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Characterization of Miniemulsion Polymerization by Small-Angle Neutron Scattering

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Summary

Emulsion polymerization is one of the major techniques for the manufacture of adhesives, coatings, thermoplastics and elastomers. In miniemulsion polymerization, relatively stable oil droplets within a size range of 500 to 5000 Å are prepared by emulsifying a monomer in a medium, generally water, with the aid of a surfactant and a hydrophobic compound. Droplet size and size distribution are by far the most important parameters of miniemulsion because they affect directly both the miniemulsion stability and droplet nucleation. Therefore, the understanding of the mechanism ruling miniemulsion polymerization strongly depends on an accurate determination of the particle size.
Small-angle neutron scattering has been used for the polymerization study of the 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) . In particular, the shape and the size of the particles before and after the anionic polymerization were sought. Surprisingly, the sizes obtained are of the order of 250 Å which ranges this system rather into the microemulsion domain and the observed growth in the mean particle size (25%) implies that there is no full preservation of the particles during the polymerization reaction .On the other hand, the contribution to the scattering of a second population of smaller particles (38 Å) with a broad size distribution in the polymerized sample is attributed to secondary products leading to a 80% polymerization reaction yield.

Introduction

Monomer miniemulsions suitable for emulsion polymerization are highly stable oil in water dispersions prepared using a mixed system comprising an efficient surfactant and sometimes a water insoluble co- surfactant [1-2]. These stable monomer droplets are the main locus for particle nucleation to produce submicrometer latex particles after adding an initiator. So, in miniemulsion polymerization, the droplet size and its distribution are considered to be the most important parameters because they affect directly both the particle nucleation and polymerization reaction. Various methods have been used to estimate the particle size [3-7], in particular dynamic light scattering is the most common method reported in the literature [8-11]. However, the necessary large dilution of the sample might affect the initial size of the particles and its distribution. Thus, small angle neutron scattering (SANS), a more powerful tool, has been applied for examining the structure of polymer solutions [12] without a prealable dilution.

The synthesis of poly (trifluoropropylmethyl)siloxane (PTFPMS) by anionic ring opening polymerization of 1, 3, 5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) was studied using dodecyldimethylbenzylammonium bromide (DDBBr) as emulsifier [13]. This polymerization has been found to produce a well-defined α,ω-dihydroxylated polymer in a very high yield and with molar masses ranging from 2000 to 30000 g.mol^{-1} [14]. In this paper, we describe the first SANS investigation of this system before and after the anionic polymerization of F_3. The data were analysed on the basis of a polydisperse homogeneous sphere model for the monomer and polymer particles which lead to satisfactory results.

Experimental

Materials

The monomer F_3 was provided by General Electrics and its nominal purity was larger than 99%. The surfactant DDBBr was purchased from Acros Organics and was 98% pur. Both compounds were used as received. The solvent is deuterated water.

Sample preparation

5.1g of the monomer F3 and 0.333 g of DDBBr were dispersed into 20.0g of deuterated water at room temperature. The sample is then sonicated for 3 minutes at 55watts in a 450 Branson Ultasonics Corporation sonicator leading to monomer emulsion sample (I). The polymer emulsion sample (II) contains additionally to the monomer emulsion the initiator NaOH at a concentration of 10^{-4}M. It is sonicated at the same intensity and time as sample (I). The emulsion is then introduced into the polymerization reactor and continuously stirred at 100 rpm at room temperature. Then a 5 mol.- % hydrochloric acid solution was added in order to stop the polymerization reaction after 1 hour.

Small angle neutron scattering

The small angle neutron scattering experiments were performed on the SANS spectrometer PAXE of the Leon Brillouin Laboratory at Saclay. The data acquisition was performed at two different samples to detector distances in order to cover a large domain of momentum transfer. The data were converted to an absolute scale through the direct determination of the incident flux. The data have been corrected for transmission, solvent and cell contributions by a standard procedure.

Theory

SANS experiments consist in measuring the neutron intensity scattered at small angles. The scattering pattern from a given sample can be described in terms of the Fourier transform of the scattering length density distribution [15] and is given in the case of a system of homogenous polydisperse spheres [16] in a solvent by:

$$I(Q)=n\cdot P(Q)\cdot S(Q) \tag{1}$$

with the magnitude of the scattering vector given by:

$$Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{2}$$

Here n is the number of particles per unit volume, λ is the neutron wavelength and θ is the scattering angle. *S(Q)* is the structure factor and is related to the correlations between the positions of the particles. The contribution of *S(Q)* has been estimated on the basis of the classical excluded volume interaction [17] among monodisperse homogeneous spheres of radius R = $\overline{R}$ which is the mean sphere radius of the form factor. *P(Q)* is the particle form factor of a particle and is given in the case of a polydisperse homogeneous sphere model by:

$$P(Q) = \int_0^\infty V^2 (\rho - \rho_s)^2 \left[3 \frac{(\sin(Qr) - QR\cos(QR))}{(QR)^3} \right]^2 h(R)\,dr \tag{3}$$

