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Guillermo E. Elicabe^a; Fernando Otero^a

^a Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Mar del Plata, Argentina

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Static Light Scattering of Concentrated Particle Systems in the Rayleigh-Debye-Gans Regime: Modeling and Data Analysis

GUILLERMO E. ELIÇABE AND FERNANDO OTERO

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Mar del Plata, Argentina

In this work we give an overview of the Rayleigh-Debye-Gans (RDG) theory applied to the analysis of static light scattering (SLS) data of different types of concentrated particle systems. First some useful models needed to analyze SLS data under the RDG regime for concentrated particle systems are presented. We consider monodisperse as well as polydisperse systems of spherical particles. Then we present some techniques for analyzing the SLS data in different contexts with the aim of gathering information about: particle size and shape, particle size distribution, particle concentration, and some other useful parameters characterizing the particle systems. Finally, we report an application of some of the models and methods illustrated previously. They were used to characterize a system of concentrated polymer particles embedded in a polymer matrix, formed as the result of a phase separation induced by polymerization in a polymer blend.

Keywords concentrated particles, particle size distribution, Rayleigh-Debye-Gans, static light scattering, structure factor

Introduction

Static light scattering (SLS) is an optical particle characterization technique in which the average value of the light scattered by a mixture of particles suspended in a medium is collected at different angles and used to extract information about the mixture. SLS techniques have been extensively used to characterize particle systems in a range of particle sizes from 0.1 to 10 μm with great success. The experimental arrangement for SLS may be mainly of two kinds: the goniometer (Glatter and Hofer 1988) and the flat cell-based setups (Lehner et al. 1998, Eliçabe et al. 2007). The goniometer setup allows covering a wide range of angles, typically varying from 10° to 150°, but imposes the limitation that the sample holder must be cylindrical. With this geometry the sample cannot be too thin and then its thickness cannot

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Address correspondence to Guillermo E. Eliçabe, Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina. E-mail: elicabe@fi.mdp.edu.ar

be used to control the negative incidence of multiple scattering. In the flat cell geometry this restriction is at the expense of limiting the range of available angles to approximately 3° – 60° . When SLS is employed with a flat sample holder, it may also be referred to as small-angle light scattering (SALS).

In order to obtain a reliable picture of the particle system under study in terms of size, shape, and composition of the particles and their spatial distribution in the surrounding medium, scattering data must be analyzed using models that accurately represent the experimental conditions. In many applications particles are diluted and then single particle scattering can be directly applied to model the behavior of the system. When the particles have spherical symmetry, the scattering from the system is proportional to the scattering by a single particle. In the case of nonspherical particles, proper orientational averages must be performed. In both cases the individual particles are assumed to be hit only by the incident light, i.e., single scattering is considered, and the intensity scattered by the system is calculated as the sum of the intensities scattered by the individual particles.

Scattering by a single particle has been rigorously treated in the so-called Mie theory, mainly for spherical particles and for a few nonspherical but regularly shaped particles (van de Hulst 1981; Bohren and Huffman 1983). Approximations of the rigorous solutions are available for very small particles (Rayleigh scattering), for small and low-contrast particles (Rayleigh-Debye-Gans scattering), and for large particles (diffraction theory). In general, scattering by a single particle of irregular shape must be treated numerically using some of the methods available to solve Maxwell equations (Wriedt 1998; Mishchenko, Travis, and Lacis 2002).

When the particles are concentrated, the assumptions of single scattering and/or independent scattering may not be valid. For concentrations low enough such that independent scattering is still applicable but single scattering is not, the scattering by the system can be modeled using radiative transfer theory (Mishchenko, Travis, and Lacis 2006). For moderate to high concentrations and depending on size and optical contrast of the particles, the assumption of single scattering could be maintained, whereas that of independent scattering will not be valid anymore. In such case the Rayleigh-Debye-Gans (RDG) theory, which must be extended to the case of a concentrated mixture of particles through the introduction of a structure factor, can be adequate to model the scattering process. In general, a rigorous model for a system of particles of arbitrary size, optical contrast, and concentration must be obtained from the solution of the Maxwell equations for the ensemble of particles. This approach, which involves large computational times and for that reason was almost impracticable in the past, has been applied recently by Mishchenko et al. (2007) to calculate scattering spectra of a system of particles without any approximation.

