

# A Simple Technique for Measuring the Refractive Index of Polymer Latexes at Various Wavelengths

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## Synopsis

The refractive index of emulsions of polymers and copolymers may be estimated from absorbance readings with a UV-visible spectrophotometer. Other information needed is the weight-average particle diameter, from other techniques such as gradient disc centrifugation. A simple computer program matches the refractive index parameter so that calculated and experimental absorbances are equal at the given wavelength. The wavelength dependence of the polymer refractive index is readily obtained.

## INTRODUCTION

The refractive index of organic polymers lies within the range of about 1.3–1.6<sup>1</sup> Knowledge of the wavelength dependence of the refractive index of polymers and copolymers is required in various analyses, including the measurement of particle sizes of emulsions by hydrodynamic chromatography or gradient disc centrifugation. This article describes a simple procedure for obtaining this information. In essence, the measured absorbance of a dispersion of the polymer is compared with the theoretical absorbance from Mie scattering theory.<sup>2</sup> Mie theory relates turbidity (or absorbance) of a dispersion to the mean particle size of the dispersed material through a scattering coefficient. The magnitude of the scattering coefficient depends on a number of factors, including the refractive index of the dispersed polymer. Therefore, the refractive index of the polymer may be extracted from absorbance measurements if the mean particle size of the polymer dispersion is known from other measurements. In practice, the refractive index parameter in Mie theory calculations is chosen so that the calculated absorbance matches the measured value at the given wavelength. Alternatively, as is well known, mean particle size information is available from the measure absorbance if the polymer refractive index is known.

Most published refractive indices of polymers have been measured at the wavelength of the sodium D line (589.3 nm). There is little information on the refractive index of polymers as a function of wavelength. In this study, a UV-visible spectrophotometer was used to characterize refractive indices of various polymer latexes at a number of different wavelengths. The polymers

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examined included polystyrene, poly(methyl methacrylate), and a copolymer of vinyl acetate and dibutyl maleate. The technique described may also be used to calibrate spectrophotometer absorbance readings for mean particle sizes of emulsions of different polymers.

### THEORY

There are a number of theories to account for the scattering of light by dissolved or suspended material. Most theories are restricted to certain conditions in their application. These conditions are conveniently described by values of  $m$  and  $\alpha$ , where  $m$  is the ratio of the refractive indices of the scattering particle and surrounding medium and  $\alpha$  is defined as equal to  $\pi D/\lambda$ , with  $\lambda$  being the wavelength of light that is scattered by an entity with diameter  $D$ .

The earliest theory of light scattering by small particles was developed by Lord Rayleigh.<sup>3</sup> Rayleigh scattering is restricted to values of  $\alpha \leq 0.4$  for any value of  $m$ . Rayleigh scattering equations, as amended by Einstein, Debye, and others, are the basis for use of light scattering measurements to estimate weight-average molecular weights of dissolved polymers.<sup>4</sup> Rayleigh theory is not applicable to polymer latexes, which are usually comprised of particles with sizes of the order of the wavelength of the light that is used.

A theory of Gans, Roman, and Debye<sup>5</sup> accounts for observed behavior when  $\alpha \leq 0.4$  and  $m \leq 1.05$  while the Rayleigh-Gans theory<sup>4,5</sup> is applicable to any particle size if  $m$  is small enough. The only current theory that is generally useful for polymer latices is that of Mie.<sup>2</sup> This treatment places no restrictions on the values of  $m$  and  $\alpha$ . However, the calculations that are involved are quite complex and applications of the Mie theory require use of a computer. (A microcomputer is adequate in the present case.)

The scattering functions calculated from Mie theory express an extinction coefficient  $Q$  as a function of the size of the scatterer. These functions have the general form shown in Figure 1. The scattering function rises to a maximum at a certain value of  $\alpha$  (defined above) and then decays into smaller, secondary maxima. We are concerned with the region up to the first maximum, with polymer latices in the size range of 0.1–1  $\mu\text{m}$ .

