Environmentally adaptable pathway to emulsion polymerization for monodisperse polymer nanoparticle synthesis

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A B S T R A C T

An environmentally adaptable method is proposed for emulsion polymerization to produce monodisperse polymer nanoparticles at surfactant concentrations much lower than conventional emulsion polymerization. The present method is based on an idea of employing a surfactant with a low critical micelle concentration (CMC) to generate a large number of polymer particles in the presence of micelles at low surfactant concentrations and to cease the particle generation by the micelle disappearance in early reaction stage for attainment of high monodispersity of particles. A hydrophobic monomer of styrene (St) and a less hydrophobic monomer of methyl methacrylate (MMA) were used in the present emulsion polymerization at a total monomer concentration of 0.3 M with an initiator of ammonium persulfate (APS) and a long alkyl chain surfactant of sodium octadecyl sulfate (SOS). The polymerization was conducted at a high APS concentration of 20 mM that gave the CMC as low as 0.085 mM for SOS. An increase in the monomer mole fraction of MMA increased the number of polymer particles, while the high monomer mole fraction of MMA failed to stabilize the dispersion of particles. The polymerization for a monomer ratio of St/MMA = 1/1 could produce monodisperse polymer particles of 33 nm at a surfactant concentration of 1 mM that was higher than its CMC (0.085 mM) but much lower than several ten mM of surfactant concentrations in conventional emulsion polymerization.

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1. Introduction

Polymer nanoparticles have a wide variety of applications such as coating, adhesives, drug delivery, controlled release, biomedical separations and nano-structured template materials [1–8]. Since particle size is an important parameter which determines physical and chemical properties, high uniformity in particle sizes is required to regulate particle properties within a narrow range. To produce polymer nanoparticles with a narrow size distribution, various methods have been proposed [3,6,8–11]. In spite of the progress in synthetic techniques, it is still challenging to develop synthetic methods for producing small polymer particles with highly monodisperse sizes less than 100 nm.

Emulsion polymerization is suitable for production of small particles, because micelles formed of surfactants provide the loci of particle generation [12–14]. Typical use of emulsion

polymerization employs surfactant concentration much higher than the critical micelle concentration (CMC) to produce small polymer particles with high dispersion stability. However, the high surfactant concentration broadens particle size distributions. Advanced methods have been proposed for emulsion polymerization to produce small polymer particles with high monodispersity [15,16]. However, these production processes are not simple but multistage polymerization with the use of considerable amount of surfactants.

Polymer nanoparticles can also be produced with microemulsion polymerization [17–19] or miniemulsion polymerization [20–22]. These methods are difficult to produce highly monodisperse particles [18,20,22]. In addition, the methods are required to use large amount of surfactants and other additives such as alcohols and hydrophobes.

Surfactant-free polymerization is an environmentally adaptable process that can produce highly monodisperse polymer particles in water solvent without the addition of surfactant [23–26]. Although specific methods with extremely low monomer concentrations [8] or the use of organic cosolvent [27] can be applied to production of highly monodisperse nanoparticles in surfactant-

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free polymerization, production of monodisperse particles are, however, mostly limited to a particle size range of submicron-meters [28–31] to micron-meters [32–35].

Another method that restricts the use of surfactants is emulsion polymerization conducted at surfactant concentrations less than CMC. This method is applicable to the production of highly monodisperse polymer particles with small sizes [36–41]. Recently, the authors conducted the emulsion polymerization that employed a hydrophobic monomer of styrene and surfactants with low CMC under conditions of low ionic strength with an amphoteric initiator (VA-057) around neutral pH [41]. The use of the surfactants with low CMC was effective to produce monodisperse polymer particles less than 100 nm at low concentrations of submillimolar surfactant.

The present work is intended to further develop the emulsion polymerization applicable to the production of monodisperse particles less than 50 nm. The method proposed here is schematically shown in Fig. 1. Although our previous work employed styrene monomer [41], use of less hydrophobic monomer such as methyl methacrylate (MMA) is advantageous in a viewpoint of the production of large number of polymer particles due to its higher solubility in water [42,43]. Use of a low CMC surfactant in emulsion polymerization allows the operation at low surfactant concentrations, which may create an environmentally desirable process with the following merit. Since the polymerization is started in the presence of micelles that provide loci of particle generation, a large number of particles would be generated in an early stage of the polymerization but followed by deep suppression of the particle generation after the disappearance of micelles at a significantly low monomer-to-polymer conversion. This may enable production of polymer nanoparticles with a narrow size distribution. This idea is examined in the present emulsion copolymerization of St and MMA. Sodium octadecyl sulfate (SOS) is employed as a low CMC surfactant, and ammonium persulfate (APS) is used as a polymerization initiator to increase ionic strength in the system for lowering the CMC of the surfactant.