In this work we will focus on the case of concentrated particles that have sizes of the order of the wavelength of the incident light and present a low optical contrast with respect to the surrounding medium. In this situation multiple scattering can be neglected up to relatively high concentrations and only particle interference must be considered. The scattering of light under these circumstances is correctly described by the RDG theory (Hobbie and Lipiin 1996). In general this theory is valid when $kd(m-1) \ll 1$ and $(m-1) \ll 1$, where k , the magnitude of the propagation vector, is defined as $2\pi n_L/\lambda_0$, and m , the relative refractive index, is equal to n_p/n_L ; λ_0 is the wavelength of the incident radiation in vacuum, n_p is the refractive index of the particles, n_L is the refractive index of the suspending medium, and d is some characteristic linear dimension of the particles.

In what follows we will give first some useful derivations needed to analyze SLS data under the RDG regime for concentrated particle systems. We will consider monodisperse as well as polydisperse systems of spherical particles. Then we will present some techniques for analyzing SLS data in different contexts with the aim of gathering information about: particle size and shape, particle size distribution (PSD), particle concentration, and some other parameters that describe the particle system. Finally, we will report an application of some of the models and methods illustrated previously. They will be used to characterize a system of concentrated polymer particles embedded in a polymer matrix, formed as the result of a phase separation induced by polymerization in a polymer blend.

Scattering Models in the Concentrated RDG Regime

For a particle system of identical spheres, the differential scattering cross section (DSCS) per unit volume of sample, which is the absolute measurement in a light scattering (LS) experiment, is given by (Pusey 2002)

$$\frac{d\Sigma(q)}{d\Omega} = N_p \Delta\rho^2 \left(\frac{4\pi}{3} R^3 \right)^2 P(q) S(q) \quad (1)$$

where N_p is the number of particles per unit volume of sample, R is the radius of the particle, $P(q)$ is the form factor of one particle, $S(q)$ is the structure factor of the system, $q = \frac{4\pi n_0}{\lambda_0} \sin \frac{1}{2}\theta$, θ is the scattering angle, n_0 is the average refractive index of the whole suspension, λ_0 is the wavelength of the incident radiation in vacuum, and $\Delta\rho$ is the contrast scattering length density of the particles, which expressed in terms of refractive index is given by $\Delta\rho = k^2(2\pi n_0)^{-1}(n_p - n_L) = k^2(2\pi n_0)^{-1}\Delta n$. The form factor for a spherical particle is given by

$$P(q) = \left[\frac{3}{(qR)^3} (\sin qR - qR \cos qR) \right]^2 \quad (2)$$

A commonly used structure factor for hard spheres is that calculated under the Percus-Yevick (PY) approximation and given by (Kinning and Thomas 1984)

$$[S(q)]^{-1} = 1 - 24\eta \left\{ \frac{(\alpha + \beta + \delta)}{u^2} \cos u - \frac{(\alpha + 2\beta + 4\delta)}{u^3} \sin u - \frac{2(\beta + 6\delta)}{u^4} \cos u + \frac{2\beta}{u^4} + \frac{24\delta}{u^5} \sin u + \frac{24\delta}{u^6} (\cos u - 1) \right\} \quad (3)$$

with

$$u = 2qR, \quad \alpha = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad \beta = -6\eta \frac{(1 + \frac{\eta}{2})^2}{(1 - \eta)^4}, \quad \delta = \frac{\eta(1 + 2\eta)^2}{2(1 - \eta)^4}$$

where η is the volume fraction of particles in the sample, $\eta = N_p 4/3\pi R^3$.