The turbidity,  $\tau$ , of a solution or a dispersion is given by

$$\tau = \frac{1}{l} \ln \left( \frac{I_0}{I} \right) \quad (1)$$

where  $I_0$  and  $I$  are, respectively, the intensities of the incident and transmitted light and  $l$  is the path length of the transmission cell. Mie theory predicts the following expression for  $\tau$ :

$$\tau = Q_{\text{ext}} \pi r^2 N \quad (2)$$

Here  $r$  is the radius of the scattering particles,  $N$  is the number of particles per cubic centimeter, and  $Q_{\text{ext}}$  is the scattering efficiency of the particles.<sup>6</sup> Letting  $c$  be the concentration of the scattering particles and  $\rho$  their density, then

$$c = \frac{4}{3} \pi r^3 \rho N \quad (3)$$

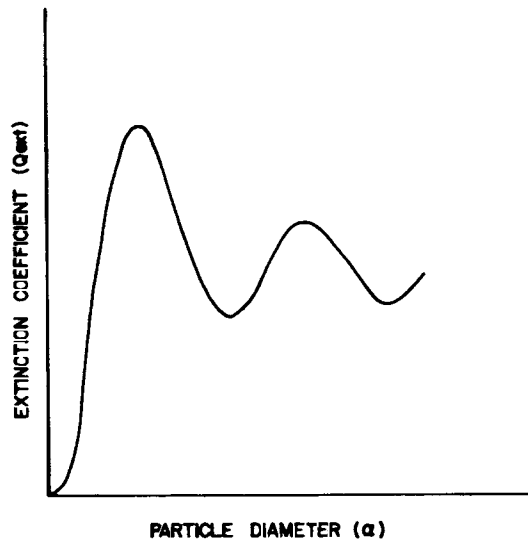


Fig. 1. Extinction coefficient as a function of the size parameter  $\alpha$  for Mie scattering.

and eq. (2) becomes

$$\tau = \frac{3Q_{\text{ext}}c}{4\rho r} = \frac{3Q_{\text{ext}}c}{2\rho D} \quad (4)$$

where  $D$  is the particle diameter. Multiplication of both sides of eq. (4) by  $\lambda_m/\pi$  ( $\lambda_m$  is the wavelength of light in the continuous medium) and rearrangement leads to

$$\left(\frac{\tau}{c}\right) \frac{2\rho\lambda_m}{3\pi} = \frac{Q_{\text{ext}}}{\alpha} \quad (5)$$

Recall that

$$\alpha = \pi D/\lambda \quad (6)$$

The turbidity is related to the absorbance  $A$  by

$$\tau = 2.303A/l \quad (7)$$

Introducing eq. (7) into eq. (5) and changing the concentrations from grams per cubic centimeter,  $c$ , to grams per liter,  $C$ , one obtains

$$\frac{A}{C} = \frac{3\pi l}{4606\lambda_m\rho} \left(\frac{Q_{\text{ext}}}{\alpha}\right) \quad (8)$$

The scattering efficiency  $Q_{\text{ext}}$  of the particles depends on a number of factors:

1. The ratio of particle diameter  $D$  to the wavelength of the radiation in the continuous medium  $\lambda$ . This ratio is most usually represented by the quantity  $\alpha$ .