Where

$$h(R) = \frac{(z+1)^{z+1}}{\overline{R}^{z+1}\,\Gamma(z+1)} \cdot \exp\left[\frac{-(z+1) \cdot R}{\overline{R}} \right] \tag{4}$$

(ρ-ρ_s) is the contrast term; it is given by the difference between the scattering length densities of the dissolved particle (ρ) and the solvent (ρ_s). *R* is the particle radius and *h(R)* the Schulz-Zimm distribution characterized by an average particle radius $\overline{R}$ and a polydispersity p = $(z+1)^{-1/2}$. This distribution is chosen because it is the most common one used for colloidal systems.

Results and Discussion

The measured SANS spectra of monomer and latex emulsions are shown on figure (1).

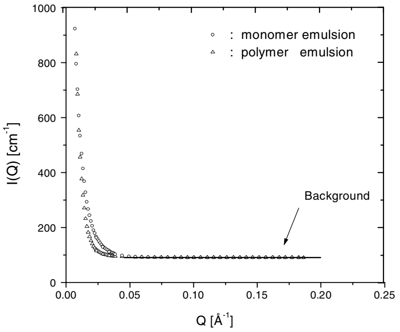

Figure 1 SANS spectra of monomer and polymer emulsions.

The transmissions of samples (I) and (II) measured at high Q values are equal to 0.722 and 0.727 respectively, meaning that multiple scattering was negligible. The data are then corrected for the flat incoherent background evident at the highest Q values in figure (1) and plotted on a logarithmic scale in figure (2).

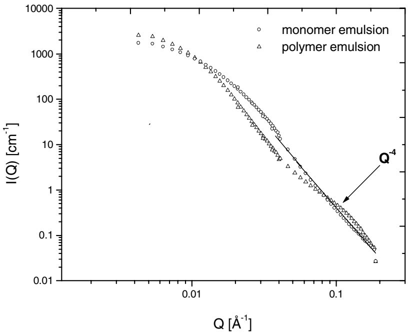

Figure 2 SANS Spectra after background correction. The Porod's law Q^{-4} behaviour, is also shown.

The spectra of samples (I) (spectrum(I)) and (II) (spectrum(II)) show a Q^{-4} dependence at high Q which corresponds to Porod's law [18] and indicate the presence of a sharp interface between two different regions of scattering length densities (solvent and particles). However, this dependence is visible down to $Q \sim 10^{-2}$ Å^{-1} for spectrum (I) only, whereas spectrum (II) is characterized by a large oscillation around Q^{-4} in the same Q-range. At small Q values ($\leq 5\ 10^{-3}$ Å^{-1}), the Guinier region [19] appears, but is too small to yield an accurate evaluation of the average radius of gyration of the particles. Moreover, it is probably affected by particle interactions through $S(Q)$.

Following equation (1), the monomer emulsion spectrum (I) is well fitted by a model of polydisperse homogeneous spherical particles [15] as shown on figure (3a). The best fit is obtained with a mean droplet size $\overline{R}$ = 240Å and a polydispersity p =40 %, and $S(Q)$ as shown on figure (3b).

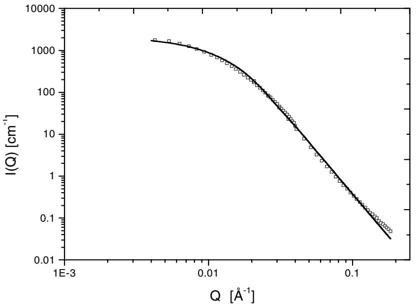

Figure 3a Fitting of spectrum (I) with a polydisperse homogeneous sphere model with mean radius $\overline{R}$ =240 Å and polydispersity p =40% for P(Q) .

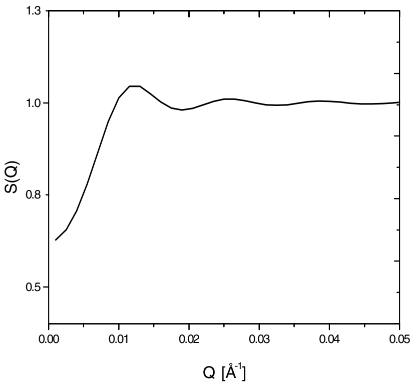

Figure 3b Fitting S(Q) for spectrum (I) : $\overline{R}$ = 240 Å and volume fraction = 6%.