For a mixture of particles of different size, the complete solution for the DSCS per unit volume of sample under the PY approximation, assuming hard sphere

interaction, was given by Vrij (1979) and can be summarized as follows for the case of spherical particles:

$$\frac{d\Sigma(q)}{d\Omega} = -D(q)\Delta(q)^{-1} \quad (4)$$

where

$$\begin{aligned} -\frac{\pi}{6}(1 - \langle d^3 \rangle)^4 D(q) = & \langle b(q)^2 \rangle T_1 T_1^* + \langle d^6 \phi^2 \rangle T_2 T_2^* + 9 \langle d^4 \psi^2 \rangle T_3 T_3^* \\ & + \langle b(q) d^3 \phi \rangle (T_1 T_2^* + T_1^* T_2) + 3 \langle b(q) d^2 \psi \rangle (T_1 T_3^* + T_1^* T_3) \\ & + 3 \langle d^5 \phi \psi \rangle (T_2 T_3^* + T_2^* T_3) \end{aligned} \quad (5)$$

and

$$\Delta(q) = \frac{1}{(1 - \langle d^3 \rangle)^4} (F_{11} F_{22} - F_{12} F_{21}) (F_{11}^* F_{22}^* - F_{12}^* F_{21}^*) \quad (6)$$

with

$$\begin{aligned} T_1(q) &= F_{11} F_{22} - F_{12} F_{21} \\ T_2(q) &= F_{21} \langle db(q) e^{iX} \rangle - F_{22} \langle b(q) e^{iX} \rangle \\ T_3(q) &= F_{12} \langle b(q) e^{iX} \rangle - F_{11} \langle db(q) e^{iX} \rangle \end{aligned} \quad (7)$$

$$\begin{aligned} F_{11}(q) &= 1 - \langle d^3 \rangle + \langle d^3 \phi e^{iX} \rangle \\ F_{12}(q) &= \langle d^4 \phi e^{iX} \rangle \end{aligned} \quad (8)$$

$$\begin{aligned} F_{22}(q) &= 1 - \langle d^3 \rangle + 3 \langle d^3 \psi e^{iX} \rangle \\ F_{21}(q) &= \frac{1}{2} (1 - \langle d^3 \rangle) i q - 3 \langle d^2 \rangle + 3 \langle d^2 \psi e^{iX} \rangle \end{aligned} \quad (9)$$

$$\begin{aligned} d &= 2R \\ X &= qR \\ \psi &= \frac{\sin X}{X} \\ \phi &= \frac{3}{X^3} (\sin X - X \cos X) \end{aligned} \quad (10)$$

$$b(q) = \Delta \rho \left(\frac{4\pi}{3} R^3 \right) \left[\frac{3}{(qR)^3} (\sin qR - qR \cos qR) \right] \quad (11)$$

The brackets in this case indicate in general that $\langle A_1 A_2 \dots A_n \rangle = \frac{\pi}{6} \sum_{j=1}^M N_p^{(j)} A_1^{(j)} A_2^{(j)} \dots A_n^{(j)}$, where $A_k^{(j)}$ is the value of function A_k evaluated for the size of species j , $N_p^{(j)}$ is the particle number density of species j , and M is the number of different species in the sample.

The DSCS of a mixture of spherically symmetric particles can be also written in terms of partial structure factors, S_{jk} , as follows:

$$\frac{d\Sigma(q)}{d\Omega} = N_p \sum_{j=1}^M \sum_{k=1}^M b_j(q) b_k(q) S_{jk}(q) \quad (12)$$

These partial structure factors can be explicitly calculated under the same scheme as in the previous paragraph. It is also interesting to note that an effective structure factor, $S^{eff}(q)$, can be defined if (12) is formally written as in the monodisperse case:

$$\frac{d\Sigma(q)}{d\Omega} = N_p \overline{b(q)^2} S^{eff}(q) \quad (13)$$

where

$$\overline{b(q)^2} = \sum_{j=1}^M \frac{N_p^{(j)}}{N_p} b_j(q)^2 \quad \text{and} \quad S^{eff}(q) = \frac{1}{\overline{b(q)^2}} \sum_{j=1}^M \sum_{k=1}^M b_j(q) b_k(q) S_{jk}(q)$$

Equation (13) has been used by Brunner-Popela and Glatter (1997) as a model for multicomponent systems of particles and was also extended to treat nonspherical particles.

