6)$$

where k_B is the Boltzmann constant, λ is the wavelength of the incident light in vacuum, V_0 is the partial molecular volume of the solvent, c is the mass concentration of the solute, and μ_0 is the chemical potential of the solvent. In this work, the values of isothermal compressibility of the solution κ_T at finite concentrations are calculated from

$$\kappa_T = \kappa_{T,\text{Tot}} + (\kappa_{T,\text{PS}} - \kappa_{T,\text{Tot}}) v_{\text{PS}}^0 c \quad (7)$$

where the physical constants $\kappa_{T,\text{Tot}}$ ($9.23 \times 10^{-4} \text{ cm}^3/\text{J}$ for toluene at 25°C)⁷ and $\kappa_{T,\text{PS}}$ ($4.3810 \times 10^{-4} \text{ cm}^3/\text{J}$ for polystyrene at 25°C)¹⁰ are the isothermal com-

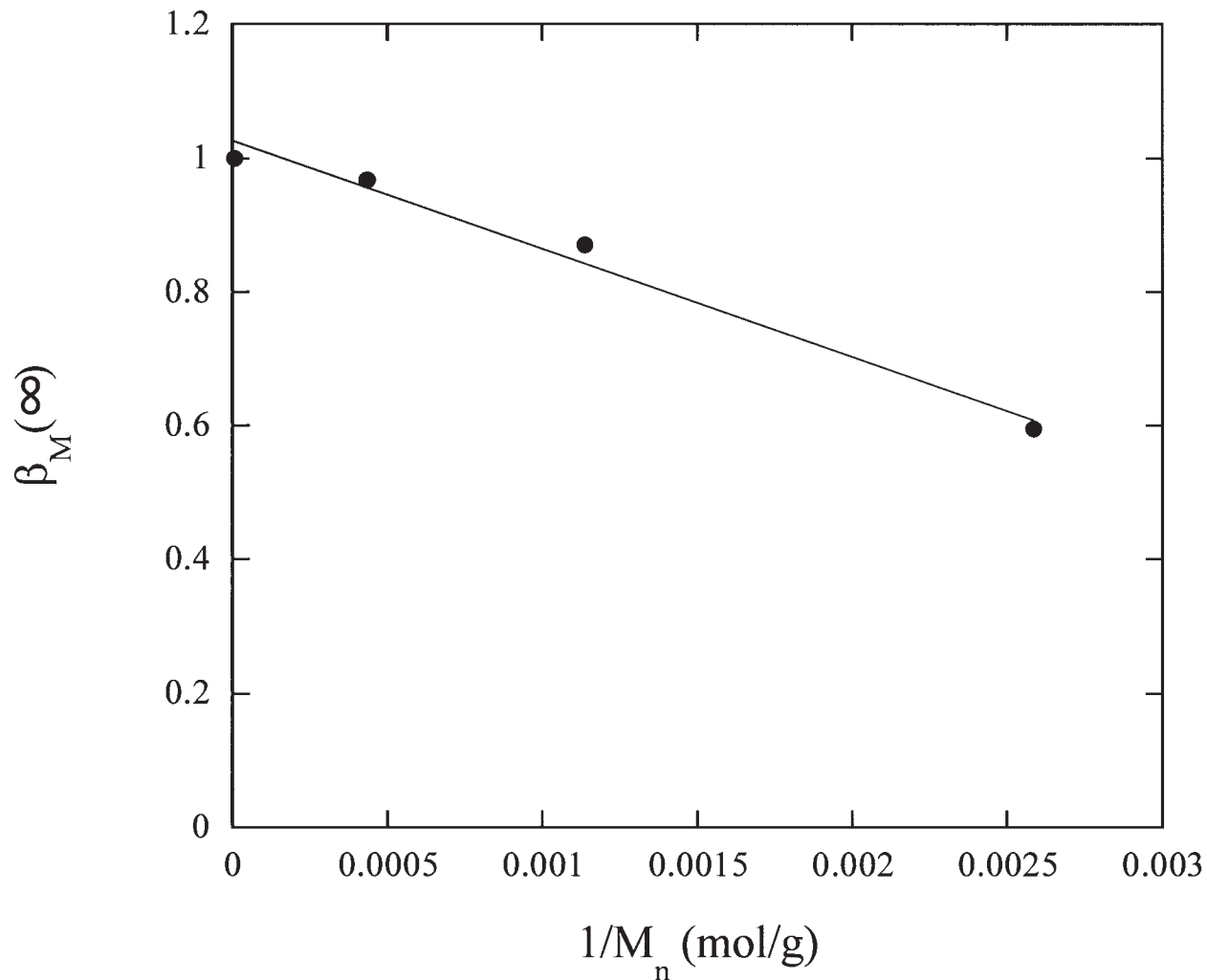


Figure 1 Molecular mass dependence of refractive index increment. Vertical axis shows $\beta_M(\infty) = (1 - d/M_n)$ at eq. (18) against M_n . These data were measured for monodisperse polystyrene reference material. Each data was measured at 5 concentrations and was extrapolated to zero concentration. The solid line represents the least squares fits and (dn/dc) of each i th component was calculated from this curve.