2. Experimental

2.1. Materials

Initiator (APS, 98%), styrene (St, 99%) and methyl methacrylate (MMA, 98%) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Anionic surfactant (SOS, 99%) was obtained from Alfa Aesar (Ward Hill, MA, USA). St and MMA were used after removing inhibitor with an adsorption column equipment. The other chemicals were used as received. Water was deionized to have an electric resistance higher than 18 MΩ·cm.

2.2. Synthesis of polymer nanoparticles

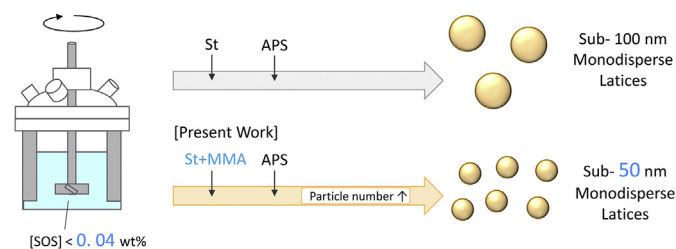All the polymerizations were conducted in a half liter reactor

Fig. 1. Schematic illustration on the proposed method using a combination of hydrophobic and less hydrophobic monomers. Sodium octadecylsulfate (SOS) was employed as an anionic surfactant with a low CMC.

with an inner diameter of 7.5 cm. The reactor was equipped with four baffle (0.7 cm in width) and four-blade-pitched paddle impeller (5 cm in length) located at 1 cm above the bottom. Aqueous solution of SOS (220 ml) was poured into the reactor placed in a constant temperature bath. The aqueous solution was bubbled with N_2 gas under stirring for 30 min. Then, monomers of St and MMA were added to the aqueous solution, which was kept stirred for 20 min under N_2 atmosphere. To initiate polymerization, 30 ml of aqueous APS solution was added into the reactor. The initial concentrations of chemicals in the polymerizations are listed in Table. Typical weights of St, MMA, SOS and APS to produce monodisperse nanoparticles were 3.9 g, 3.75 g, 9.3 mg and 1.14 g, respectively, for 250 g water, corresponding to Run 12 in the Table. The polymerizations were performed for 6 h at a fixed APS concentration of 20 mM and 70 °C with stirring at 360 rpm under N_2 atmosphere. Table 1.

2.3. Characterization

In each polymerization, a small amount of reaction mixture (less than 20 ml) was withdrawn from the reactor to measure particle size distribution and polymer yield. Hydroquinone was added to the reaction mixture to terminate the polymerization. The polymer yield was determined from the weight of polymer contained in the mixture with a freeze-drying method. More than 150 diameters of particles were measured with a transmission electron microscope (TEM mode on FE-SEM Hitachi, S-4800) to determine volume-averaged diameter, d_V, and the coefficient of variation of particle size distribution, C_V, defined as follows:

$$d_v = \left(\sum n_i \, d_i^3 \Big/ \sum n_i \right)^{1/3}$$

$$C_v = \frac{\left[\sum \{ d_i - (\sum n_i d_i / \sum n_i) \}^2 \right]^{1/2}}{\sum n_i d_i / \sum n_i} \times 100$$

where n_i is the number of particles with diameter d_i. Volume average diameter, d_V, and a coefficient of variation of particle size distribution, C_V, were calculated from the particle diameters. The number of particles in each polymerization, N_p, was calculated from d_V and the yield. The calculated values are summarized in Table together with the chemical concentrations in the polymerization.

The CMC of SOS was measured at 70 °C with an electrical conductivity method, in which a concentrated aqueous surfactant solution SOS solution with 20 mM APS was dropwisely added to 20 mM APS solution and the solution conductivity was measured with a conductivity meter (D-50, Horiba Ltd., Kyoto, Japan). The CMC was determined as an inflection point of conductivity−concentration curve (Fig. S1, see electronic supporting information).

3. Results and discussion

Copolymerization of MMA and St were conducted at [SOS] = 0.1 mM in a range of MMA mole fraction, X_{MMA}, for a total monomer concentration of 0.3 M on the basis of water volume. The CMC of SOS was 0.085 mM at the APS concentration of 20 mM and 70 °C (see again Fig. S1). At $X_{MMA} \geqq 2/3$, the polymer particles coagulated at late stage of the polymerization, as shown in Fig.2(a). Since PMMA is less hydrophobic than PSt, it is considered that the PMMA-rich particles were not stabilized due to poor adsorption of the SOS surfactant. The poor adsorption of alkyl sulfates to PMMA was reported by soap titrations for PSt, PMMA and their copolymer particles [43,44]. The individual particles in the figure can be distinguished as spheres that have definite sizes. The d_V and C_V