Several models have been proposed to approximate the scattering of a multicomponent particle system with number density radii distribution $D(R)$. For systems with small polydispersities, a decoupling approach that considers that interactions are independent of size was proposed by Kotlarchyck and Chen (1983). Another approximate model is the local monodisperse approximation (LMA), proposed by Pedersen (1994). The LMA holds the assumption that a particle of a certain size is surrounded only by particles of the same size. In this form the DSCS is approximated by that of monodisperse subsystems weighted by the PSD. When the particles, assumed as spherical, interact with their actual radius the scattered intensity under this approximation is given by

$$\frac{d\Sigma(q)}{d\Omega} = \Delta\rho^2 \left[\int_0^\infty D(R) [4/3\pi R^3]^2 P(q, R) S(q, R) dR \right] \quad (14)$$

$S(q, R)$ in this equation corresponds to that of a monodisperse system and depends also on the total volume fraction of particles. It has been shown that the LMA works better than the decoupling approximation for systems with larger polydispersities and higher concentrations (Pedersen 1994).

Data Analysis in the Concentrated RDG Regime

Scattering data of particle systems must be analyzed using models that accurately represent the experimental conditions in order to estimate parameters related to the shape, orientation, and size or size distribution of the particles. Additionally, in a concentrated system, parameters that describe the distribution of the particles in the medium such as particle concentration, interaction radius, and stickiness must be also included in the estimation process.

LS data of concentrated particle systems are usually processed to obtain the size distribution of the actual particles and the parameters describing the structure of the particle system. Depending on the models used, structure parameters such as particle concentration, interaction radius, and stickiness can be considered.

The PSD may be modeled using a fixed-form approach with Gauss, Weibull, or lognormal functions, which are described with a few parameters. If a free-form distribution is desirable, the number of parameters strongly increases and the estimation problem may become unstable (Glatter 1977). In the first case the estimated distribution has a shape limited by the selected function, which stabilizes the estimation at the expense of restricting the space of solutions. The free-form approach allows a wider range of solutions but must include a regularization scheme to stabilize the estimation.

The previous approaches are completely general and can be applied to any of the LS models described in the preceding section. However, some models have particular structures that can be helpful to develop specific approaches. This is the case for the LMA model with a free-form PSD. Since the PSD appears linearly in the LMA model, the problem can be solved iteratively in two stages (Pedersen 1994). First the PSD is estimated using linear least squares with regularization for fixed values of the parameters related to the particle system structure, which appear in the LS model in a nonlinear fashion. Then, with the estimated distribution as a fixed function, new values for the structural parameters are calculated in an iterative form. This procedure is continued until the unknowns no longer change significantly.

Another scattering model that can be solved in two steps, one linear and the other nonlinear, is the one of Equation (13). In the work of Brunner-Popela and Glatter (1997), $S^{eff}(q)$, which is expressed as a function of partial structure factors, is approximated in different forms. Weyerich, Brunner-Popela, and Glatter (1999) used four parameters to describe $S^{eff}(q)$: the volume fraction, the interaction radius, the polydispersity parameter, and the charge of the particles. The estimation scheme used in the work of Weyerich, Brunner-Popela, and Glatter (1999) is similar to the one used for estimating the PSD in the LMA approach.

