Poly(methyl methacrylate) Nanoparticles Prepared through Microwave Emulsion Polymerization

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ABSTRACT: The emulsifier-free emulsion polymerization of methyl methacrylate (MMA) was conducted with microwave irradiation. Superfine and monodisperse poly(methyl methacrylate) (PMMA) microspheres were obtained. Microwave irradiation notably promoted the polymerization reaction. This phenomenon was ascribed to the acceleration of the initiator [potassium persulfate (KPS)] decomposition by microwave irradiation. The experimental results revealed that the apparent activation energy of KPS decomposition decreased from 128.3 to 106.0 kJ/mol with microwave irradiation. The average particle size of the prepared PMMA latex was mainly controlled with the MMA concentration; it increased linearly from 103 to 215 nm when the MMA concentration increased from 0 to 0.3 mol/L and then remained almost constant at MMA concentrations of 0.3–1.0 mol/L. The KPS concentration had no effect on the average particle size, but the particle size dispersity was significantly reduced by a high KPS concentration. With a mixed polymerization phase (water/acetone = 1:3 v/v) or a redox initiation system, PMMA nanoparticles were obtained with an average particle size of 45 or 67 nm, respectively. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2815–2820, 2004

Key words: emulsion polymerization; microwave

INTRODUCTION

The number of applications of microwave-heating techniques in chemistry is growing rapidly. Many reactions thought to require lengthy heating periods in biochemical applications and polymer and organic chemistry are ideal for microwave promotion for rapid transformation and do not require extensive heating.[1,2] Microwave-assisted emulsion polymerization has the advantages of rapid reactions, high conversions, and low energy consumption.[3–5] As recent studies by Zhang et al.[6,7] indicated, polystyrene particles prepared by microwave-assisted emulsifier-free emulsion polymerization have narrow molecular weight and particle size distributions. Microwave-assisted polymerization is another way of preparing clean, superfine polymer particles.

As methacrylate is more hydrophilic and water-soluble than styrene, its nucleation procedure in emulsifier-free emulsion polymerization is thought to be homogeneous nucleation caused by the precipitation of growing oligomers;[8,9] this is different from that of styrene. A systematic study of methyl methacrylate (MMA) is required for a comprehensive understanding of microwave-assisted emulsion polymerization in a soap-free system. For clarity, a microwave reactor capable of controlling the temperature and microwave power was used in this study. Data from control experiments were provided to identify the relationship between the initiator decomposition and the polymerization rate and to permit a comparison of the microwave results with those obtained under classical conditions. One major purpose of this study was to prepare polymer nanoparticles. After the factors affecting the particle size were determined, two methods were tested to reduce the particle size to less than 100 nm.

EXPERIMENTAL

MMA, purified by distillation under reduced pressure, was stored in a refrigerator. Potassium persulfate (KPS) was purified by recrystallization in water. Copper sulfate and acetone were analytical-grade and were used as received.

The microwave reactor was reconstructed from a Whirlpool T120 microwave oven (Department of Radio Electronics, Sichuan University, China). The electromagnetic energy was produced by a magnetron at 2.45 GHz; the power could be adjusted between 0 and 700 W continuously. The temperature of the reaction system was monitored with an IR temperature pickup. With an internal cooling flask, the temperature could be adjusted precisely and independently of the micro-
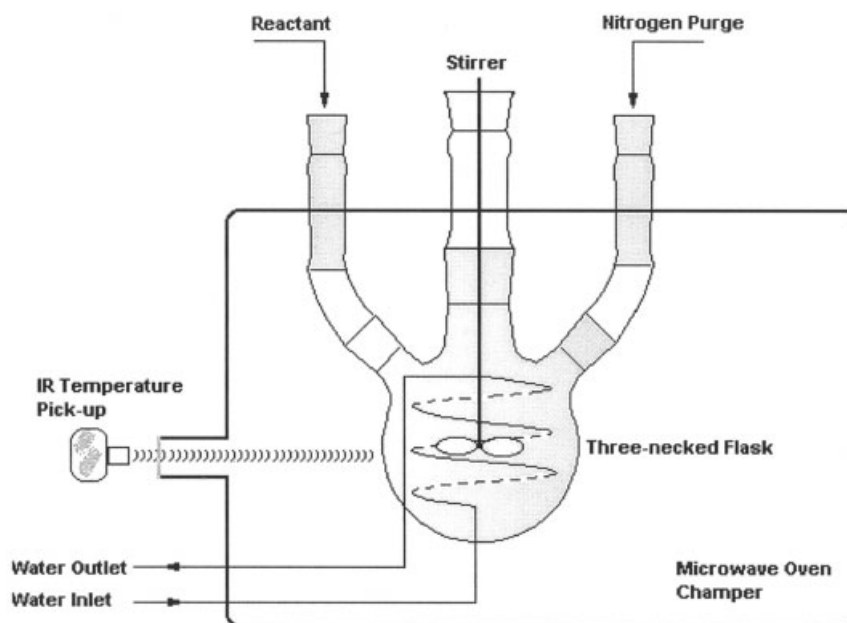
Figure 1 Sketch of the microwave reactor.