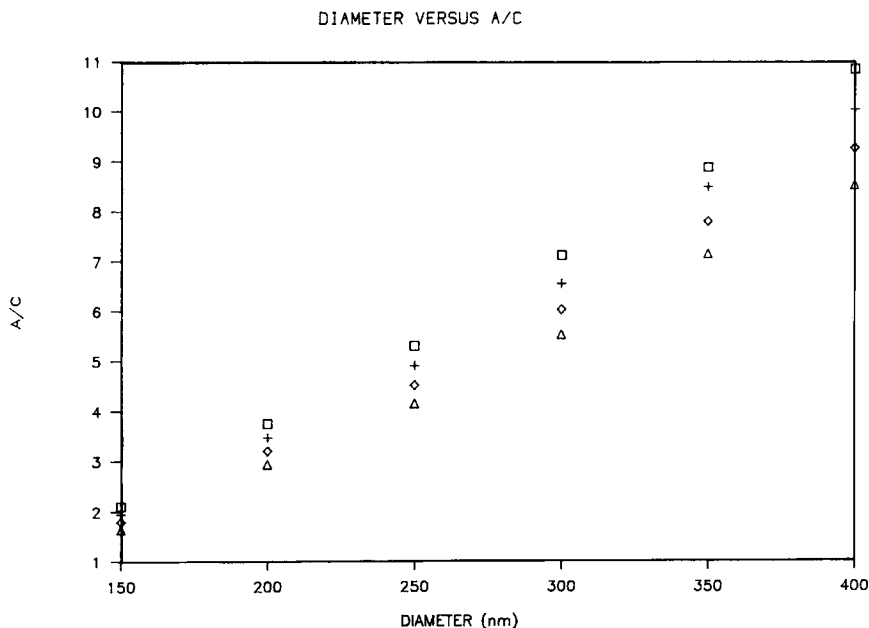


Fig. 2. Plot of  $A/C$  vs. particle diameter for polystyrene latexes at 589 nm. Various values of the refractive index of polystyrene have been assumed for these calculations, which are based on Mie scattering and eq. (8). RI: (□) 1.60; (+) 1.59; (◇) 1.58; (△) 1.57.

2. The refractive index  $\eta$  of the particles.

3. The shape of the particle and its orientation in the light beam (with spherical particles this consideration may, obviously, be neglected).

In a given system there is a high sensitivity of  $Q_{\text{ext}}(\eta, \alpha)$  on refractive index. The sensitivity of the estimated particle size to the refractive index of the particles is illustrated in Figure 2, where  $A/C$  is plotted against  $D$  for polystyrene latices. Here the particle diameter  $D$  is entered through eq (3), and  $A/C$  is calculated as a function of  $D$  using Mie theory calculations for given  $\eta$  values. The true value for the polystyrene refractive index is 1.59 at 589-nm wavelength (see below). Evidently, considerable error in estimating  $D$  from  $A/C$  can be introduced if an incorrect refractive index is assumed for the polymer particles.

The present procedure for estimating  $\eta$  involves the calculation of values for  $Q_{\text{ext}}$  using Mie theory, for given  $\alpha$  and  $\eta$  values, and comparing the results with experimentally measured  $A/C$  values. A computer program eliminates the more tedious aspects of curve fitting in the calculation of  $Q_{\text{ext}}$ .<sup>7</sup> The refractive index value that yields good agreement between the experimental and calculated  $A/C$  is taken to be the refractive index of the polymer at the particular wavelength. An independent measure of  $D$  is needed, of course, to calibrate the method.

The effect of particle size distribution of refractive index of the polymer is small. The measured  $D$  corresponds to the turbidity that would be obtained from a corresponding monodisperse latex with the same diameter as an average value of the real, polydisperse emulsion. Our results indicate that  $D$  measured using the UV-visible spectrophotometer corresponds to the weight average diameter  $D_w$  as measured by gradient disc centrifugation.

## EXPERIMENTAL

A polystyrene latex of narrow particle size polydispersity and a mean particle size of 236 nm was obtained from Seragen Diagnostics. A poly(methyl methacrylate) latex of narrow particle size distribution was synthesized with the use of a mixture of anionic and nonionic surfactants. The technique used in this synthesis is essentially that of Woods et al.<sup>8</sup> A polydisperse poly(vinyl-acetate-co-dibutylmaleate) (85/15 ratio by weight) latex was synthesized using an emulsion polymerization recipe published elsewhere.<sup>9</sup>