An Application: Polymer Particles in a Polymer Matrix

We will show here some of the results obtained in an SLS study of free-radical polymerization of a solution of polyisobutylene (PIB) in isobornyl methacrylate (IBoMA) that produces poly(isobornyl methacrylate) (PIBoMA). This polymer system has been extensively studied in the works of Soulé et al. (2007) and Soulé and Elicabe (2008), and the results presented here are taken from those publications. In this polymerization, as the reaction takes place and more PIBoMA is formed, the PIB molecules are phase separated from the matrix, forming droplets of growing sizes in the submicron regime.

The system studied is one in which: its parameters evolve in time, particles and medium are made of polymer, particles are more or less spherical, particle concentration is relatively high, and there is a distribution of particle sizes. In what follows we will show the results of the application of the models and methods described in the previous sections to estimate the more relevant parameters of the particle system. The use of the RDG theory to model the experimental results obtained with this particle system was supported by the findings reported by Lindner, Fritz, and Glatter (2001). In that work a transition from RDG regime to Mie theory is verified

for samples with particle radii of about 0.5 μm . The study indicates that when the relative refractive index of the particles, m , is equal to 1.04, the PSDs estimated with the RDG and Mie theories are very similar. Because in the present study m was no larger than 1.02 and the mean radii was in all cases smaller than in that study, it was assumed that RDG was a valid approach to investigate this particle system.

In the study, the effects of particle concentration and polydispersity in the particle size were considered through the use of the LMA, as described in the previous sections of this article, which was used to estimate the PSD of the polymer particles. For the interpretation of the SLS results, a log-normal distribution function was selected to fit the PSD in the LMA model of Equation (14):

$$D(R) = \frac{(g/\pi)^{1/2}}{R} \exp\left\{-g[\log(R/R_0)]^2\right\} \quad (15)$$

The use of a two-parameter PSD gives the model four adjustable parameters: (i) the product $N_p \Delta \rho^2$; (ii) the volume fraction of particles, η , that acts as an effective parameter that describes the interference effects; and (iii) the two parameters, g and R_0 , that define the shape of the PSD used in this study. Blends with different wt.% of PIB and with PIBs of different molar mass averages were used in the study. Here the results corresponding to two types (PIB5, PIB025) and two values of wt.% (30% and 50%) of PIB will be reported. The following blends are considered: (a) 30 wt.% PIB5 in IBoMA (30PIB5), (b) 50 wt.% PIB5 in IBoMA (50PIB5), and (c) 50 wt.% PIB025 in IBoMA (50PIB025 and 50PIB025(Replica)). Samples 1.2 mm in thickness were measured with a time-resolving flat cell static light scattering (FCSLS) apparatus described in the work of Eliçabe et al. (2007) and schematically depicted in Figure 1.

First, the time-resolving SLS results corresponding to the evolution of the particle system during polymerization will be shown. The measured and fitted spectra corresponding to formulation 30PIB5 of the PIB-IBoMA solution are shown in Figure 2 for increasing IBoMA conversion values. An optimum set for the four adjustable parameters was obtained for every one of the selected spectra using a

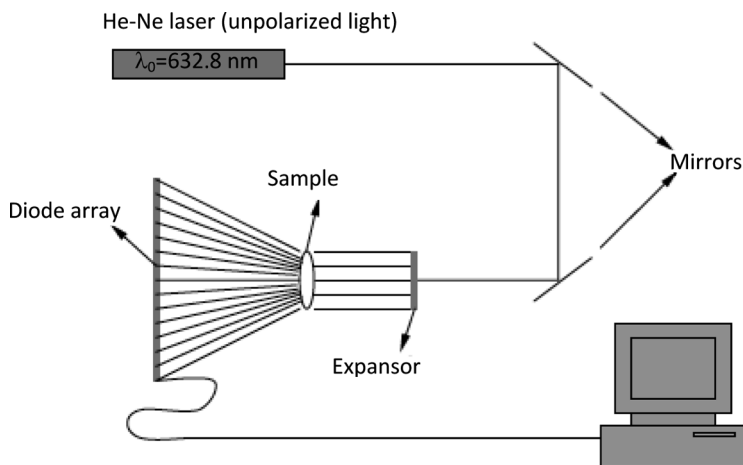


Figure 1. Schematic representation of the FCSLS apparatus.

