

WIDE ANGLE LIGHT SCATTERING INVESTIGATION OF THE INTERNAL STRUCTURE
OF POLYMER LATEXES

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ABSTRACT

A new apparatus has been developed for the measurement of wide-angle and low-angle scattering from colloidal suspensions. The instrument employs an argon ion laser source, single photon counting detection, data acquisition by minicomputer and has an easily accessible angular resolution of 0.6° . The accuracy of the light scattering apparatus along with the reliability of the data-inversion procedure has been tested by comparison of measurements on a standard polystyrene latex by four independent methods on the same sample as well as comparison with numerous reports in the literature. An improvement of the inversion procedure of Rowell and Levit has been used in a double blind analysis of a control latex with no shell structure and the subject latex of pH-dependent shell structure. Both control and subject latex were analyzed using both homogeneous sphere theory and concentric sphere theory. The results conclusively established the existence of a concentric-shell structured latex and were in agreement with an independent study of the system by sedimentation methods, which is reported elsewhere in this book.

INTRODUCTION

A problem of great practical as well as theoretical interest is the determination of the structure of polymer latex particles in situ. Unfortunately, there are few satisfactory means of probing directly the structure of particles in suspension. The most successful techniques involve viscosity or sedimentation but these are indirect measurements which lead only to an average hydrodynamic or effective hydrodynamic size.

Light scattering appears to offer a new and direct approach to the problem. We may distinguish two main approaches. The recent photon-correlation spectroscopy methods (also known as Rayleigh linewidth, quasielastic light scattering and dynamic light scattering) have been mainly applied to molecular systems but an application to polymer latex suspensions leads to a hydrodynamic size which can be compared with the viscosity and sedimentation approaches. The second approach which is the subject of the present work utilizes wide angle light scattering. Angular variation of the light scattering intensity patterns may be fitted to various theoretical models as a direct probe of the internal structure of latex particles.

EXPERIMENTAL

Rayleigh-Gans-Debye Approximation

The Rayleigh-Gans Debye approach has been concisely described by Kerker.¹ The basic approximation is a small phase shift $2ka(m-1) \ll 1$ where a is the diameter of the particle, m the refractive index of the particle relative to the medium and k the propagation constant $2\pi/\lambda$. For our larger latexes with $a = 0.35 \mu\text{m}$, $\lambda = \lambda_0/n = 0.4880/1.337 = 0.3650 \mu\text{m}$, $m \approx 1.05$, we found $2ka(m-1) = 0.60$ so that the Rayleigh-Gans-Debye approach could not be used.

For smaller particles where the Rayleigh-Gans-Debye approximation is valid, the angular scattering patterns become less sensitive to particle parameters making it difficult to obtain a reliable fit.

The same general considerations applied to concentric spherical particles so that it was necessary to use the exact treatment. The RGD approach was useful mainly in investigating general trends, rough-checking and debugging during computer program development.

Exact Computations

The initial derivation by Aden and Kerker² for the angular dependence of the light scattered from coated spherical particles has been reviewed and updated by Kerker.¹ The concentric spherical