wave power. A schematic drawing is shown in Figure 1. In microwave-assisted polymerization, MMA, deionized water, KPS, and other ingredients were mixed in a flask stirred at 200 rpm, and then the flask was heated with 700-W microwave irradiation. After a temperature of 70°C was attained in 1 min, the microwave power was reduced to 40 W to maintain the temperature. The polymerization was accomplished in 2 h. Polymerization with a water bath, used for comparison, was performed according with the same temperature-rising procedure.

The monomer conversion was determined by a gravimetric method. The KPS decomposition rate was measured by an iodometric method. After being dyed with phosphotungstate, a poly(methyl methacrylate) (PMMA) latex was transferred to an electron microscope grid and observed with a JEM CX-100 transmission electron microscope. The particle size distribution parameters, include the number-average particle diameter (D_n), weight-average particle diameter (D_w), particle size diversity index (ε), and monodispersity index (U), were calculated on the basis of the digital graphical analysis results of transmission electron microscopy (TEM) photographs.[10] The liquid surface tension was determined with a Krüss K10ST digital liquid interfacial force meter:

$$D_n = \sum_{l-1}^{k} n_i D_i / \sum_{i-1}^{k} n_i \tag{1}$$

$$\varepsilon = \{\sum_{i-1}^{k}(D_i - D_n)^2/(k-1)/\}D_n \tag{2}$$

$$D_w = \sum_{i-1}^{k} n_i D_i^4 / \sum_{i-1}^{k} n_i D_i^3 \tag{3}$$

$$U = D_w / D_n, \tag{4}$$

where D_i, is the diameter of i species particle, n_i is the number of i species particle, and k is the total number of particle species with different diameters.

RESULTS AND DISCUSSION

Polymerization procedure

A graph of the fractional conversion of the monomer to the polymer as a function of time is shown in Figure 2. The polymerization was accomplished with microwave and convection heating at 70°C with 1.0×10^{-3} mol/L KPS and 0.30 mol/L MMA in a 200-mL water solution. The polymerization based on MMA/KPS/H_2O in the presence of microwaves had a higher rate of polymerization than that performed with convection heating. The induction period was 2 min for microwave polymerization but 15 min for convection heating. After 20 minutes reaction, the monomer conversion for microwave polymerization was 60%, whereas the corresponding conversion for convection heating polymerization was only 5%.

The increase of reaction rate was attributable to a dual effect: the activation of MMA polymerization and the acceleration of initiator decomposition, driven by the polar moieties in the radical oligomers or KPS with dipolar relaxation under 2.45 GHz electromagnetic wave. The second effect was systematically examined
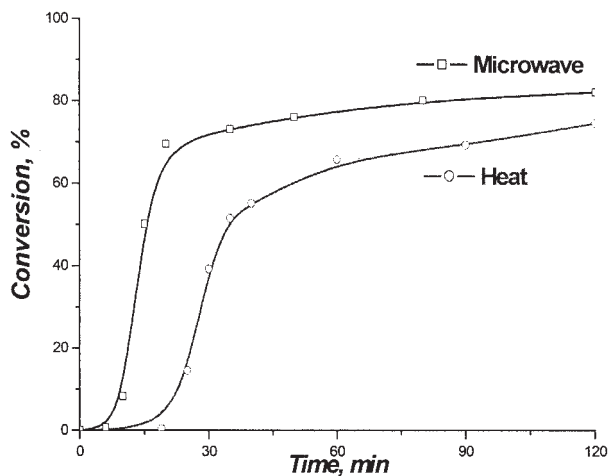
Figure 2 Conversion curves of MMA during microwave-irradiation polymerization and conventional thermal polymerization.