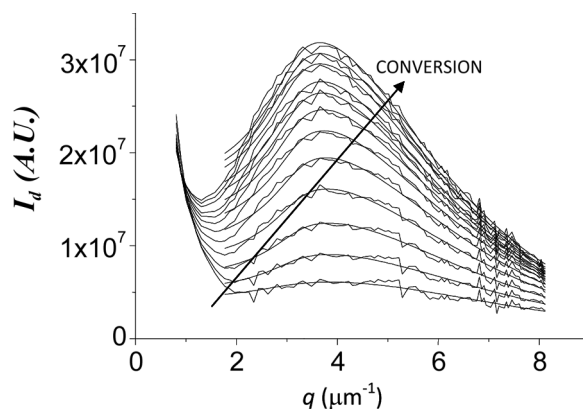


Figure 2. SLS spectra plotted as intensity (arbitrary units) as a function of the modulus of the scattering vector q . Non-smooth curves are experimental results and smooth curves represent the fitting of the SLS model for polymer blend 30PIB5 for the following monomer conversions: 0.512, 0.536, 0.558, 0.58, 0.601, 0.621, 0.641, 0.66, 0.678, 0.712, 0.788, and 0.881. Data adapted from Soulé et al. (2007).

typical least squares scheme. The estimated SLS spectra as shown by the smooth curves in Figure 2 agreed quite well with the measured ones in almost all regions of the q range analyzed.

The evolution of the corresponding PSD calculated by the model is shown in Figure 3. The authors found that the predicted shift of the PSD to the right, in the conversion range between 0.512 and 0.58, a sign that growth-coarsening mechanisms are still active in this range, and the prediction that for conversions higher than 0.62 there is practically no further evolution of the PSD, meaning that phase separation was practically arrested when the system reached this conversion, are in excellent agreement with the reported evolution of the volume fraction of dispersed phase predicted on thermodynamic grounds and verified by scanning electron microscopy (SEM) (Soulé et al. 2007). These conclusions were also supported by the result

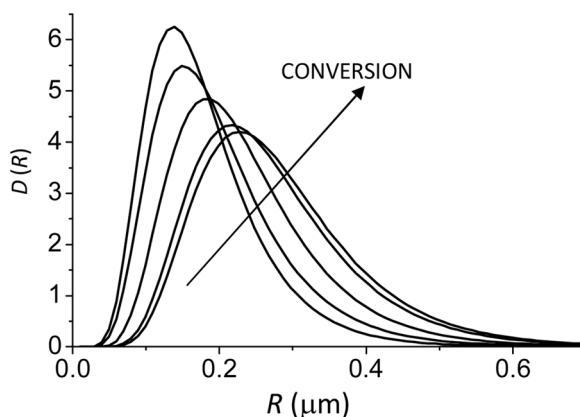


Figure 3. Evolution of the number PSDs calculated by the SLS model for polymer blend 30PIB5 for the following monomer conversions: 0.512, 0.536, 0.558, 0.621, and 0.80. Data adapted from Soulé et al. (2007).

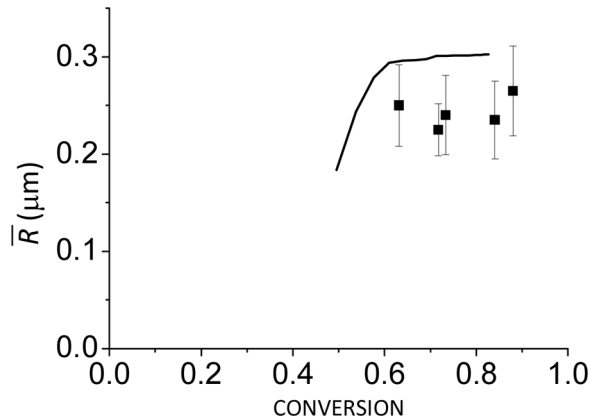


Figure 4. Comparison of number average radii calculated from the log-normal distribution with experimental values obtained from SEM micrographs for polymer blend 30PIB5. Data adapted from Soulé et al. (2007).

shown in Figure 4. This comparison of average sizes calculated from the log-normal distribution with experimental values obtained from SEM micrographs revealed a reasonable agreement between estimations and experiment and put in evidence the predictive capability of the scattering model.

