

One-Step Preparation of Highly Monodisperse Micron-Size Particles in Organic Solvents

Hua Hu* and Ronald G. Larson

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

Received June 11, 2004; E-mail: huhuadce@umich.edu

In this communication, we report the first simple and fast one-step method for synthesizing highly monodisperse micron-size PMMA particles dispersible in organic media through dispersion polymerization in the presence of PHSA (a polyhydroxyl-stearic-acid graft PMMA copolymer) as a stabilizer. There are two significant advantages of our method over earlier methods.^{1–2} First, by optimizing the composition of a solvent mixture of hexane and dodecane, we were able to increase the concentration of monomer up to 50–56% and obtain unusually large (up to 10 μm in diameter) PMMA particles. Second, by strictly controlling the nucleation time, we were able to make PMMA particles with a low polydispersity of around 1%, much lower than has ever before been achieved for such large particles.² We also report an unusual apparent metastable state in the nucleation stage.

Highly monodisperse particles are used as model systems for studying crystallization, melting, freezing, gelation, vitrification, and rheology of colloidal materials.^{3–9} Monodisperse large particles are also very useful in making toners, films, coatings, paints, chromatographic media, LCD displays, and optical materials. For example, they can be used as spacers for LCD displays and templates of porous structures to produce photonic band gap materials in telecommunication industries.^{7–9} With monodisperse large particles, new advanced materials such as binary crystals¹⁰ or well-defined and highly reproducible structures and clusters¹¹ can be made. When monodisperse particles are stained with fluorescent dyes, one can directly observe and study the behavior of individual colloidal particles to obtain deep insight into colloidal structures and dynamics. Therefore, highly monodisperse particles are preferred for both industrial applications and scientific research.

PMMA particles, because of their excellent hard-sphere properties and ability to be matched with solvent media in terms of density and refraction index, have drawn much attention in colloidal studies. There are numerous publications describing the preparation of PMMA particles with a size range of 100–2000 nm in organic media^{1,11–18} via dispersion polymerization. The preparation of particles larger than this is rarely mentioned. Although Williamson and co-workers² reported the preparation of PMMA particles of up to 8 μm in nonpolar media, the particle images in their paper show large polydispersities. Thus, despite much progress in the preparation of smaller monodisperse PMMA particles, preparation of monodisperse micron size ($>2 \mu\text{m}$) PMMA particles is still a major challenge.

In our method, monomers, methyl methacrylate (MM, Sigma), and methacrylic acid were used after removing inhibitors. The initiator, azo-diisobutyronitrile, was recrystallized in acetone. The solvents, hexane and dodecane (Aldrich), were used as received. A stabilizer PHSA was synthesized using the method described in our previous paper.¹⁸ The following detailed procedure was used to synthesize PMMA particles: (1) All reactants were mixed by a magnetic stirrer in a 50 mL flask at room temperature in the presence of nitrogen. (2) The mixture of reactants was heated to

and refluxed at 80 °C in an oil bath, which was equipped with a magnetic stir bar. The reactant mixture was stirred during the whole synthesis process to avoid the settlement of particles, and the stirring speed was set at a low level. The mixture of reactants became turbid shortly (about less than 3 min) after the temperature reached 80 °C, and the reaction was continued under reflux for 2 h until almost all the monomers in the solution were consumed. (3) An inverted fluorescent microscope (Nikon TE200) and SEM (Philips XL30 FEG) were used to measure the particle size and its polydispersity σ .

By optimizing the solvent ratio and by varying the monomer concentrations, highly uniform large particles were prepared simply, rapidly (the total reaction time is less than 2 h), and successfully in the range of 2–10 μm . The particle size was able to be precisely controlled using the method in our previous paper.¹⁸ After synthesis, a drop of PMMA particle suspension was deposited on a glass coverslip, and a monolayer of particles was then formed as the droplet dried, see Figure 1. Using the algorithm we described in the previous paper,¹⁸ we found the particle sizes in Figures 1a and 1c to be 3.89 μm with $\sigma = 1.4\%$ and 6.01 μm with $\sigma = 1.06\%$, respectively. The size of particles in Figure 1a is close to the SEM measurement of 3.81 μm in Figure 1b. The particles in Figures 1a–c are arranged into well-ordered two-dimensional crystal structures, which demonstrates that the particles are very uniform in size. Normally, for smaller particles ($<1 \mu\text{m}$), the polydispersity can be as high as 5% and yet generate a crystal structure, while for larger particles a lower polydispersity (less than 2%) is necessary if a colloidal crystal is to form. For example, Figure 1d is an image of 4.1 μm aqueous polystyrene particles (purchased from IDL, Inc.) deposited on a glass coverslip. These particles are not ordered into a crystal structure because σ is 4.5%, which is too large.

