Environmentally adaptable pathway to emulsion polymerization for monodisperse polymer nanoparticle synthesis

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Abstract

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 1mM that was higher than its CMC (0.085mM) but much lower than several ten mM of surfactant concentrations in conventional emulsion polymerization.

Keywords: monodisperse polymer nanoparticle; low CMC surfactant;

emulsion copolymerization

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 [3,6,9-11]. 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-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 Figure 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.

Experimental

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 $18 \text{ M}\Omega \cdot \text{cm}$.

Synthesis of polymer nanoparticles. All the polymerizations were conducted in a half liter reactor with an inner diameter of 7.5cm. 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 N₂ 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 N₂ 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 3.9g, 3.75g, 9.3mg and 1.14g, respectively, for 250g water, corresponding to Run 12 in the Table. The polymerizations were performed for 6h at a fixed APS concentration of 20 mM and 70 °C with stirring at 360 rpm under N₂ atmosphere.

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

$$d_v = (\sum n_i d_i^3 / \sum n_i)^{1/3}$$

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

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:

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 supporting information).

Results and discussion

Copolymerization of MMA and St were conducted at $[\text{SOS}] = 0.1 \text{ mM}$ 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 $X_{\text{MMA}} \geq 2/3$, 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 values of the particles, including the data of $X_{\text{MMA}} = 2/3$, are plotted in Fig.2(b). All the C_v values measured were $< 5\%$ much lower than the typical criterion of 10% for monodispersity of particle sizes. The particle size, d_v , in the St polymerization ($X_{\text{MMA}}=0$) was large in comparison with the other data. Solubility of monomer in water solvent affects the generation of particles. High solubility of monomer tends to promote desorption of polymer radicals from small particles [43,45], which enables new generation of particles not only in the presence but also in the absence of micelles. Consequently, the high solubility can lead to a decrease in particles size. On the other hand, the C_v at $X_{\text{MMA}} = 0$ was similar to or slightly smaller than those at $X_{\text{MMA}} > 0$.

Figure 3 shows TEM images of PSt particles ($X_{\text{MMA}} = 0$) in a range of $[\text{SOS}]$ from 0.025 to 1.0 mM . Although the St polymerization was also conducted at $[\text{SOS}] = 0$ and 0.01 mM , polydisperse

particles were produced (see Fig.S2). The polydispersity implies that the particle coagulation proceeded for long period after particle generation in the polymerization. However, the surfactant addition had striking effects on particle size distributions. As shown in Fig.3, even an increase in [SOS] to 0.025 mM generated monodisperse particles with $C_V < 10\%$ and the monodispersity was continued up to [SOS] = 0.2mM, followed by a change in d_V from 218 to 67 nm. The SOS concentration of 0.2 mM is more than twice of the CMC (0.085 mM). Thus, the present work could prepare monodisperse particles at surfactant concentrations exceeding the CMC. However, the average particle size did not fall below 50 nm. At the concentrations of [SOS] ≥ 0.4 mM, the particle sizes became polydisperse, again as seen in Fig.3.

Figure 4 shows TEM images of polymer particles in emulsion copolymerization at $X_{MMA} = 0.5$. In Fig.4, the particles were monodisperse in a range of [SOS] up to 1mM while d_V fell below 50 nm and attained 33 nm at [SOS] = 1 mM that is more than 10 times higher than the CMC (=0.085 mM). When [SOS] exceeded 1mM, particle size distribution became polydisperse.

The values of N_p and C_V obtained in the polymerizations at $X_{MMA} = 0$ and 0.5 are plotted against surfactant concentration, C_S , in Figures 5 and 6, respectively. The same figures contain the data obtained with a short chain length surfactant of SDS (see Fig.S3 for size distributions) of particles formed at $X_{MMA} = 0.5$. The CMC of SDS measured at the initiator concentration of [APS] = 20 mM in water was 1.97mM at 70 °C. Even though the CMC was suppressed by the high ionic concentration of APS, 1.97 mM was almost 20 times higher than the CMC (0.085 mM) of SOS.

In Fig.5, N_p for SDS remarkably increased with an increase in C_S around the CMC. On the

other hand, the increase in C_S around the CMC for SDS gave rise to the sharp increase in C_V shown in Fig.6. The tendency of N_p is the common behavior reported in the emulsion polymerizations of hydrophobic monomers with short chain length surfactants [14, 36, 39, 42,46]. Appearance of micelles increases the number of particles, which elongate the period of polymer particle generation, eventually resulting in an increase in C_V [47] .