compressibility of solvent and polymer for the pure components, respectively. v_{PS}^0 is the specific volume of the pure polymer (0.96, 153 cm³/g for polystyrene at 25°C).¹¹

Approximation of relationship between density and refractive index

It is very difficult to calculate R_d because we cannot measure the $(\partial n/\partial P)_{T,m}$ easily. Instead of determining R_d directly from eq. (5), we calculate R_d from $R_{d,0}$ of pure solvent using the following equation:

$$\frac{R_d}{R_{d,0}} = \frac{\kappa_T f(n)}{\kappa_{T,Tol} f(n_{Tol})} \tag{8}$$

where

$$\begin{aligned} f(n) &= (n^2 - 1)^2(n^2 + 2)^2 \text{ Lorentz-Lorenz} \\ &= \frac{n^2(n^2 - 1)^2(n + 0.4)^2}{(n^2 + 0.8n + 1)^2} \text{ Eykman} \\ &= n^2(n - 1)^2 \text{ Gladstone-Dale} \\ &= \frac{n^4(n^2 - 1)^2(2n + 1)^2}{(2n^4 + 1)^2} \text{ Oster} \\ &= (n^2 - 1)^2 \text{ Laplace} \end{aligned} \tag{9}$$

These functions are introduced approximately by the use of a relation between n and the solution density ρ_w .

$$h(n) = \text{constant} \times \rho_w \tag{10}$$

where the proportionality constant is assumed to be independent of the pressure p .¹² For the function $h(n)$, various approximate expressions have been given as:

