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Characterization of a miniemulsion by DLS and SANS

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ABSTRACT

Dynamic light scattering (DLS), small angle neutron scattering (SANS) and transmission electronic microscopy (TEM) were used for the size determination of the poly(trifluoropropylmethyl)siloxane (PTFPMS) nanoparticles obtained by miniemulsion polymerization. The presence of large particles with a narrow size distribution as deduced from the DLS experiments on the latex sample was taken into account in the SANS data analysis by the introduction of a bimodal size distribution including a small particle population. It was shown that the contribution to scattering of the large particle component consistent with the SANS data should be less than about 45% of the total particle volume fraction. These results were corroborated by the spherical particle shape and the quite large particle size distribution observed on the TEM images. The DLS experimental procedures exploiting merely the cumulant analysis of the autocorrelation function for size determination in routine usage in the field of miniemulsions should thus be practiced with caution.

1. Introduction

Monomer miniemulsions suitable for miniemulsion polymerization are stable oil- in-water dispersions obtained under sonication and addition of an efficient surfactant and occasionally a water insoluble co-surfactant (hydrophobe) [1]. These miniemulsion monomer droplets are the main locus for particle nucleation producing submicrometer latex particles with a presumed size of 500–5000 Å upon addition of an initiator [2] in the polymerization process. Since the droplet mean size and size distribution affect directly both the particle nucleation and polymerization reaction [3], they are considered to be the most important parameters and are commonly measured by dynamic light scattering (DLS) experiments [4,5]. DLS is a non-intrusive, sensitive and powerful analytical tool used to characterize macromolecules and colloids in solution [6]. However, in the case of miniemulsions the results may suffer from some inconveniences such as the required high aqueous dilution of the samples in order to eliminate, or at least minimize, the effect of particle interactions. In addition, the hydrodynamic size of the particles obtained this way includes all the water layers that are coupled with the particle displacement. With regards to these drawbacks and sought goals, small angle neutron scattering (SANS) appears to be a more adequate tool. The choice of SANS is motivated by its higher spatial resolution besides its capacity to investigate the miniemulsions in their native states since particle interactions in concentrated media may be generally straight forwardly taken into account [7]. Last but not least, the measured sizes are independent of hydration effects.

In this paper, the particle structure of a miniemulsion previously characterized is investigated with the help of complementary techniques: DLS [8], SANS and TEM. The image method normally used for diluted miniemulsion samples is here experienced [9] on a concentrated one in order to examine its particle morphology and size distribution.

Hence, the structure of poly(trifluoropropylmethyl)siloxane (PTFPMS) synthesized by anionic ring opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) in the presence of hexadecyltrimethylammonium bromide (HTAB) as emulsifier [10], is followed with regards to the droplet mean size and size distribution as well as particle interactions.

2. Experimental

2.1. Materials

The monomer F_3 was supplied by General Electrics with a nominal purity larger than 99%. The surfactant HTAB was 98% pure and furnished by Acros Organics. Both compounds were used as

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received. The solvent is deuterated water for SANS and demineralized distilled water for the other experiments.

2.2. Sample preparation

5.160 g of F_3 and 0.266 g of HTAB were dispersed into 20.0 g of heavy water at room temperature. Then, 50 μL of the initiator, NaOH solution at 10^{-3} mole/L in D_2O, were added. The mixture was sonicated for 4 min at 55 W in a 450 Branson Ultrasonics Corporation sonicator and then introduced into the polymerization reactor under continuous stirring at 100 rpm for 1 h at 40 °C. 50 μL of a HCl solution at 10^{-3} mole/L prepared in D_2O was subsequently added in order to stop the polymerization reaction.

2.3. Instruments

2.3.1. Dynamic light scattering

The experiments were performed in the homodyne mode at 90° scattering angle on a Malvern Zetasizer-4. The sample dilution about 1/100 was performed in order to avoid counter saturation and particle interactions, as already mentioned.

2.3.2. Transmission electron microscopy

The latex particle morphology was observed through a Philips CM 30 TEM at a maximum accelerating voltage of 100 kV. The samples were prepared by casting a sample solution drop onto a 200-mesh copper grid covered with a carbon film. The drops were absorbed on a filter paper no. 41 and immediately deepen in liquid ethane cooled by liquid nitrogen and then transferred to the electron microscope.

