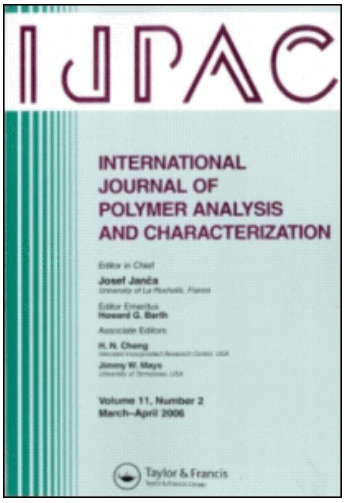

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Particle Size Analysis using Continuous-Angle Laser Light Scattering*

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The estimation of particle size from the particle scattering factor was performed using a recently developed continuous-angle laser light scattering instrument. The angular dependence of the scattered intensity between $\theta = 10°$ and 170° was measured with an angular resolution of 0.6°. Latices of 0.212, 0.262 and 0.777 μm diameters were used and the data compared with Mie theory. For monodisperse samples of 0.212 and 0.777 μm latices, measured data show good agreement with the theoretical curve. A mixture of monodisperse latices was also evaluated. Two different mixing ratio in particle number, 0.262 μm : 0.777 μm = 9 : 1 and 26 : 1 were calculated as 11 : 1 and 32 : 1, respectively, from fitting the theoretical curve.

Keywords: Continuous-angle laser light scattering; Mie theory;
Particle scattering factor; Particle size measurement; Particle size distribution

INTRODUCTION

Light scattering is a useful method to measure particle size and the size distribution of polymers and colloidal suspensions. Dynamic light scattering is used widely for relatively small particles. For dynamic light scattering, the decay time of the autocorrelation function is measured by means of photon correlation spectroscopy (PCS).

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The autocorrelation function from the polydisperse system can be represented as a sum of correlation functions. Many data analysis processes, such as cumulative[1] and histogram[2] methods, are applied to calculate the size distribution of a polydisperse system. However, the resolution and the reproducibility are relatively poor due to the ill-conditioning of the inversion of PCS data; these are still long-term issues to be addressed.

On the contrary, static light scattering, a method of particle size determination from a measurement of the particle scattering factor (PSF) is an alternative way that has an advantage over PCS in speed and resolution. Several attempts[3–6] have been reported for the particle size distribution measurement from static light scattering data. The PSF data is analyzed by Rayleigh–Gans–Debye theory and Mie theory for the particles of diameter up to a few microns. For the determination of the precise PSF, the measurement of angular dependence of the scattering intensity in a wide angular range with high resolution is required.

The PSF can be measured by conventional static light scattering instrument with high resolution, but the measurement takes an impracticably long time. Multi-angle light scattering instruments using fiber optics or a multi-detector measure the PSF with a sufficiently high speed. However, the precise PSF determination is difficult because the angular resolution is limited.

We have recently developed a new light scattering instrument, continuous-angle laser light scattering (CALLS). The CALLS instrument shows good performance in both angular resolution and measurement speed and is suitable for the precise measurement of PSF. In this paper, we report the results concerning particle size measurement of the latex suspension using the CALLS instrument and discuss the applicability of the PSF to particle size estimation.

THEORY AND APPARATUS

Mie Theory

From Mie theory, the PSF for a vertically polarized incident light can be represented as follows:[7,8]

$$I_S(\theta) = \frac{I_0}{k^2 r^2} |S_1(\theta)|^2 \tag{1}$$

where k is the wavenumber, r is the distance between the scattering particle and the point of intensity measurement, and

$$S_1(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos\theta) + b_n \tau_n(\cos\theta)]. \tag{2}$$

The angle-dependence functions are

$$\tau_n(\cos\theta) = \frac{\mathrm{d}}{\mathrm{d}\theta} P_n^{(1)}(\cos\theta), \tag{3}$$

$$\pi_n(\cos\theta) = \frac{P_n^{(1)}(\cos\theta)}{\sin\theta}, \tag{4}$$

where $P_n^{(1)}(\cos\theta)$ is the Legendre polynomial. The scattering coefficients a_n and b_n for a homogenous sphere are

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)}, \tag{5}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)} \tag{6}$$

where m is the relative refractive index. The size parameter, x, is represented by $x = ka$ where a is a radius of sphere. $\psi_n(\rho) = \rho j_n(\rho)$ is Riccati–Bessel function and $\xi_n(\rho) = \rho h_n^{(1)}(\rho)$ is Hankel function.