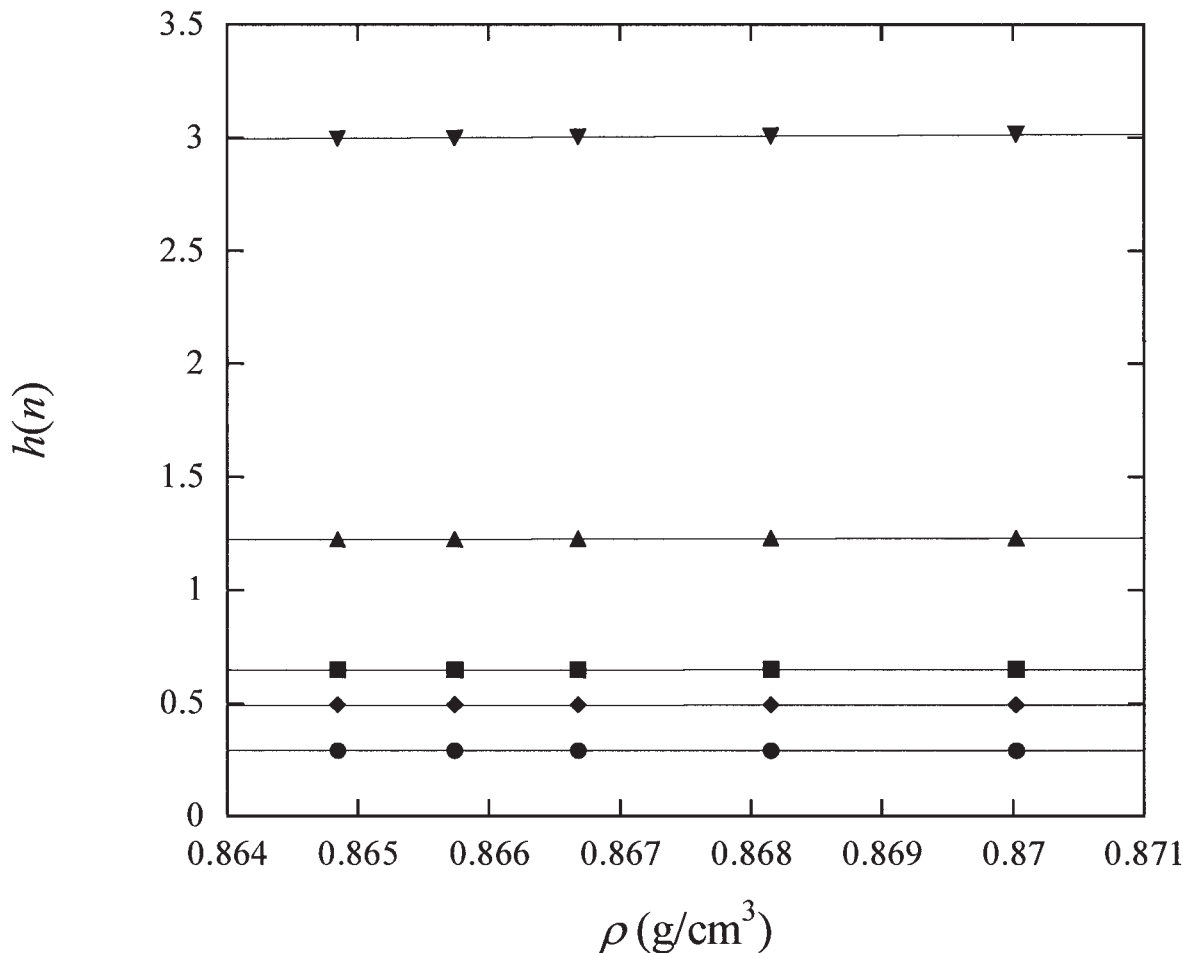


Figure 2 Relationship between density and refractive index. The solid lines represent the fitting curves by $h(n)$ function. [● Lorentz-Lorenz, ■ Eykmán, ◆ Gladstone-Dale, ▲ Laplace, and ▼ Oster at eq. (8)].

$$\begin{aligned}
 h &= (n^2 - 1)/(n^2 + 2) \text{ Lorentz-Lorenz} \\
 &= (n^2 - 1)/(n + 0.4) \text{ Eykmán} \\
 &= n - 1 \text{ Gladstone-Dale} \\
 &= (n^2 - 1)(2n^2 + 1)/n^2 \text{ Oster} \\
 &= n^2 - 1 \text{ Laplace}
 \end{aligned} \tag{11}$$

Differentiation of both sides of eq. (10) with respect to p leads to

$$\begin{aligned}
 \kappa_T^{-1} \left(\frac{\partial n}{\partial p} \right)_{T,m} &= \frac{(n^2 - 1)(n^2 + 2)}{6n} \text{ Lorentz-Lorenz} \\
 &= \frac{(n^2 - 1)(n + 0.4)}{n^2 + 0.8n + 1} \text{ Eykmán} \\
 &= n - 1 \text{ Gladstone-Dale} \\
 &= \frac{n(n^2 - 1)(2n^2 + 2)}{2(2n^4 + 1)} \text{ Oster} \\
 &= \frac{n^2 - 1}{2n} \text{ Laplace}
 \end{aligned} \tag{12}$$

Substituting eq. (12) into eq. (5), we obtain eq. (8) for the ratio $R_d/R_{d,0}$

Since it is very difficult to measure an accurate refractive index (n) of solution, n was calculated from the refractive index increment ($\partial n/\partial c$), the concentration c of polymer, and the refractive index of toluene (n_{Tol}) by the following equation:

$$n_{\text{sol}} = n_{\text{Tol}} + c \left(\frac{\partial n}{\partial c} \right) \tag{13}$$