2.3.3. Small angle neutron scattering

The data acquisition was performed on the spectrometer PAXE of the Léon Brillouin Laboratory at Saclay in three different setups in order to cover a large domain of momentum transfer. Despite a convenient transmission (around 0.7), the very high-scattered intensity at very small angles generated a small but significant saturation of the electronics which was not corrected during the experiment. Thus, the corresponding data were not taken into account in the data fitting process. The raw data were corrected for sample transmission, solvent and empty cell (2 mm thickness) contributions and detector efficiency by a standard procedure, then normalized and converted to an absolute scale of scattered intensity.

3. Theory/calculation

3.1. Dynamic light scattering

The field autocorrelation function obtained was well represented by a single exponential decay attributed to the presence of a monomodal particle scattering source. The mean apparent diffusion coefficient (D) deduced from the second order cumulant data analysis [11] is related to the mean (intensity weighted) hydrodynamic radius (R_H) of the globular particles by the well known Stokes–Einstein relation:

$$R_H = \frac{kT}{6\pi\eta D}$$

where η is the viscosity of the dispersion medium, k the Boltzmann constant and T the absolute temperature. The data treatment yields also an estimation of the width of the particle size distribution through the value of the polydispersity index (pdi) deduced from the second moment of the cumulant expansion.

3.2. Small angle neutron scattering

SANS experiments consist in measuring the static neutron intensity scattered at small angles. The scattering pattern from a given sample can be described in terms of the Fourier transform of the correlations of the scattering length density distribution [12]. In the case of a system made of homogeneous polydisperse spheres [13] dispersed in a solvent, the isotropic coherent scattered intensity is given by the following equation:

$$I(Q) = n\left[\left\langle \left|F(Q)\right|^2\right\rangle - \left|\left\langle F(Q)\right\rangle\right|^2\right] + n\left|\left\langle F(Q)\right\rangle\right|^2 S(Q) \quad (1)$$

Here n is the number of particles per unit volume of the sample and Q is the magnitude of the scattering vector. $S(Q)$ is the particle structure factor which takes into account the inter-particle interactions and $F(Q)$ is the particle diffusion function. In the case of spherical particles, it is usual to define the form factor $P(Q)$ as:

$$P(Q) = \left|\left\langle F(Q)\right\rangle\right|^2 = \int_0^\infty \left[\left(\frac{4}{3}\pi R^3\right)(\rho - \rho_s) f(Q,R)\right]^2 h(R)dR \quad (2)$$

In this expression, ρ and ρ_s are respectively the scattering length densities of the homogeneous particle and the solvent, and $f(Q,R)$ is the first order spherical Bessel function. $h(R)$ is the radii distribution function which is generally taken as the Schulz–Zimm distribution [14] for polymeric systems. It is characterized by the mean particle radius $\bar{R}$ and the width of the distribution is related to the size polydispersity factor p.

The contribution of $S(Q)$, associated to the correlations between the particle spatial positions, is estimated to a first approximation on the basis of the excluded volume model [15] where the particle size is taken as $\bar{R}$ and the volume fraction occupied by the particles is equal to 0.189 in our case.

4. Results and discussion

4.1. Dynamic light scattering

DLS measurements performed under the experimental conditions described above lead to a value of 1160 Å for R_H and 0.12 for pdi. Hence, according to these results, this latex sample presents a rather narrow distribution around the mean particle size whose value confers to the system the status of miniemulsion as it is generally accepted in the literature for other systems of the same kind. However, as already mentioned, our results are possibly affected by several errors, among which the considerable dilution carried out on the sample which may deteriorate the structure of the system.

4.2. Transmission electron microscopy

The stereotypes obtained with a good resolution are represented in Fig. 1 at different sample sites. At this μm-scale, a spherical morphology of the particles is observed. The size distribution is difficult to address correctly but seems nevertheless at first sight rather large in contrast with the low pdi value deduced from the DLS data treatment which suggests a narrow distribution. Furthermore, from inspection of the images, it appears that large as well as small particles seem to coexist. This feature will be taken into account in the SANS data analysis.

4.3. Small angle neutron scattering

The absolute scale latex SANS spectrum corrected for the flat incoherent background deduced from the highest Q values is depicted in Fig. 2. The scattered intensity shows two successive