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Communications to the Editor

Microwave Preparation of Narrowly Distributed Surfactant-Free Stable Polystyrene Nanospheres

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Recently, much attention has been paid to the preparation of polymeric nanoparticles in the size range of 10−100 nm. The microemulsion polymerization of polystyrene is a typical example.[1−10] It has been shown that the particle size can be quantitatively controlled by the initial fleet ratio, namely the macroscopic surfactant-to-monomer weight ratio.[1,8−10] A normal microemulsion contains at least water, monomer (oil), and surfactant. Often, a cosurfactant and/or salt are added to stabilize the microemulsion, so that the number of components could be four or more. In practice, a complete removal of the added surfactant and other components from the resulted polymeric particles is rather difficult, if not impossible. In this communication, we report, for the first time to our knowledge, a novel method of using microwave radiation to prepare narrowly distributed surfactant-free stable polystyrene nanospheres. It should be stated that using microwave radiation to initiate a reaction is not new in chemistry,[11] but it has several distinct advantages in the preparation of the surfactant-free stable polymeric nanoparticles.

In this study, a microwave oven (Whirlpool-VIP20) with a double emission system, operating at 2450 MHz with a maximum output power of 900 W, was used. A flask equipped with a glass stirrer, a reflux condenser, and feeding heads was assembled inside the oven. A mixture of proper amounts of freshly distilled styrene monomer and water inside the flask was stirred for 10 min at a speed of 3 × 10^2 rpm under N_2 before a given amount of initiator, potassium persulfate (KPS), was added to start the polymerization. The total volume of the reaction mixture is 250 mL. Typically, under the microwave radiation, the reaction temperature of ~70 °C was reached within just 2 min, and the reaction was carried out at ~70 °C under N_2 for 1 h, with a reduced microwave radiation of only 80 W. In this way, more than 98% of styrene monomer were polymerized within ~40 min. It should be stated that no surfactant was added, but the resultant polystyrene nanoparticles are stable with a constant particle size distribution over months. Moreover, such formed polystyrene nanoparticles are narrowly distributed (Figure 4). Figure 1 shows a typical hydrodynamic radius distribution $f(R_h)$ of the nanoparticles. In comparison, using a conventional heating method to polymerize the same reaction mixture under an identical condition not only took a much longer time (>10 h) to reach the same extent of conversion but also resulted in a much broadly distributed particles, as shown in Figure 1.

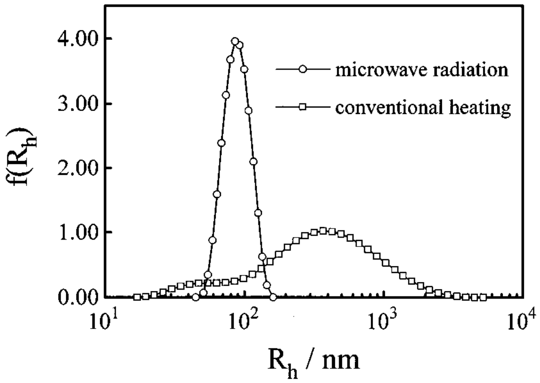

Figure 1. Comparison of the typical hydrodynamic radius distributions ($f(R_h)$) of the polystyrene nanospheres prepared by microwave radiation (○) and by the conventional heating method (□), where the styrene monomer and initiator concentrations are 1.13 × 10^{-2} and 3.02 × 10^{-4} g/mL, respectively.

Since no cross-linking agent was added, individual polystyrene chains inside the nanoparticles are soluble in toluene to form a polymer solution. Both the polystyrene nanoparticles in water and individual polystyrene chains in toluene were characterized by using a modified commercial laser light scattering (LLS) spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425 II, output power ~400 mW at $\lambda_0 =$ 532 nm). In static LLS, the weight average molecules (M_w) and the *z*-average radius of gyration ($\langle R_g \rangle$) were determined. In dynamic LLS, the measured intensity−intensity time correlation function was analyzed by both the cumulants and CONTIN (a Laplace inversion program) methods equipped with the correlator to give the average line width $\langle \Gamma \rangle$ and line-width distribution $G(\Gamma)$. Γ was further reduced to the translational diffusion coefficient (D) and the hydrodynamic radius (R_h).[8] The specific refractive index increments (dn/dC) of the polystyrene nanoparticles in water and individual polystyrene chains in toluene are 0.256 ± 0.002 and 0.110 ± 0.001 mL/g, respectively.[12,13] The details of LLS instrumentation and theory can be found elsewhere.[14,15]

The LLS results are summarized in Table 1. The ratios of $\langle R_g \rangle / \langle R_h \rangle$ are close to the theoretical value of 0.774 for a uniform hard sphere, indicating that these polystyrene nanoparticles are spherical and uniform. The small values of $(1 + \mu_2/D^2)$ clearly indicate that the resulted nanospheres are narrowly distributed, where $\mu_2 = \int_0^\infty G(D)(D - \langle D \rangle)^2 \, dD$ with D, $G(D)$, and $\langle D \rangle$ being the translational diffusion coefficient, the translational diffusion coefficient distribution, and the average translational diffusion coefficient, respectively.