Apparatus

CALLS is a novel technique that can achieve the simultaneous measurement of angular dependence of scattering light over a wide range with high resolution. Figure 1 illustrates a schematic diagram of optics for the CALLS instrument. The key components of this instrument are an ellipsoidal mirror and a charge-coupled device (CCD) detector. The ellipsoidal mirror collects the scattering light from the wide-angle range and the CCD measures the intensity of scattering light introduced by the ellipsoidal mirror The measurable angle range of the

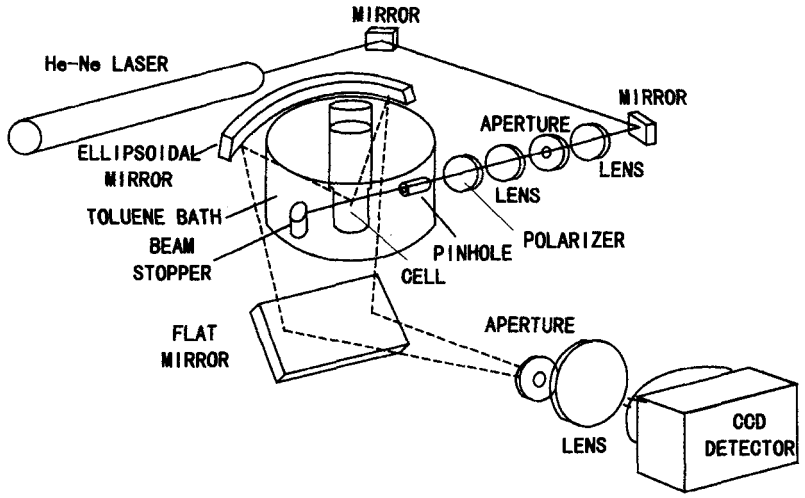

FIGURE 1 Schematic diagram of the optical portion of the instrument.

instrument is 10°–170° and the angular resolution is about 0.6°. The period for the data acquisition depends on the intensity of scattered light, and is typically less than 1 s. Detail specification and basic characteristics of the instrument are described elsewhere.[9]

EXPERIMENTAL

Aqueous suspensions of latex spheres (Dow Chemical Co., Midland, MI) of 0.212, 0.262 and 0.777 μm nominal diameters were used. The standard deviations of the diameters for the latices are 0.0029, 0.0031 and 0.0183 μm, respectively. The latex suspensions were diluted with deionized water. The mixture samples were prepared from two latices of 0.262 and 0.777 μm. From the concentration of each latex suspension, the ratio in particle numbers of the two latices in the mixture were determined as 9 : 1 (mixture 1) and 26 : 1 (mixture 2). Before the measurement, the latex suspension of 0.212 μm diameter was filtered using a 0.45-μm Durapore membrane filter (Millipore Co., Bedford, MA). A Durapore filter of 5 μm was used for the latex suspensions of 0.777 μm only and the mixture of the two latices.

In each measurement, the dark current of the CCD was measured and subtracted from the scattered intensity of the latex particles. Neutral-density filters and the exposure time of the CCD detector were adjusted not to exceed the capacity of the detector at low scattering angles where the intensity of the scattering light was more intense.

RESULTS AND DISCUSSIONS

Figures 2 and 3 show the angular dependence of scattered intensity from latex suspensions of 0.212 and 0.777 μm diameter, respectively. The intensity of scattered light is normalized by the intensity at the scattering angle of 30°. The solid lines in the figures represent the theoretical curves for the particle scattering function calculated based on Mie theory. A refractive index of 1.59 for the latex sphere was used for the calculation. A He–Ne laser was used for this experiment so that wavelength for the calculation was 632.8 nm. Figures 4 and 5 indicate the relative scattering intensity normalized at 30° obtained

