

## Notes

## Microemulsion Synthesis of Fluorinated Latex Spheres

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## Introduction

Recently<sup>1</sup> we reported the synthesis of fluorinated latex colloids by emulsion polymerization in water. The motivation for this work was that fluorinated latex has an unusually low refractive index of 1.37, compared to the typical value of 1.5 for commonly used colloidal particles such as silica, polystyrene (PS), and poly(methyl methacrylate) (PMMA). Aqueous dispersions of silica or latex are generally turbid because of the large difference between the refractive index of the particles and that of water (1.33). Instead, fluorinated particles can be relatively easily optically matched to give transparent dispersions. This allows the study of the structure and dynamics of model colloidal sphere dispersions by light scattering and microscopy even at high volume fractions. With a single-step emulsion polymerization,<sup>1</sup> the obtainable size range is limited to radii between 50 and 250 nm. Larger particles can be easily obtained by seeded growth<sup>1</sup> up to a radius of at least 1000 nm. However, extension to smaller particle sizes by emulsion polymerization is problematic because at low monomer concentrations the particles obtained are polydisperse. It is well-known that small, monodisperse particles such as PS and PMMA can be synthesized using a microemulsion (see, for instance, refs 2 and 3). In a microemulsion, the size of micelles can be controlled by varying the ratio of surfactant/cosurfactant, and with respect to a classical emulsion polymerization this allows a fine control on the final particle size and high reproducibility. Moreover, because of the transparency of microemulsion systems, UV light provides an alternative and interesting method to initiate polymerization. In this note, we demonstrate that synthesis methods similar to those reported in refs 2 and 3 can be successfully applied to fluorinated latex to obtain particles with radii between 17 and 50 nm.

## Experimental Section

**Chemicals.** 1H,1H-heptafluoro-*n*-butyl methacrylate (97% Lancaster, molar mass 254.11 g/mol) was distilled under a reduced pressure at 30–40 °C in a nitrogen atmosphere.

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<sup>†</sup> Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University.<sup>‡</sup> Experimental Soft Condensed Matter Group, Harvard University, 9&15 Oxford Street, Cambridge, MA 02138.(1) Koenderink, G. H.; Sacanna, S.; Pathmamanoharan, C.; Rasa, M.; Philipse, A. P. *Langmuir* **2001**, *17*, 6086–6093.(2) Guo, J. S.; Elaasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 691–710.(3) Capek, I. *Adv. Colloid Interface Sci.* **2001**, *92*, 195–233.Table 1. Particle Radius  $R_{DLS}$ , Mobility  $\mu$ , and Zeta Potential  $\zeta$  of Fluorinated Latex Spheres

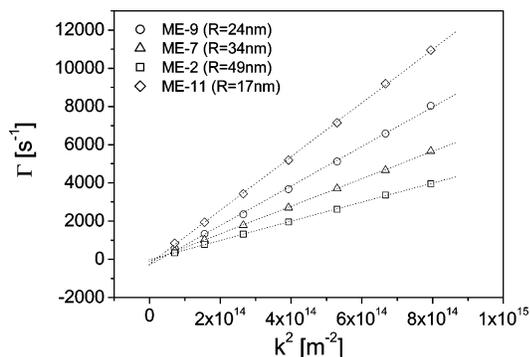
composition, wt % [water/1-pentanol/ monomer]	SDS wt %	$R_{DLS}$ [nm]	$\mu$ [ $\mu\text{m cm s}^{-1} \text{V}^{-1}$ ]	$\zeta$ [mV]	sample
77.9/3.64/9.89	8.57	52	−5.1	72	ME-1
89.0/4.16/6.79	8.98	49	−4.9	70	ME-2
90.9/4.27/4.80	9.19	48	−5.1	73	ME-3
89.7/5.22/5.05	8.98	35			ME-5
90.1/5.04/4.88	5.72	34			ME-6
92.8/3.58/3.58	8.98	34			ME-7
93.3/5.22/1.44	8.98	24			ME-9
91.4/7.18/1.44	8.98	17			ME-11
89.6/8.98/1.44	8.98	19			ME-12
91.8/6.80/1.36	3.92	19	−5.9	114	ME-13
89.0/4.19/6.76	8.98	50	−4.3	61	ME-15
91.3/3.65/5.06	8.98	30	−4.6	71	ME-16

Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , 99+%, Acros Organics) was used as a water-soluble initiator, and sodium dodecyl sulfate (SDS, 99%, BDH Laboratory Supplies, critical micelle concentration  $\sim 8 \text{ mM}$ )<sup>4</sup> and 1-pentanol (J.T Baker), surfactant and cosurfactant, respectively, were used as received without further purification.