Figure 2 shows that the plot of the average hydrodynamic volume ($\langle V_h \rangle$) of the nanospheres vs the initial monomer concentration (C_{monomer}) is a straight line for a given initiator concentration of 3.02 × 10^{-4} g/mL,

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Table 1. Summary of the LLS Results of the Polystyrene Nanospheres in Water and the Polystyrene Chains in Toluene at 25 °C[a]

			polystyrene nanospheres					polymer chains		
sample	C_m, g/mL	C_i, g/mL	$\langle R_h \rangle$, nm	$1 + \mu_2/D^2$	$\langle R_g \rangle$, nm	$M_{particle}$, g/mol	ρ_{app}, g/cm^3	$10^{-5}M_w$, g/mol	M_W/M_n	$10^{-3}N_c$
1	5.44×10^{-4}	3.02×10^{-4}	35.2	1.10						
2	1.81×10^{-3}	3.02×10^{-4}	39.2	1.10						
3	3.62×10^{-3}	3.02×10^{-4}	56.6	1.01						
4	1.13×10^{-2}	3.02×10^{-4}	82.1	1.01	69.4	7.57×10^{8}	0.54	1.06	1.8	7.96
5	1.45×10^{-2}	3.02×10^{-4}	87.9	1.03						
6	2.26×10^{-2}	3.02×10^{-4}	105	1.01	93.8	1.68×10^{9}	0.57	2.11	1.6	7.20
7	3.04×10^{-2}	3.02×10^{-4}	113	1.01						
8	1.13×10^{-2}	1.39×10^{-4}	73.4	1.01						
9	1.13×10^{-2}	6.08×10^{-4}	91.2	1.01				1.01	1.6	
10	1.13×10^{-2}	1.17×10^{-3}	117	1.01				0.71	2.0	

[a] The relative errors: $\langle R_h \rangle$, ±2%; $\mu_2/\langle D \rangle^2$, ±5%; $\langle R_g \rangle$, ±5%; $M_{particle}$, ±5%; M_w, ±5%; and M_w/M_n, ±10%.

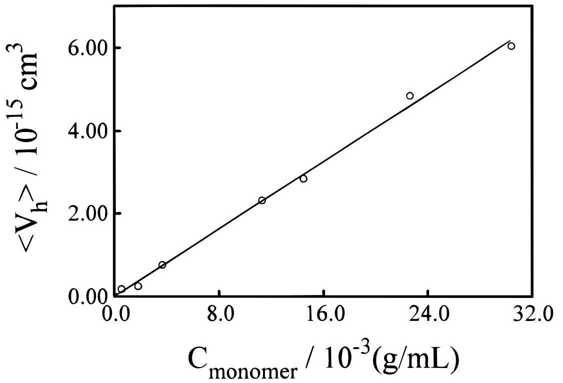

Figure 2. Monomer concentration ($C_{monomer}$) dependence of the average hydrodynamic volume ($\langle V_h \rangle$) of the polystyrene nanospheres, where the initiator concentration was kept at 3.02×10^{-4} g/mL and $\langle V_h \rangle$ is defined as $(4/3)\pi\langle R_h \rangle^3$ with $\langle R_h \rangle$ being the average hydrodynamic radius of the nanospheres. The line represents a least square fitting of $\langle V_h \rangle = 2.03 \times 10^{-15} C_{monomer}$.

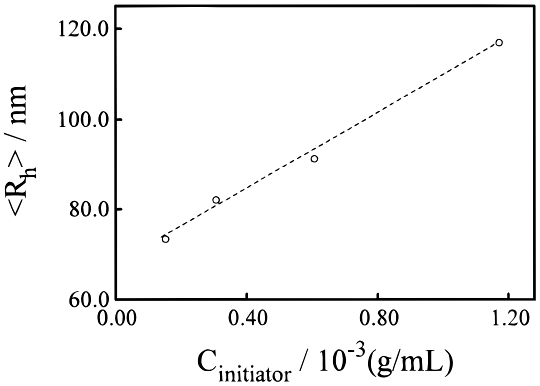

Figure 3. Initiator concentration ($C_{initiator}$) dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the polystyrene nanospheres, where the monomer concentration was kept at 1.13×10^{-2} g/mL.

where $\langle V_h \rangle$ is defined as $(4/3)\pi\langle R_h \rangle^3$. $C_{monomer}$ should be proportional to the number (N_p) of the nanospheres per unit volume and ($\langle V_h \rangle$), i.e., $C_{monomer} \propto N_p \rho \langle V_h \rangle$, where ρ is the average density of nanospheres. The straight line of $\langle V_h \rangle = 2.03 \times 10^{-15} C_{monomer}$ indicates that N_p is a constant which is independent of $C_{monomer}$. Moreover, a constant N_p implies that on average each nanosphere contains a constant number of individual polystyrene chains since the initiator concentration (or in approximation, the total number of the polymer chains) was kept as a constant. This interesting result leads us to look for other advantages of using microwave radiation besides the rate of polymerization.