Soulé et al. (2007) also gave an explanation of the further evolution of the spectra of scattered light plotted in Figure 2 in the conversion range where the PSD and the volume fraction of dispersed phase became almost constant. In this conversion range the only adjustable parameter that varied was the proportionality constant mentioned before, which includes $(\Delta\rho)^2$. With this support, the increase in the intensity of the SLS spectra in the range of high conversions was assigned to an increase in the difference of refractive indices between the particles and the matrix due to the continuous purification of both phases in the corresponding neat components.

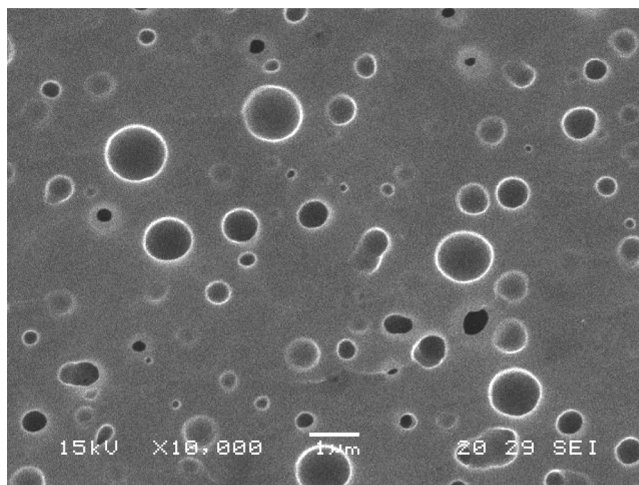


Figure 5. SEM micrograph of sample 50PIB025 completely reacted. Adapted from Soulé and Eliçabe (2008).

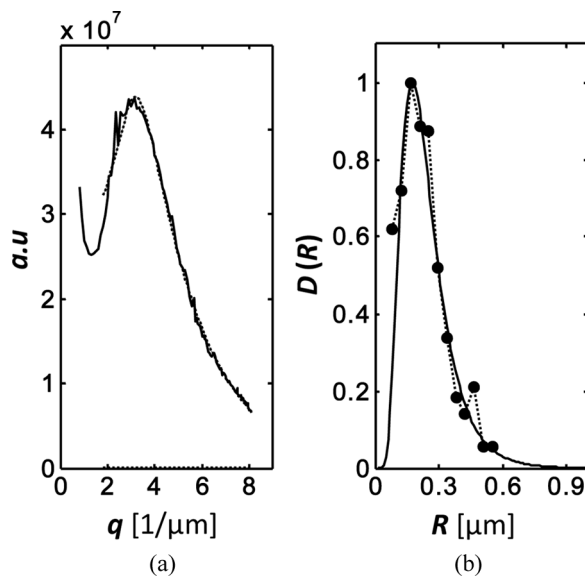


Figure 6. Results for sample 50PIB025: (a) experimental SLS data, full line curve; fit of the model, dotted line curve; (b) normalized number PSD estimated from the model fitting, full line curve; normalized number PSD calculated from SEM, dotted line curve with full circles. Data adapted from Soulé and Eliçabe (2008).

In a subsequent publication, Soulé and Eliçabe (2008) reported the characterization of the particle system obtained at the end of the polymerization, when the PIBoMA has vitrified and the PIB droplets have reached their final size. A SEM micrograph of one of the samples is shown in Figure 5.