**Microemulsion Polymerization.** Following the approach of Guo et al.<sup>2</sup> for microemulsion polymerization of styrene, stable oil-in-water microemulsions were prepared in a 100-mL round-bottom reaction flask, by adding mixtures (see Table 1) of 1H,1H-heptafluoro-*n*-butyl methacrylate and 1-pentanol to an aqueous solution of SDS, previously prepared by dissolving 2.75 g of SDS in 26 g of doubly distilled water. The contents of the flask were vigorously stirred and sonicated for several minutes to obtain a homogeneous microemulsion that was then stored at 4 °C for 24 h to attain equilibrium. In some cases, the microemulsion composition was then fine-adjusted by titration with pentanol. Before the polymerization was started, the microemulsion with the required amount of the persulfate initiator (0.65 mM) was degassed at low pressure for about 10 min by using a vacuum pump and then kept under nitrogen. The microemulsion was irradiated at room temperature for 8 h (entire reaction time) by an 8-W UV lightbulb (Sylvania blacklight blue) to promote the radical polymerization. Alternatively, the polymerization in the above-described microemulsion systems can be thermally initiated by heating the microemulsion to 70 °C. The microemulsion particles were purified by dialysis against deionized water for at least 3 days, to remove free monomer, 1-pentanol, emulsifier, and residual electrolyte. The small particle size makes concentration of the dispersions by centrifugation unfeasible. The high spinning rates necessary to sediment the particles irreversibly aggregate the particles. However, concentrated latex dispersions can be obtained by removing solvent with a rotavapor, followed by a cross-flow diafiltration using MicroKros hollow fibers modules with a molecular-weight cutoff of 400 kDa. The hollow fibers retain the particles above this cutoff and allow the free electrolyte and surfactant molecules, concentrated during the solvent evaporation, to permeate through the membrane. We found the resulting purified concentrated dispersions much more suitable for electron microscopy imaging than the original reaction mixtures.

**Light Scattering.** Light scattering cuvettes were cleaned by sonication in water (10 min) and afterward flushed with freshly distilled acetone. Dilute sphere dispersions were filtered in a dust-free hood, through a Millipore filter with a pore size of about

(4) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80* (9), 905–922.



**Figure 1.** Decay rate  $\Gamma$  of the electric field autocorrelation functions measured with DLS at various wavevectors  $K$ , for different particles (see Table 1).

five times the particles diameter. Dynamic light scattering (DLS) measurements were done at a temperature of 25.0 °C with an argon laser operating at a wavelength of 514.5 nm. Hydrodynamic radii  $R_{\text{DLS}}$  were obtained from the Stokes–Einstein diffusion coefficients measured by fitting DLS intensity autocorrelation functions to the second-order cumulant expression  $\ln g_i(K, t) = \beta_1 + \beta_2 t + \beta_3 t^2$  with fitting parameters  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ .

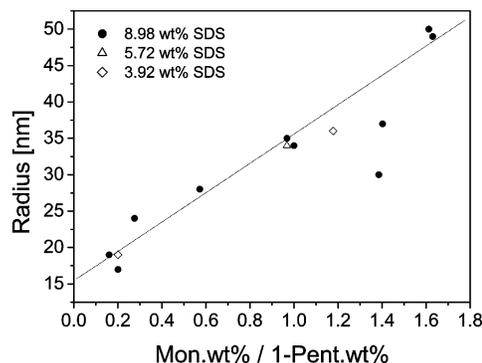
**Electrophoresis.** The zeta potential,  $\zeta$ , of the particles was estimated from electrophoretic measurements (Coulter DELSA 440 SX) on dilute samples, at a pH of 6, a temperature of 25 °C, and an ionic strength of 20 mM NaCl (i.e., a Debye–Hückel screening length of  $\kappa^{-1} = 2$  nm). A typical measurement was performed at a constant electric field of 20 V in both stationary layers of a 1-mm-thick gold cell, and the two independently measured mobilities were averaged. The electrophoretic mobilities,  $\mu_e$ , were converted to zeta potentials using the Smoluchowski equation ( $\kappa R \gg 1$ ) with Henry's correction term, as further explained in our previous paper on fluorinated latex spheres.<sup>1</sup>

**Particle Imaging.** The particle morphology was examined with a Philips TECNAI 12 transmission electron microscope (TEM) operating typically at 100 kV. Samples were prepared by dipping glow-discharged TEM grids in concentrated latex dispersions and drying for a few minutes under an infrared lamp.

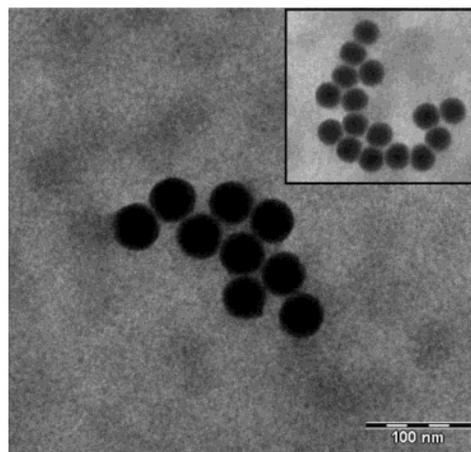
## Results and Discussion

Stable dispersions of fluorinated particles were prepared following the procedure described in the Experimental Section. After some preliminary synthesis work, using thermal decomposition of the water-soluble initiator (KPS), we made use of the optical transparency of the microemulsion systems to replace the thermal initiation by a more convenient photochemical polymerization at room temperature. In fact, KPS is known to be decomposed upon absorption of ultraviolet light at about 350 nm.<sup>5,6</sup> The stability of the dispersions was sensitive to the dialysis time. Typically, after 1 week of dialysis, some flocs were present in all dispersions. After removal of the flocs by filtration, the dispersion was stable during several months, as evidenced by DLS measurements.