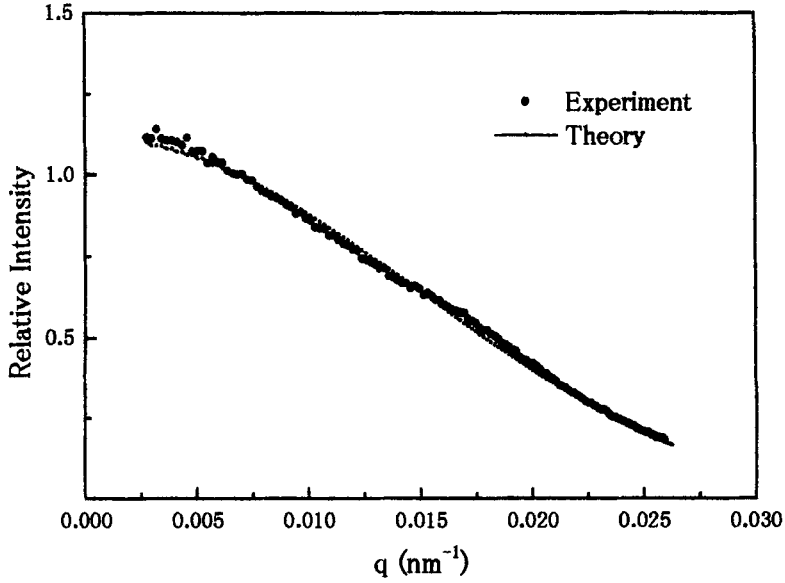

FIGURE 2 Plots of the relative intensity vs. q for 0.212 μm latex spheres.

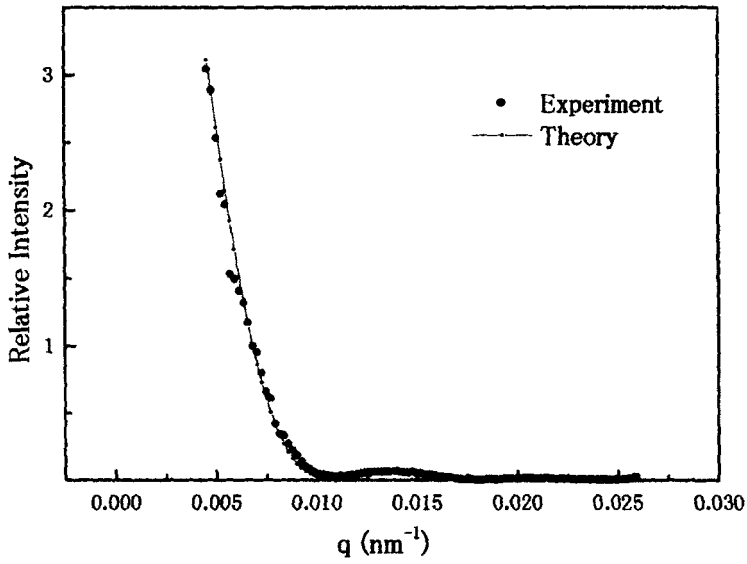

FIGURE 3 Plots of the relative intensity vs. q for 0.777 μm latex spheres.

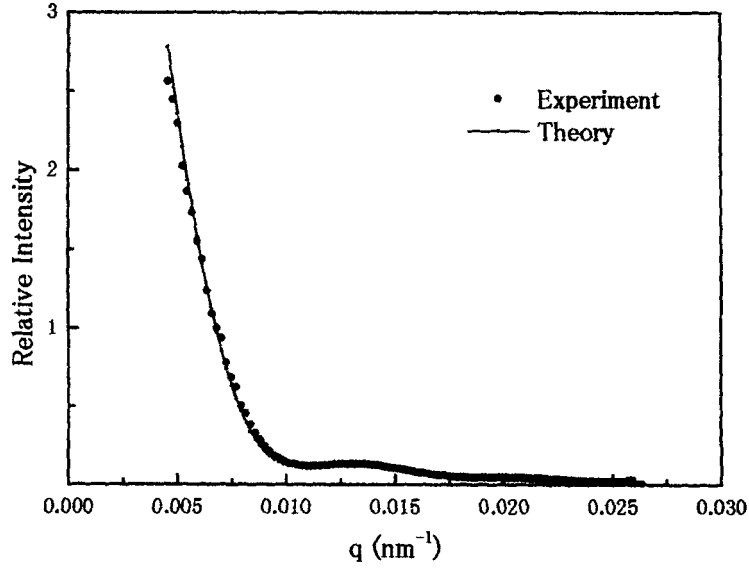

FIGURE 4 Plots of the relative intensity vs. q for the mixture of 0.262 and 0.777 μm latex spheres. Mixture ratio is 0.262 : 0.777 = 9 : 1 (mixture 1).