It is known that microwave radiation can uniformly heat the entire solution. Therefore, it is reasonable to assume that the polymerization of styrene would be simultaneously initiated, presumably at the monomer droplet/water interface. For a given initiator concentration, the rate of the initiation should be a constant, resulting in relatively narrowly distributed polymer chains. Table 1 shows that the polydispersity index of the polystyrene chains inside the nanospheres is in the range of 1.5−2.0, relatively low for free radical polymerization. Further aggregation of these polystyrene chains would lead to the nanospheres stabilized by the ionic initiators at the chain ends. For a given dispersion energy and a fixed amount of the initiators, it is expected that, on the one hand, the average number of free radicals produced per droplet under the microwave should be a constant, resulting in a nearly constant number of the polymer chains inside each droplet; on the other hand, as the monomer concentration increases, each monomer droplet on average contains more monomers, so that each polystyrene chain could grow longer, resulting in larger particles. The average number (N_c) of individual polymer chains inside each nanosphere can be estimated from the ratio of the average molar masses of the nanospheres ($M_{particle}$) to individual polystyrene chains (M_{chain}), i.e., $N_c = M_{particle}/M_{chain}$. As shown in Table 1, M_{chain} is doubled when $C_{monomer}$ increases twice (samples 4 and 6), but N_c is nearly a constant, supporting our supposition. The fact that the apparent particle density (ρ_{app}) is nearly a constant suggests a similar packing of the polystyrene chains inside the nanospheres in spite of the variation of the chain length.

On the other hand, Figure 3 shows that the size of the nanospheres is nearly a linear function of the initiator concentration ($C_{initiator}$) for a given styrene monomer concentration. It is expected that the number of the polystyrene chains formed increases as the initiator concentration increases, so that the polymer chains have more chances to come together to form larger particles, i.e., N_c increases as $C_{initiator}$ increases. Moreover, on the basis of our previous discussion and Figure 2, the average length of the polymer chains depends on the monomer concentration. Therefore, for a given monomer concentration, the length of the polystyrene chains should be similar. As shown in Table 1 (samples 4, 9, and 10), it is true that the average molar mass of the polymer chains is close to ~1×10^5 g/mol.

In conclusion, narrowly distributed surfactant-free stable polystyrene nanospheres can be prepared by microwave radiation. In comparison with the conventional heating method, using microwave radiation can shorten the synthesis time by a factor of ~20. The size

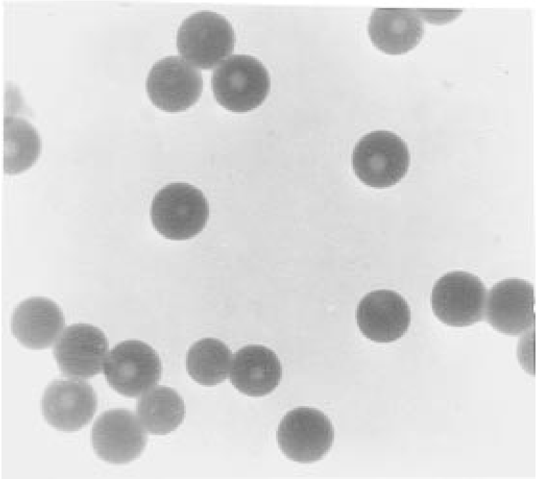

Figure 4. Electron microscopy micrograph of surfactant-free polystyrene nanoparticles prepared under microwave radiation. The magnification of 50 000 times.

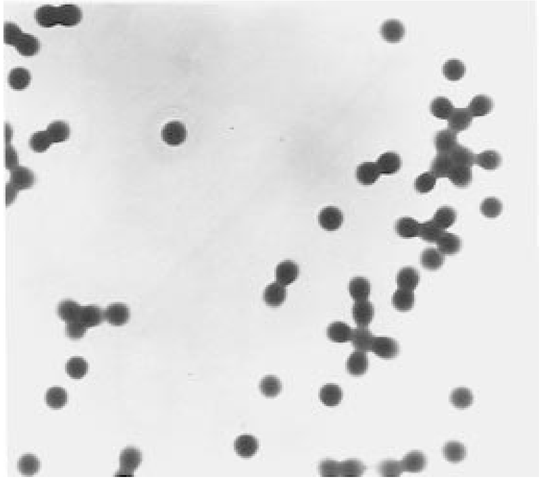

Figure 5. Electron microscopy micrograph of surfactant-free poly(methyl methylacrylate) nanoparticles prepared under microwave radiation. The magnification is 25 000 times.

of the nanospheres can be well controlled by varying the macroscopic monomer-to-initiator weight ratio. Our results indicate that the average number of individual polystyrene chains inside each nanosphere is independent of the monomer concentration but increases as the initiator concentration, and the average length of the polystyrene chains inside the nanospheres is independent of the initiator concentration but increases as the monomer concentration. Further studies are undergoing to reveal possible structural difference between the particles prepared by microwave radiation and by the conventional heating method. The method presented here is ready to be used to prepare other types of colloid particles, such as narrowly distributed stable surfactant-free poly(methyl methylacrylate) nanoparticles (Figure 5).

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