in our work. A solution with $1.0 \times 10^{-2}M$ KPS in water was used, and the decomposition rates for KPS undergoing convection heating, 40-W microwave irradiation, and 300-W microwave irradiation at 60, 70, 80, and 90°C were measured with an iodometric method. Figure 3 presents curves illustrating the relationship between the temperature and decomposition rate of KPS; the slopes of the curves are the apparent decomposition activation energy. The decomposition rates of KPS undergoing microwave irradiation showed no apparent divergences, but they were all higher than the rate of KPS undergoing conventional heating. Moreover, the variation of the heat was quite linear, but that of the microwave shifted between 60 and 70°C. The apparent activation energy, based on Figure 3, for conventional heating and 40- and 300-W micro-
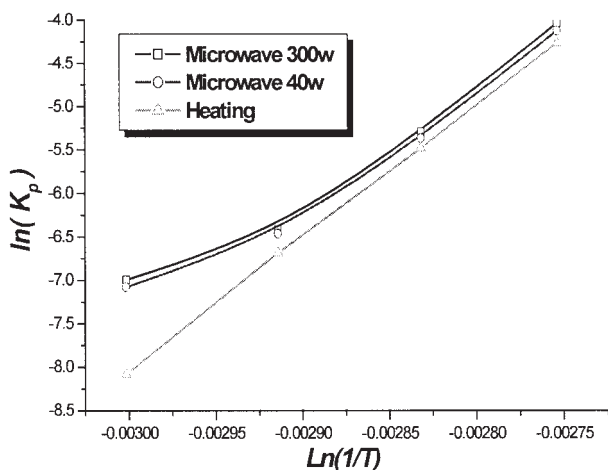

Figure 3 Decomposition curves of KPS with different heating methods [k_p = decomposition rate of KPS (min^{-1}); T = temperature (K)].

wave irradiation were 128.3, 106.0, and 97.1 kJ/mol, respectively.

Lewis et al.[11] studied the imidization reaction with microwave radiation and concluded that the apparent activation energy of the solution imidization reaction decreased from 105 to 55 kJ/mol when microwave radiation was used instead of conventional thermal processing. They proposed that because the predominant mechanism for the absorption coupling of microwave radiation to dielectric materials was forced oscillation of the dipole moments, the energy of the dipole moments of the reactants on a local scale was higher than that for nonpolar bonds or groups in the molecule; this resulted in an apparent activation energy reduction. The higher, localized energy would be observed as an enhanced statistical temperature at the dipole (ΔT). An equation was proposed to estimate ΔT:[11]

$$\Delta T = \frac{\left[T_{observed}^2 R \ln\left(\frac{k_{microwave}}{k_{thermal}} \right) \right]}{\left[E_a - RT_{observed}\left(\frac{k_{microwave}}{k_{thermal}} \right) \right]} \quad (5)$$

The determined decomposition rates of KPS were substituted into eq. (5). The ΔT values was determined to be 9.0, 2.0, 1.1, and 1.5°C for 40-W microwave irradiation at 60, 70, 80, and 90°C, respectively; ΔT for 300-W microwave radiation was a little higher. The results implied that the effect of microwaves was more significant at reaction temperatures lower than 70°C. At a higher temperature, the microwave effect was weakened by thermal factors.

Microscopic observations

Typical latex particles obtained by microwave polymerization are shown in Figure 4. Samples A and B were synthesized with two different MMA concentrations (0.30 and 0.23 mol/L, respectively) at a constant KPS concentration of 1.0×10^{-3} mol/L. The particles were spherical and very monodisperse. D_n and U of the latex particles were 214.8 nm and 1.03 and 169.3 nm and 1.03, respectively.