This S(Q) appears to be significantly different from unity only for Q smaller than 0.009 Å^{-1}. When the interactions are negligeable, $S(Q)$ approaches unity.

The polymer emulsion spectrum (II) shown on figure (4a) is well fitted by a model where two distinct populations of polydisperse homogeneous spheres having the same scattering length densities but different mean sizes coexist. 80 wt.-% of the total polymerized mass is constituted by the largest particles with a mean size $\overline{R}_1$= 300Å and p_1= 33 %, and the remainder by the smallest particles with $\overline{R}_2$ =38Å and p_2 = 40%.

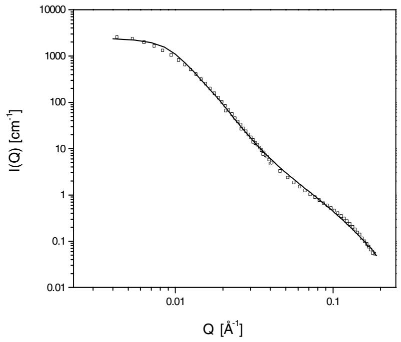

Figure 4a Fitting of spectrum (II) according to the sum of two spherical particle contributions for P(Q) (80wt.-% with $\overline{R}_1$=300Å and p_1= 33% , and 20wt.-% with $\overline{R}_2$= 38Å and p_2= 40%).

The fitting S(Q) is shown on figure (4b) and possesses the same features as $S(Q)$ of spectrum (I) . It should be noted that this structure factor $S(Q)$ is used here merely as a phenomenological function to obtain the best fit of $I(Q)$ and hence its fitting parameters should not be taken as exact physical values.

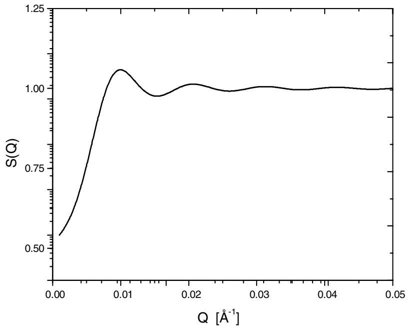

Figure 4b Fitting S(Q) for spectrum (II) : $\overline{R}$ = 300 Å and volume fraction = 8%.

These results can be interpreted in the following way. In anionic polymerization of cyclosiloxanes an interfacial mechanism [13] has been proposed in order to explain its main features. Initiation reaction occurs at the droplet surface by attack of the cyclosiloxane molecules by hydroxyl ions forming active silanolate centers. Propagation involves the diffusion of the monomers to the active centers, and then termination occurs with water molecules. Hence the silanolate chains lose their amphiphilic character and precipitate in the particle core. Besides this polymerisation reaction, secondary reactions occur and yield secondary products. Indeed, after the total consumption of the monomers, intermolecular redistribution or back-biting reactions occur producing mainly F_4 and F_5 cycles and other ramified molecules. Thus, it can be assumed that the smaller particle population corresponds to these secondary products and its high polydispersity indicates the presence of a large product spectrum. At equilibrium, the proportion of secondary compounds is 20wt.-% after 1 hour of polymerization as deduced from the fitting data. This result is in good agreement with the data of Barrère et al. [14] who obtained 90% polymerization yield. With regards to the size of the main particles, it must be pointed out that the polymer density has been taken equal to that of the monomer but this could not account for this large size difference. The observed growth in the mean particle size (25%) implies that there is no full preservation of the particles during the polymerization reaction as reported in other systems [20, 21] .

Concerning the size distributions two processes can be invocated: firstly, monomer mass transport or Oswald ripening due to monomer diffusion [22] ; secondly, droplet coalescence due to droplet collisions caused by Brownian motion and van der Waals forces. The last one is the most important mechanism and is also implicated in the increase of the droplet size during the polymerization reaction [23].

Conclusion

The primary and latex droplet particle mean sizes and size distributions have been determined by SANS experiments for a fluorinated tricyclosiloxane. The obtained sizes are rather located in an intermediate range between micro and miniemulsion.

The observed variation in the mean particle size with polymerization reaction as concluded from the data fitting cannot be accounted for by the difference between monomer and polymer densities. The concept of one- to-one copy process [24] as reported in other systems in favour of the idea of the independent nanoreactor does not seem to be an adequate model for this polymerization. This result is in good agreement with TEM data for polystyrene miniemulsion [25] and suggests the presence of the Oswald ripening and droplet and particle coalescence. Consequently, our system seems to behave in a continuous variation along the polymerization reaction. With regards to the second population (the presumed secondary products), these smaller particles appearing with a large size distribution are in favour of the idea that various side reactions occur.

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