We attribute our success in preparing monodisperse micron-size particles, shown in Figure 1a–c, to our strict control of nucleation time, the higher concentrations of monomers used, and our optimization of the optimal composition of the solvent mixture. Nucleation is the most complex and important stage of particle preparation and also difficult to track experimentally because of the small size of typical particle nuclei. In our synthesis of large particles using carefully controlled solvency, we obtained nuclei that were unusually large and were able to observe stages of nucleation and growth that are normally not visible. We accomplished this by extracting samples of the reaction mixture at various time points and observing particles under an optical microscope. We found that under conditions leading to highly monodisperse large particles, after around 2 min of reaction, deformable droplets appeared whose size was highly polydisperse; see Figure 2a. These persisted until around 4–5 min, at which time a rather abrupt (~ 30 s) transition occurred from a light turbid to a milky turbid reaction mixture, and particles withdrawn after this transition were apparently solid and relatively monodisperse (polydispersity around 3.9%). Thereafter, the particles grew in size and

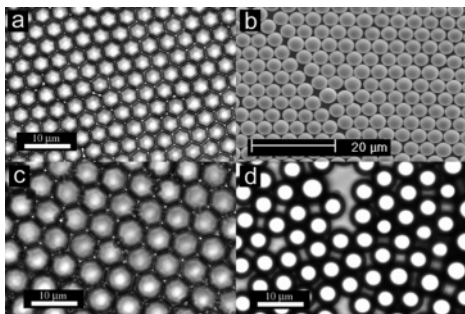


Figure 1. Highly monodisperse micron-size PMMA particles. (a) Image taken by an inverted fluorescent microscope. The size of the particles is $3.89 \mu\text{m}$ with $\sigma = 1.4\%$. (b) SEM image of the particles in a. The particle size measured by SEM is $3.81 \mu\text{m}$. (c) Highly ordered PMMA particles with a size of $6.01 \mu\text{m}$ and $\sigma = 1.06\%$. (d) Image of commercial $4.1 \mu\text{m}$ PS particles with $\sigma = 4.5\%$.

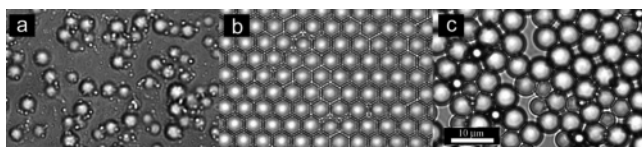


Figure 2. (a) Particle image in the metastable nucleation stage. (b) Highly monodisperse particles at a nucleation time of less than 2–3 min. (c) Polydisperse particles at a nucleation time of longer than 6 min.

in monodispersity until monomers were consumed; see Figure 2b. It was very surprising that the polydisperse droplets decreased their polydispersity so abruptly at the milky transition and that not only small droplets but also large ones disappeared from the population of particles at this transition. Conditions that do not lead to monodisperse large particles (see Figure 2c) had a longer phase (6–10 min) in which droplets persisted and a more gradual transition from light turbid to milky appearance. We do not understand the thermodynamics of these transitions but believe that the droplet phase is a metastable intermediate between the initial nuclei and the first well-defined particles. Further study of the transition from polydisperse droplets to relatively monodisperse particles at the milky transition is under way.

One major way to limit the nucleation time is to adjust solvency, which is especially important in a high monomer-concentration regime. Because monomers are good solvents for their own polymers, a higher concentration of monomers can make the particle nuclei more compatible with the solvent medium in which they are suspended. The solvency can be carefully tuned by varying the composition. We have found that a mixture of hexane and dodecane with a ratio of around 4:1 can produce highly monodisperse micron-size particles even at high monomer concentrations of 50–56%; see Figure 1. Using methods described previously in the literature,^{1,16} it was not possible to produce monodisperse micron-size PMMA particles in this higher monomer concentration regime. In addition, we also found that strict control of the reflux rate was necessary to maintain a consistent solvency.

Two-stage methods¹³ that include a seeding stage and a feeding stage were also unable to produce monodisperse micron-size PMMA particles. The difficulty was first caused by the unmanageably large feed of monomers used to increase the particle size beyond that of the seeding stage (around 300–1000 nm). The feed of additional monomers must be proportional to the cube of the

particle diameter since the number of particles does not change once nucleation is finished. Thus, to grow 3–10 μm particles, an additional 1000-fold charge of monomers over that in the initial seeding stage should be fed into the reaction system. A typical lab-scale reactor cannot tolerate such a huge change in the weight of the reactants. Even if one could manage these large charges, the addition of monomers and other components into the reaction system tends to change the solvency. The chance to renucleate is very high, and it is therefore easy to produce polydisperse particles. On the other hand, in our one-step method, since the monomers are consumed gradually and the solvency does not vary drastically, particle monodispersity can be easily achieved. Therefore, the one-step method is a better choice than the two-stage method to prepare monodisperse micron-size PMMA particles.

In summary, for the first time, a simple and fast one-step method has been developed to prepare monodisperse micron-size particles through dispersion polymerization in the presence of the stabilizer PHSA. The nucleation time was controlled to be less than 2–3 min and the ratio of hexane to dodecane chosen to be around 4:1 so that highly monodisperse micron-size PMMA particles can be produced in the higher monomer-concentration regime of 50–56%. We also discovered a metastable state in the nucleation stage, whose duration dramatically affects the polydispersity of the particles. In our forthcoming paper,¹⁹ we will address dynamics of particle growth, control of particle size, creation of fluorescent particles, and nanoparticles.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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