Effects of the MMA and KPS concentrations on the particle size

Emulsifier-free emulsion polymerization is a technique derived from conventional polymerization. For conventional polymerization, the stability of the system is attributed to the addition of surfactants aggregating together to form a large number of micelles in the polymerization; the concentration of the micelles could be up to 10^{18}/mL, and the rate of radical production is typically around 10^{13}/mL/s, so that the
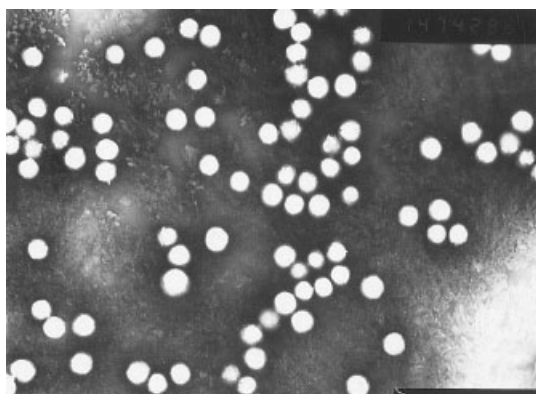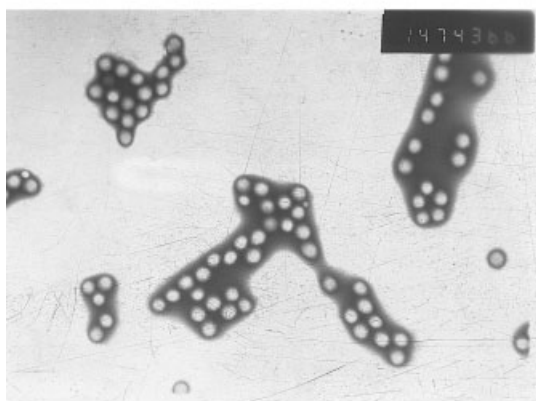
Figure 4 TEM images of PMMA particles synthesized by microwave polymerization: (A) 214.8 and (B) 169.3 nm.

probability for micelles being attacked simultaneously by radicals is low.[12] On the contrary, the concentration of primary particles in an emulsifier-free emulsion polymerization could be about 10^{12}/mL, which is much smaller than that for the radical production rate. Therefore, the diffusion of growing radicals from an aqueous phase into micelles could be uniform and lead to microspheres with monodisperse particle size distributions.

The particle size of the microspheres generated by an emulsion-free emulsion polymerization system depends mainly on the concentration of the monomer and the number of primary particles in the polymerization phase. Similar experiments were conducted with different MMA concentrations (0.01–1.5 mol/L) at a constant KPS concentration of 1.0×10^{-3} mol/L; the results are shown in Figure 5.

From these data, we can conclude that (1) for an MMA concentration lower than 0.3 mol/L, the latex particle size increased from 103 to 215 nm linearly with an increasing monomer concentration; (2) be-

tween MMA concentrations of 0.3 and 1.0 mol/L, D_n of PMMA particles remained constant at about 200 nm; and (3) for an MMA concentration beyond 1.0 mol/L, D_n increased again. However, a high MMA concentration caused instability of the latex, which led to coagulation sedimentation of the polymer during the last stage of polymerization.

At 70°C, the solubility of MMA in water is 0.15 mol/L. In the emulsifier-free emulsion polymerization of MMA, the radical oligomer or dead polymer chain exceeded the critical dimension of the primary particles, and the number of primary particles stabilized after the initial stage of the polymerization at a low monomer conversion.[8,14] The primary particles in the polymerization phase increased the solubility of MMA because of the solubilization effect. When the MMA concentration was less than 0.3 mol/L, after the initial stage of nucleation, the MMA residue could be fully absorbed by these primary particles. Therefore, there was no nucleation procedure in the following polymerization. This may explain the linear relationship of the latex particle size and the monomer concentration. There was a minimum particle size diversity at MMA concentrations between 0.23 and 0.3 mol/L, and it could be ascribed to the homogeneous and adequate swelling of all primary particles within this monomer concentration range. When the MMA concentration exceeded 0.3 mol/L, in a bulk polymerization procedure the monomer not absorbed by primary particles caused multiple nucleation procedures and consequently led to increasing particle size diversity.