The 236-nm particle size of the polystyrene latex was confirmed with a Joycel Loebl disc centrifuge and with the spectrophotometer [with eq. (8)] by taking the refractive index of the polymer to be 1.59, which is refractive index that is reported at the sodium *D* line of 589.3 nm.<sup>1,10</sup> The particle size of the poly(methyl methacrylate) latex was determined with the disc centrifuge and the spectrophotometer. The number-average diameter was 296 nm and the weight-average diameter was 307 nm. The particle size of the copolymer latex was measured by hydrodynamic chromatography and disc centrifugation. This latex has a uniformity index ( $D_w/D_N$ ) of 1.42. Equation (8) provides a good estimate of weight-average diameter of the particles for this copolymer when the refractive index of the copolymer is taken to be equal to the refractive index of poly(vinyl acetate) (1.47<sup>1</sup>), at a wavelength of 589.3 nm. The density of the polymer in these latexes was measured by the method of Seidewand and Erickson.<sup>11</sup>

Samples were prepared for spectrophotometric measurements by dilution with water to the concentration that gave absorbance readings on the most accurately read part of the scale on the spectrophotometer. That is, absorbances were read in the range of 0.0–0.7. The concentration of the latex was measured by weighing a sample of latex into a tared aluminum pan, drying in a vacuum oven overnight, and then reweighing the pan. All absorbance measurements were read on a Bausch and Lomb Spectronic 20 spectrophotometer using test tubes of path length 1.17 cm. All absorbance measurements were made at room temperature (approx. 22°C). The refractive index of the continuous medium, water, was calculated from a standard equation found in the literature.<sup>12</sup>

$$\eta = \left[ 1.762530 - 0.0133998\lambda^2 + \frac{0.00630957}{(\lambda^2 - 0.01588)} + 10^{(107.731(0.064156 - \lambda^2) - 5)} \right]^{1/2} \quad (9)$$

Conventional spectrophotometers like the one used here are not designed to reject light scattered at small angles to the incident direction. The resulting error in calculated refractive index is trivial, however, if the particles are not too large.

## RESULTS

Table I lists the refractive indices measured with this technique for the polystyrene and poly(methyl methacrylate) latexes. Good agreement between published values for the refractive indices and our values is observed. Table II illustrates the measured refractive indices of the copolymer latex.

TABLE I  
Refractive Indices of Polystyrene and Poly(methyl methacrylate)

$\lambda$ (nm)	$\eta$	Literature	Ref.
Polystyrene			
400	1.600	1.628	10
436	1.589	1.617	10
546	1.580	1.596	10
589	1.578	1.59-1.60	10-12
Poly(methyl methacrylate)			
400	1.496		
436	1.495	1.502	13
546	1.494	1.494	13
589	1.492	1.492	13

TABLE II  
Apparent Refractive Index of Poly(vinylacetate-co-dibutylmaleate)

$\lambda$ (nm)	$\eta$
400	1.473
436	1.470
546	1.468
589	1.467

## DISCUSSION AND CONCLUSIONS

The characterization of latex particles with a light scattering size analysis requires consideration of the relationship between refractive index and wavelength. The refractive index of a substance changes in a complicated manner with the wavelength of the incident radiation. The relationship between refractive index and wavelength for the three polymers were fitted to two equations, one based on electromagnetic dispersion theory<sup>13</sup> and the other on an empirical relationship developed by Cauchy.<sup>14</sup>

Electromagnetic dispersion theory gives

$$\frac{\eta^2 + 2}{\eta^2 - 1} = k_0 - \frac{k_1}{\lambda^2} \quad (10)$$

where  $k_0$  and  $k_1$  are constants related to polarizability. A plot of  $(\eta^2 + 2)/(\eta^2 - 1)$  against  $\lambda^{-2}$  should therefore be linear with a negative slope. The data from this paper is plotted in Figure 3.

The second, empirical relationship is given by

$$\eta_\lambda = \eta_0 + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (11)$$

where  $B$  and  $C$  are constants. The third term is usually neglected since it is small. A plot of  $\eta_\lambda$  against  $\lambda^{-2}$  should therefore also be linear with a positive slope. Our data is plotted in Figure 4.