In common static light scattering measurements for polymers, M_w is calculated by using a constant ($\partial n/\partial c$). For an oligomeric sample, however, it is well known that ($\partial n/\partial c$) depends on molecular mass.¹³ Therefore, a common analysis using a Zimm plot for oligomer gives an apparent mass-average molecular mass $M_{w(\text{app})}$, which is defined as follows:

$$\frac{Kc}{\Delta R_{\theta=0}} = \frac{1}{M_{w(\text{app})}} + 2A_2'c + \dots \tag{14}$$

where

$$M_{w(\text{app})} = \sum v_i^2 w_i M_i \quad (15)$$

with

$$v_i \equiv \frac{(\partial n / \partial c_i)_{T,P}}{(\partial n / \partial c)_{T,P}} \quad (16)$$

The apparent second virial coefficient A_2' is defined as

$$A_2' = A_2 - \frac{RT\kappa_{T,\text{Tot}}}{2M^2} \quad (17)$$

and the optical constant K is given by

$$K = \frac{2\pi^2 n^2}{N_A \lambda^4} \left(\frac{\partial n}{\partial c} \right)_{T,P}^2 \quad (18)$$

where $(\partial n / \partial c)_{T,P}$ is the refractive index increment at infinite molecular mass. $(\partial n / \partial c_i)$ for each oligomer i th component is generally expressed as follows¹⁰:

$$\left(\frac{\partial n}{\partial c} \right)_{T,P} = \left(\frac{\partial n}{\partial c} \right)_{M=\infty} \left(1 - \frac{d}{M_n} \right) \quad (19)$$

where d is a constant dependent on both polymer and solvent. In this study, we used a measured value 0.1065 mL/g of polystyrene in toluene as the refractive index increment at infinite molecular mass $(\partial n / \partial c)_{M=\infty}$.

We can calculate the right side of eq. (15) from the values of certified mass fraction of each component in certificate. On the other hand, we can determine $M_{w(\text{app})}$ using the literature Rayleigh ratio (R_{lit}) from light scattering measurement. Finally, we can calculate the Rayleigh ratio of toluene from the ratio as follows:

$$R_{90}^{\text{Tot}} = \frac{\sum v_i^2 w_i M_i}{M_{w(\text{app})}} \times R_{\text{lit}} \quad (20)$$

EXPERIMENTAL

Materials

An oligomeric polystyrene certified reference material PS 2400 (NMIJ CRM 5001-a; $M_w = 2423 \pm 20$) was provided by a National Metrology Institute of Japan. The molecular mass and the mass fraction of each component were exactly determined by supercritical fluid chromatography (SFC), with some corrections. A spectroscopic grade toluene (Spectrossole; Dojin Chemical Co.) was used as received. To determine the molecular mass dependence of refractive index increment in the oligomeric region, PS-300 and PS-1000

(Tosoh Co.), and SRM 705a (National Institute of Standards and Technology, NIST) were used for measurements of refractive index increment. Molecular mass of the polystyrene samples are listed in Table I. The molecular mass of these polymers were evaluated from their SFC chromatograms in our laboratory except for SRM 705a. The solutions and solvent were optically purified by filtration through Teflon membranes of pore size 0.2 and 0.02 μm , respectively.

Apparatus

Since it is difficult to measure the refractive index directly, an Otsuka Electronics differential refractometer (DRM-1030; $\lambda_0 = 632.8$ nm) was used to determine refractive indices of the polymer solution using eq. (13) with refractive index of toluene and $(\partial n / \partial c)$.

An Otsuka Electronics DLS-7000 static light scattering photometer was used to measure the angular variation of scattered light intensity. It was equipped with He-Ne laser ($\lambda_0 = 632.8$ nm) as incident light source. Intensities of unpolarized, vertical, and horizontal component of scattered light for vertically polarized incident light were measured.

A density meter (DMA-60/602; ANTON PAAR Co.) was used to measure the density of toluene and the polymer solutions to determine the concentration of solutions. Every measurement was controlled at 25°C using a circulating bath.