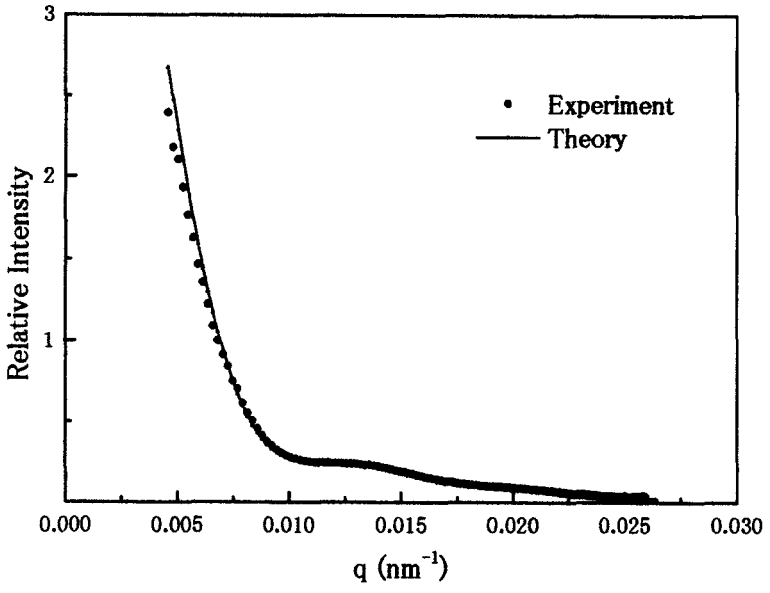

FIGURE 5 Plots of the relative intensity vs. q for the mixture of 0.262 and 0.777 μm latex spheres. Mixture ratio is 0.262 : 0.777 = 26 : 1 (mixture 2).

from the latex mixtures of 0.262 and 0.777 μm. The theoretical curves represented by solid lines in figures are estimated as the sum of the particle scattering factor for both latices. The particle scattering factor is normalized to be unity at the scattering angle of 30° for both latex and then the sum is calculated by combining two factors at a certain ratio. The ratio is variable and calculated theoretical curve is optimized to obtain the best fit to the measured data by trial and error.

For all latex suspensions, the theoretical curve shows good agreement with the measured data. The data from latex of 0.212 μm are in fair agreement over the wide scattering vector range, q, between 0.0025 and 0.025 nm^{-1} and the data for the 0.777 μm latex is fitted satisfactorily to the theoretical curve in the relatively narrow range of $q = 0.005–0.025\ nm^{-1}$. The angular dependence of the scattered intensity become more steep when the size of the particles is larger. For example, the scattering intensity ratio I_{30}/I_{90} is about 2.2 for the 0.212 μm latex and is greater than 100 for the 0.777 μm latex. For the suspension that includes the 0.777 μm latex, the scattering intensity at a very low angle, $q < 0.005\ nm^{-1}$ is too strong and may exceed the

linearity range of the detector, thus the deviation of the measured data from the theoretical curve cannot be ignored. However, the range of $q = 0.005–0.025\,\mathrm{nm}^{-1}$ is sufficiently enough to determine the particle size.

For the mixture of the two latices, the data between $q = 0.005$ and $0.025\,\mathrm{nm}^{-1}$ was used to determine the ratio of the particle number in the mixture. The ratio of two scattering factors is first determined as the theoretical curve. Since both scattering factors is normalized at 30° to be unity, the intensity ratio (normalized factor) at 30° is multiplied to the ratio determined by the intensity for the calculation of the number ratio. The number ratio of 0.262 μm : 0.777 μm obtained from the calculation are 11 : 1 (mixture 1) and 33 : 1 (mixture 2), respectively. The results show that the ratio of 0.262 μm is slightly higher than the original ratio. Although the reason of this deviation is not clear, one thing to be addressed is the concentration of the suspensions. In this experiment, the concentration of 1×10^{-4}wt% of the solid was used. It can be considered as very dilute and absolutely no multiple scattering was observed; however, the details of the concentration dependence have not been studied at present.

CONCLUSION

The data represented in this article demonstrates the possibility of determining the particle size from the particle scattering factor. The measurement of the angular dependence of the scattering light gives useful information of the particle size. Furthermore, the CALLS instrument is a novel tool for this experiment since it measures the scattering intensity from all scattering angles simultaneously, resulting in a high-speed measurement with a high angular resolution.

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