The resulting SLS spectra were fit by the model and the corresponding parameters estimated. In Figure 6 the measured and fitted spectra and the normalized PSD for sample 50PIB025 are shown. As is evident here, the fit to the data was excellent and the estimated distribution agreed very well with the one determined with SEM.

The estimated parameters of the PSD converted to number average radius, \bar{R} , and standard deviation, σ , and the estimated volume fraction of particles, $\hat{\eta}$, are displayed in Table 1 for all the studied formulations. In the table are also shown the same parameters calculated from SEM micrographs. The estimations are in quite good agreement with one another for the parameters describing the PSD.

Table 1. Estimated parameters from SLS and measured parameters from SEM for the four samples analyzed

| | 30PIB5 | | 50PIB5 | | 50PIB025 | | 50PIB025 (Replica) | |
|-----------------------------------|--------|-------|--------|------|----------|-------|--------------------|-------|
| | SLS | SEM | SLS | SEM | SLS | SEM | SLS | SEM |
| $\hat{\eta}$ | 0.28 | 0.052 | 0.35 | 0.15 | 0.29 | 0.085 | 0.35 | 0.077 |
| $\hat{\bar{R}}$ [μm] | 0.24 | 0.21 | 0.40 | 0.31 | 0.24 | 0.23 | 0.24 | 0.19 |
| $\hat{\sigma}$ [μm] | 0.096 | 0.054 | 0.11 | 0.11 | 0.12 | 0.12 | 0.11 | 0.091 |

Adapted from Soulé and Eliçabe (2008).

As mentioned before, the volume fraction of particles acts as an apparent parameter not expected to coincide with the value calculated with SEM.

Conclusions

It is interesting to note that most of the results shown in this work were initially developed in the framework of small-angle X-ray and neutron scattering (SAXS and SANS) applications, in which the conditions of validity of the RDG theory are always fulfilled because the refractive indices of all materials are very close to one at those wavelengths. However, in general this is not the case for SLS. Refractive indices of different materials at visible wavelengths may differ from one another in a way that makes the RDG approximation not valid. In SLS the conditions of validity of the RDG theory are accomplished when: the particles are not too large compared to the wavelength of light, and either the optical contrast between particles and medium is naturally low as is the case in many polymer systems in which particles and medium are both polymer materials, or the optical contrast is made sufficiently low by addition of some proper element to the system of particles. In general, low contrast precludes multiple scattering even in systems in which the concentration of particles is high. Thus, as a first approach, a low contrast system can be analyzed using RDG theory up to high concentrations without considering multiple scattering. The application presented in this work is a good example of how the natural fact that polymers have refractive indices very similar to one another allows one to use the simplified models developed for the RDG regime to characterize complex particle systems using light.

Nomenclature

| | |
|-------------|---|
| D | number radii distribution |
| d | characteristic linear dimension |
| g | parameter of log-normal distribution |
| k | magnitude of the propagation vector |
| M | number of different species in sample |
| m | relative refractive index |
| N_p | number of particles per unit volume of sample |
| $N_p^{(j)}$ | particle number density of species j |
| n_0 | average refractive index of whole suspension |
| n_L | refractive index of suspending medium |
| n_p | refractive index of particles |
| P | form factor |
| q | magnitude of scattering vector |
| R | radius |
| R_0 | parameter of log-normal distribution |
| S | structure factor |
| S_{ij} | partial structure factor |

Greek letters

| | |
|--------------|--|
| $\Delta\rho$ | contrast scattering length density |
| Δn | difference of refractive index between particle and medium |
| η | particle volume fraction |

| | |
|---------------------------|---|
| θ | scattering angle |
| λ_0 | wavelength of incident radiation in vacuum |
| σ | standard deviation |
| $\frac{d\Sigma}{d\Omega}$ | differential scattering cross section per unit volume |

Superscripts/Subscripts

| | |
|-------------|----------------|
| eff | effective |
| $^{\wedge}$ | estimated |
| — | number average |

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