RESULTS AND DISCUSSION

Density and differential refractive index of polymer solutions as a function of polymer concentration was determined by following equations, respectively.

$$\text{Density}(\text{g}/\text{cm}^3) = 0.8621 \pm 2.183 \times 10^{-7} + 0.1705 \pm 0.5360 \times 10^{-3} \times c(\text{g}/\text{g}) \quad (21)$$

$$\Delta n = -2.383 \times 10^{-5} \pm 2.334 \times 10^{-7} + 0.1016 \pm 0.633 \times 10^{-4} \times c(\text{g}/\text{mL}) \quad (22)$$

These equations were derived by the least-squares fitting for our measured data. To determine the concentration of the solutions, the density of every solution is calculated from eq. (21). The refractive index of each solution is calculated by combining eq. (13) and (22).

Figure 1 shows molecular mass dependence of $(\partial n / \partial c)$ of the polystyrene oligomers in toluene. It was found that the linear fitting can be given by the following equation:

$$\left(\frac{\partial n}{\partial c} \right)_{T,P} = \left(\frac{\partial n}{\partial c} \right)_{M=\infty} \left(1 - \frac{157.16}{M_n} \right) \quad (23)$$

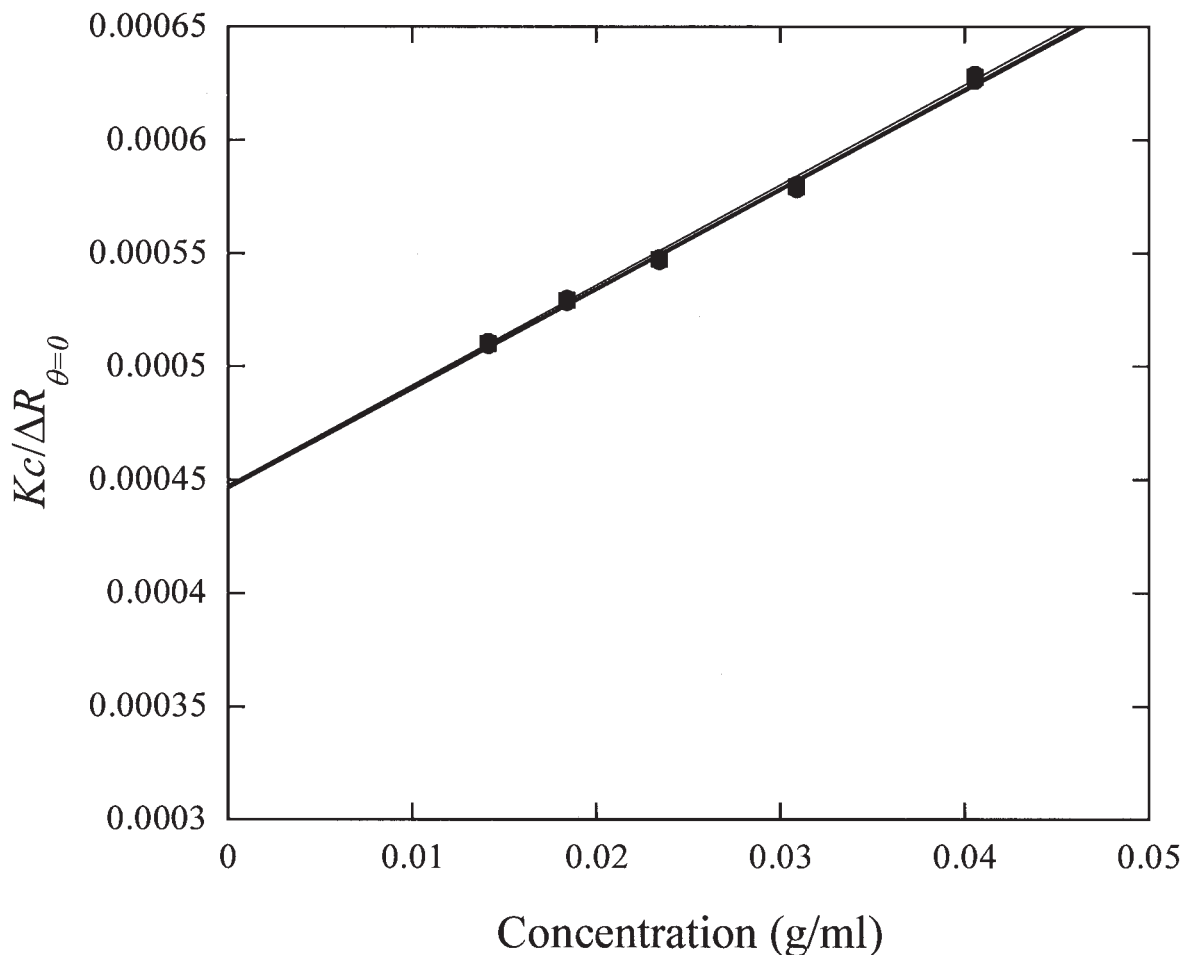


Figure 3 Zimm type plot at scattering angle θ as a function of polymer concentration. (Approximation function: ● Lorentz-Lorenz, ■ Eykmán, ◆ Gladstone-Dale, ▲ Laplace, and ▼ Oster).

Figure 2 shows $h(n)$ fitted with various approximate expressions of eq. (8) as a function of density. Although the Lorentz-Lorenz or Eykmán equations were recommended for oligomers by Einaga et al., there was no significant difference among these equations in our study, probably because of the narrow concentration range. For toluene, they showed that the corrected M greatly depends on the type of equations for $f(n)$. The observed relative difference between the maximum and minimum of the corrected M is over 10%.

In Figure 3, a Zimm type plot is shown as a function of concentration. Each data was extrapolated to the dilute limit to calculate intercepts. The Rayleigh ratios of toluene were evaluated from eq. (21) as the intercepts of corresponding equations.