The influence of the KPS concentration on the particle size is shown in Figure 6; the KPS concentration had no apparent effect on the average particle size. This was different from the emulsifier-free emulsion polymerization of styrene; there, the more KPS was used, the larger the particle size was for the resulting
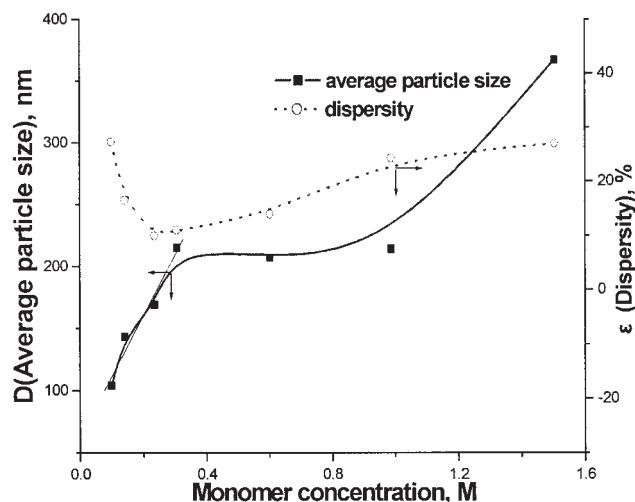

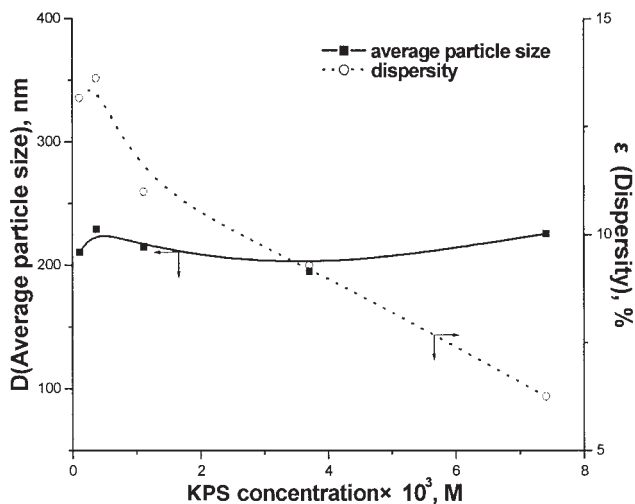**Figure 5** Effect of the MMA concentration on the emulsion particle size and size distribution.

Figure 6 Effect of the KPS concentration on the emulsion particle size and size distribution.

Figure 8 Conversion of MMA during microwave emulsion polymerization with acetone as the cosolvent.

polystyrene.[6,7] When the solid content for an emulsifier-free emulsion polymerization is fixed, the particle size of the microspheres mainly depends on the nucleation number in the polymerization phase. In this case, although increasing the ionic strength in the polymerization phase lessened the electrostatic repulsion of primary particles, the additional stability attained from the hydrophilicity of PMMA prevented the initial nucleus from coagulating and maintained the number of primary particles.[8,13] A high KPS concentration significantly reduced the particle size diversity. Because a higher KPS concentration generated a higher rate of radical production, it brought about a higher probability of primary particles being attacked simultaneously and consequently a higher uniformity for the resulting microspheres. We also deduced that because microwave irradiation promotes the decomposition of KPS, microwave-assisted polymerization
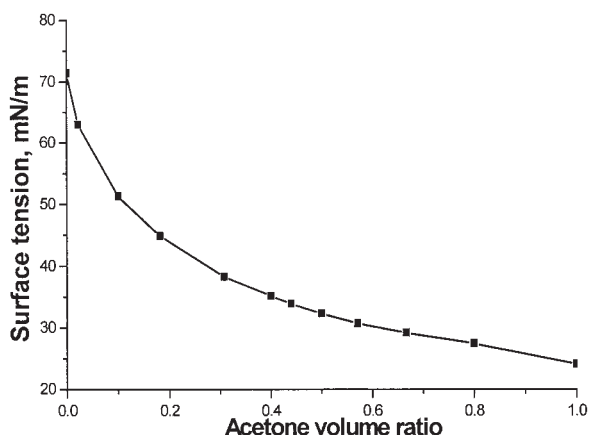
would also improve the uniformity of prepared latex particles. Therefore, we have a promising way of enhancing the effect of microwaves with a more sensitive initiation system.