Figure 1 displays the decay rate  $\Gamma$  of the electric field autocorrelation functions measured with DLS, as a function of the wavevector  $K$ . In all cases, we found a linear dependence of  $\Gamma$  on  $K^2$ , as expected for monodisperse particles. The slope of the  $\Gamma(K)$  plots equals the translational diffusion coefficient  $D$  of the particles. Using the Stokes–Einstein relation, we derived the particle radii collected in Table 1. Varying the relative composition of the ternary mixture water/1-pentanol/monomer, at different surfactant concentrations, inside the microemulsion stability one-phase region, we always obtained particle



**Figure 2.** Particle radius from DLS versus the concentration ratio of monomer/1-pentanol for particles prepared using different amounts of the surfactant SDS. The dotted line is to guide the eye.



**Figure 3.** Transmission electron microscopy picture of fluorinated latex spheres with a DLS radius of 42 nm, prepared by a UV-initiated microemulsion polymerization. In the inset, more particles are shown.

sizes in a range between 17 and 50 nm. Figure 2 shows that the particle radius appears to increase almost linearly with increasing monomer/cosurfactant concentration ratio, whereas it seems to be not particularly affected by variations in SDS concentration.

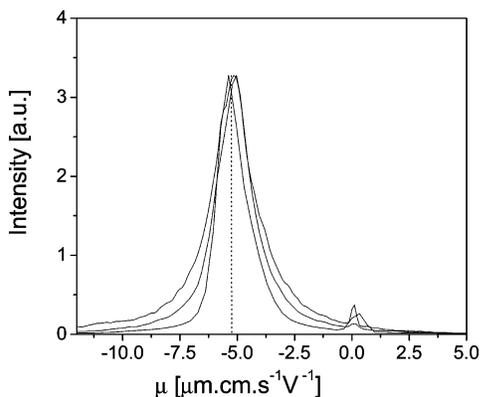
Attempts to visualize the fluorinated latex particles with electron microscopy were complicated by the rapid melting of the particles under the electron beam. Figure 3 shows one of the few samples we could image, containing fluorinated latex particles with a DLS radius of 42 nm prepared by a UV-initiated microemulsion polymerization. The particles look spherical and fairly monodisperse, confirming the narrow size distribution seen in DLS measurements.

We attempted to image the particles also by atomic force microscopy (AFM). However, the softness of the latex particles, also observed for larger fluorinated latex spheres,<sup>1</sup> made AFM probing unfeasible. Moreover, the particles are negatively charged (see Figure 4 and Table 1) and hardly stick to the mica surface used for AFM measurements, resulting in aggregation of the particles, probably due to capillary forces. Recently,<sup>7</sup> poly-L-lysine-coated mica substrates have been successfully used for bigger particles to reduce clustering during drying. However, particles with a radius around 30 nm flatten to objects of a few nanometers in height and can hardly be distinguished from the poly-L-lysine coating.

(5) Kubota, H.; Hariya, Y.; Kuroda, S.-i.; Kondo, T. *Polym. Degrad. Stab.* **2001**, *72*, 223–227.

(6) Livingston, J.; Morgan, R.; Crist, R. H. *J. Am. Chem. Soc.* **1927**, *49*, 338–346.

(7) Rasa, M.; Kuipers, B. W. M.; Philipse, A. P. *J. Colloid Interface Sci.* **2002**, *250*, 303–315.



**Figure 4.** Electrophoretic mobility of ME-3 ( $R = 48$  nm) particles. The three lines represent mobility measurements at different scattering angles.

As expected because of the anionic surfactant (SDS) used and the sulfate end groups  $[R-OSO_3]^-$  generated by the radical initiator system, the particles have a strong negative surface charge. Despite the different synthetic pathways, particles prepared by surfactant-free emulsion polymerization<sup>1</sup> and particles prepared by microemulsion polymerization show a comparable electrophoretic mobility (see Figure 4 and Table 1) of about  $-5.2 \mu\text{m cm s}^{-1} \text{V}^{-1}$ . This may indicate that the electrostatic particle stabiliza-

tion is mainly due to the anionic groups generated by the initiator system during the particle formation rather than to surfactant absorption.

In conclusion, we have shown that polymerization in a microemulsion provides a useful technique for the synthesis of very small fluorinated latex particles in the size range 17–50 nm. DLS and TEM measurements show that the resulting particles are monodisperse and spherical. The stability of the particles is provided by a negative surface charge. As a result of the low refractive index of fluorinated latex, this colloidal system may be useful, for instance, as a well-defined, optically transparent host suspension for diffusion studies on tracer particles by light scattering experiments. These “nano-latexes” further extend the presently available size range for fluorinated particles prepared by emulsion polymerization and seeded growth<sup>1</sup> to cover almost the complete colloidal size domain.

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