The values of R_{90}^{tol} determined by our method and the values that were determined by other authors using specially designed optical system are listed in Table II and III, respectively. The Rayleigh ratio of the toluene determined by our method is $1.34 \times 10^{-5} \text{ cm}^{-1}$. This value shows good agreement with previ-

ous values, especially Pike et al.'s value. Furthermore, our method also had small standard deviation of repeatability. One can determine Rayleigh ratio in an arbitrary condition with small uncertainty more than the values in the previous papers, because the uncertainty is very small for PS-2400 also, which is used as standard polystyrene.

TABLE II
Rayleigh Ratio of Toluene Calculated from Approximate Expressions

	Rayleigh Ratio of Toluene (cm^{-1})
Lorentz-Lorenz	$1.342 \times 10^{-5} \pm 1.9 \times 10^{-7}$
Eykmán	$1.340 \times 10^{-5} \pm 1.9 \times 10^{-7}$
Gladstone-Dale	$1.340 \times 10^{-5} \pm 1.9 \times 10^{-7}$
Oster	$1.338 \times 10^{-5} \pm 1.9 \times 10^{-7}$
Laplace	$1.338 \times 10^{-5} \pm 1.9 \times 10^{-7}$
Average	$1.340 \times 10^{-5} \pm 1.9 \times 10^{-7}$

TABLE III
Rayleigh Ratio of Toluene from the Literature

Investigator	$R_{90}^{\text{tol}} \times 10^5$ (cm^{-1})	Temperature ($^{\circ}\text{C}$)	Reference No.
Pike et al.	1.359	22	[14]
Huglin et al.	1.41	25	[15]
Kaye and McDaniel	1.406	23	[16]
Kaye and Havlik	1.345	22	[17]
Standard deviation	0.033	—	—

CONCLUSIONS

The Rayleigh ratio of toluene at 25°C for wavelength 632.8 nm was successfully determined using a conventional method on the basis of the well-established theory of fluctuations in multi component systems. The values of Rayleigh ratio had a good agreement with previous literature values. In this method, we can get good repeatability with small variation. Since the value of Rayleigh ratio does not depend on the type of approximate relations between density and refractive index in this study, we can average the values calculated from all the approximate equations for the Rayleigh ratio. The present procedure will be applied to the determination of the Rayleigh ratio for arbitrary experimental condition, wavelength of laser, and calibration solvents, without using any complicated optical systems.

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