Methods used to reduce the particle size

The PMMA microspheres prepared with this method had a minimum particle size of about 100 nm. For an emulsifier-free emulsion polymerization based on the MMA/KPS/H$_2$O system, a way of preparing smaller particles was to interfere with the nucleation mechanism through the addition of polar solvents. The higher the number was of the stable nucleus during the nucleation stage, the smaller the particle size was of the resulting microsphere. Acetone was used in our experiments. The dielectric coefficient of acetone (20.7) was lower than that of water (80.0), and the reduced
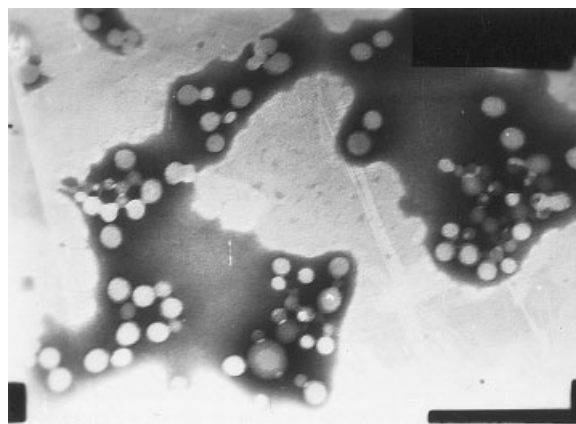

Figure 7 Surface tension of water mixed with different amounts of acetone.

Figure 9 TEM image of PMMA particles synthesized in a mixed medium (30% acetone and 70% water). The average particle size was 45 nm.
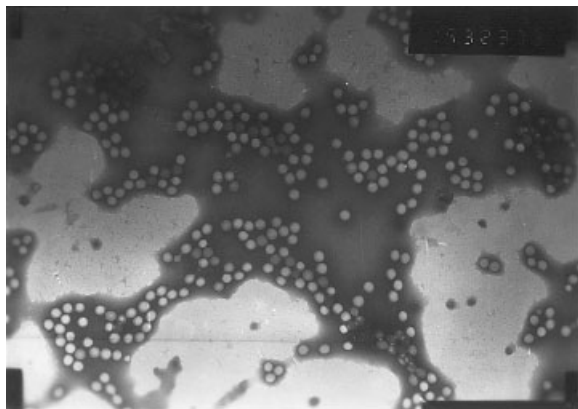
Figure 10 TEM image of PMMA synthesized with a $K_2S_2O_8/NaSO_3/CuSO_4$ redox initiation system. The average particle size was 67 nm.

polarity of the polymerization system enhanced the solubility of MMA in water. Acetone also reduced the surface tension of the polymerization system, as shown in Figure 7, and consequently stabilized the latex particles. Subsequently, adding acetone notably increased the formation of primary particles.

Figure 8 shows a time–conversion curve of MMA in a 30:70 acetone–water medium at a monomer concentration of 0.30 mol/L and a KPS concentration of 1.0×10^{-3} mol/L. The polymerization temperature was 65°C (the azeotropic point). The conversion curves obtained in this work did not conform to a typical shape; there was no rapid growth period at the start of the reaction. Arai et al.[15] studied the emulsifier-free emulsion polymerization of MMA in this system, and they indicated that the rate of polymerization increased gradually because of autoacceleration. In the water–acetone phase, the plasticization of acetone enhanced the mobility of the oligomer radicals and prohibited apparent autoacceleration in the polymerization procedure. Because of the higher number of primary particles, the monomer conversion reached a high level of about 99% after 2 h. Therefore, with acetone as a cosolvent, the emulsifier-free emulsion polymerization of MMA could be smoothly carried out in a short time.

The polymerization of MMA in the water–acetone phase provided a stable latex with spherical particles whose average particle size was about 45 nm, as shown in Figure 9, but there was some polydispersion in the particle sizes. Further work is needed to improve this method.

Using a $K_2S_2O_8/NaSO_3/CuSO_4$ redox initiation system effectively reduced the particle size of MMA/ethyl acrylate copolymer microspheres produced by a conventional emulsion polymerization.[16] We believe that the copper ion absorbed by the latex particles might increase their surface charge and overcome the van der Waal forces between any nearby particles. A reaction using a redox initiation system with 1.0×10^{-3} mol/L $K_2S_2O_8$, 1.0×10^{-3} mol/L $NaSO_3$, and 3.5×10^{-3} mol/L $CuSO_4$ was conducted. The results showed this effect was also significant in microwave-assisted emulsifier-free emulsion polymerization. As shown in Figure 10, the size of the generated PMMA particles was 67 nm, and they were very monodisperse; the diversity index was only 5.1%. The resulting emulsions prepared by these two methods also showed improved latex stability. Generally, an emulsifier-free emulsion sedimented after 90 days; the emulsion prepared in the acetone–water system or with copper salt remained stable even after 270 days.

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