For both the electromagnetic dispersion equation and the Cauchy approach the correlation coefficient from linear regression analysis is good ( $> 0.98$ ). The limitations on the wavelengths that may be used to determine the refractive

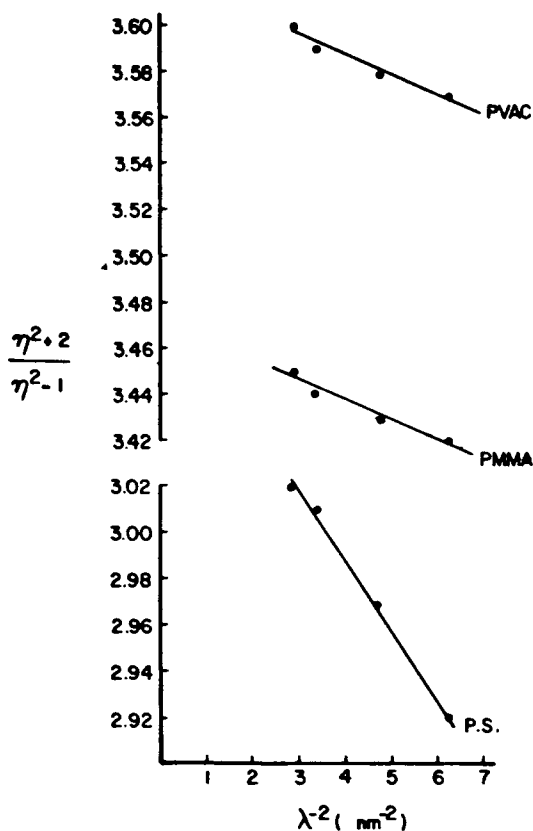


Fig. 3. Plots of refractive index function against wavelength according to eq. (10).

index are determined by the absorption maximum of the polymer and the absorption of the continuous medium.

The slope of the lines in Figures 2 and 3 are dependent on parameters such as density and dielectric constant. Since poly(methyl methacrylate) and poly(vinyl acetate) have similar density and dielectric constants, their lines in Figures 2 and 3 have the same slope. Polystyrene, being a material with a different density and dielectric constant, has a different slope in both figures. Plots such as those in Figures 2 and 3 can be used to extrapolate the refractive indices to wavelengths outside the measured range, if this should be needed.

After this research was completed it has come to our attention that a somewhat similar technique has been reported by Griffin and Griffin<sup>10</sup> for estimation of refractive indices of casein micelles of bovine milk. We believe that the present report is also worth recording because it will be of use to workers in polymers and coatings, who will not likely note the potential for use of the cited report in their own research.

A listing of the BASIC program for calculation of scattering efficiencies is available from the authors on request. This program is adapted from one given in Reference (7).

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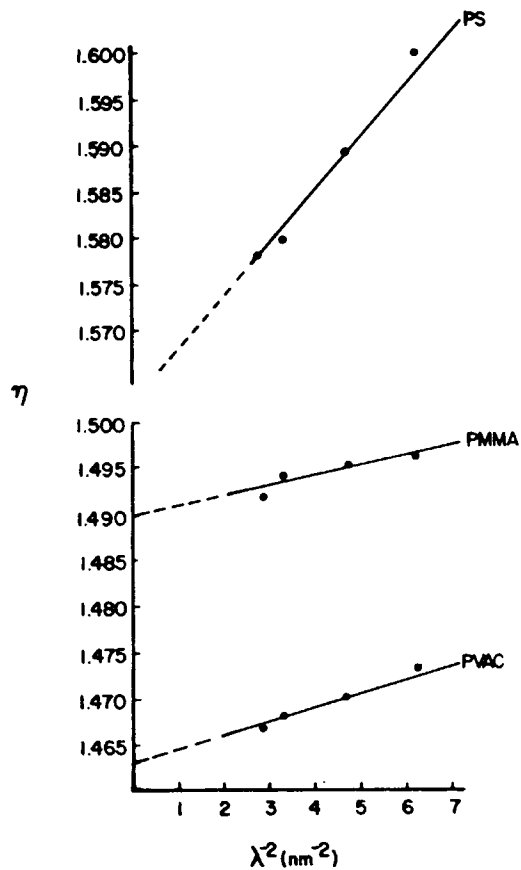


Fig. 4. Cauchy equation [eq. (11)] plots.

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