In Fig.5, the N_p curve of the St polymerization with SOS had a bending point clearly above its CMC. The particle formation mechanism below the CMC is expected to follow homogeneous nucleation that is polymer precipitation in the water solvent [36, 39, 42,47]. In a range of surfactant concentrations much higher than the CMC, the formation mechanism should be the heterogeneous nucleation caused by radical entrance into micelles. Smith-Ewart theory regarding N_p vs C_S is applicable to emulsion polymerization with hydrophobic monomer such as St. In the figure, the slope of the N_p curve above the bending point was almost consistent with 0.6 predicted by the theory. The high dependence of N_p on C_S around CMC is reported for the homogeneous nucleation in the polymerization of hydrophobic monomers [14,36,39,42,46]. For conventionally employed surfactants with a high CMC, the bending point appears on the CMC [36,42,46]. However, in the present case, the CMC of SOS is so small that the reduction in actual surfactant concentration in water phase, due to the surfactant adsorption on polymer particles [48], can shift the transition from the homogeneous nucleation to the heterogeneous nucleation toward the side of high surfactant concentrations. In Fig.6, C_V value of the St polymerization with SOS increased with C_S in the range above the CMC, and the C_V increase was gradual in comparison with the one

with SDS around its CMC.

In Fig.5, the bending point of the N_p curve for $X_{MMA} = 0.5$ with SOS is not clearly seen. It was reported that polymerization of monomers with a high solubility to water solvent tended to lose a bending point for the number of polymer particles plotted against surfactant concentration [42].

Nomura *et al.* reported that the Smith-Ewart theory was not applicable to the emulsion copolymerization of St and MMA with SDS and potassium persulfate (KPS) because of desorption of radicals from polymer particles and surfactant micelles [43,45]. In their reports, the slope of N_p curve at $X_{MMA} = 0.51$ was 0.76, with N_p value approximately 1.5 times higher than that at $X_{MMA} = 0$ [43]. The present polymerizations with SOS have a tendency of N_p similar to those reported by Nomura *et al.*

In Fig.6, C_V for $X_{MMA} = 0.5$ with SOS increases with C_S and its slope above the CMC is most moderate among the three polymerizations. This suggests transition from the homogeneous nucleation to heterogeneous nucleation. Since large numbers of particles were produced for $X_{MMA} = 0.5$ with SOS in Fig.5, it can be expected that the generation of polymer particles quickly reduces actual surfactant concentration in the water phase.

The equilibrium isotherms of surfactant adsorption onto polymer particles were reported for a variety of normal sodium alkyl sulfates ($C_nH_{2n+1}SO_4Na$) [44], providing the area (A_m) occupied by a surfactant at saturation adsorption to polymer particles. Using the A_m of normal sodium alkyl sulfates, the particle size of micelle disappearance, d_m , in the present polymerizations are estimated under the assumption of monodispersity for particles sizes (also see electronic supplementary

material for detailed calculation procedure). The calculated values of d_m for SOS were less than 7.6 nm for the copolymerizations of St and MMA at $[\text{SOS}] \leq 1.0\text{mM}$, whereas those for SOS were less than 6.0 nm for the St polymerizations at $[\text{SOS}] \leq 0.2\text{ mM}$. The low values of d_m suggest that the micelles disappeared in a very early stage of the polymerization. The polymer yield corresponding to the micelle disappearance was 1% at most in the present polymerizations.

The surface coverage of PSt particles with SDS was reported for conventional emulsion polymerization that was conducted at various St concentrations for $[\text{SDS}] = 40\text{ mM}$ with KPS initiator [48]. In the polymerization experiments, the saturated adsorption, corresponding to the surface coverage (θ) = 1, was maintained until the completion of polymerization at $[\text{St}] \leq 96.4\text{ g/dm}^3$. In this range of monomer concentration, the existence of micelles generated new particles until the end of polymerization, and the number of polymer particles increased with St concentration. If we calculate d_m for $N_p = 4.8 \times 10^{20}\text{ m}^{-3}$ of the polymerization, which was conducted at $[\text{St}] = 0.36\text{ M}$ (37.9 g/dm^3) similar to our case of 0.3 M St, the use of the A_m (0.42 nm^2) in the report [48] indicates a large value of $d_m = 75\text{ nm}$. This datum is further applied to the confirmation of the small d_m in the present polymerization. For instance, the d_m for PSt particles at $[\text{SOS}] = 0.2\text{ mM}$, estimated with the relation of $[\frac{d_m^2 N_p}{A_m(C_s - \text{CMC})}]_{\text{SDS}} = [\frac{d_m^2 N_p}{A_m(C_s - \text{CMC})}]_{\text{SOS}}$, is less than 8 nm because the A_m of SOS is smaller than the one of SDS. It is clear that the small d_m in the present polymerization is mainly due to the low surfactant concentration.

Since the present method generates particles in the presence of micelles and complete the generation for a very early period, it could have features of emulsion polymerization for large

number production and of soap-free emulsion polymerization for high monodispersity in particle sizes. With the features, the present work could produce monodisperse polymer particles with $d_v = 33\text{nm}$. The process is environmentally adaptable and different from conventional emulsion polymerization conducted at high surfactant concentrations.

Conclusions

A long alkyl chain surfactant of SOS with a low CMC was employed in emulsion copolymerization of hydrophobic St and less hydrophobic MMA initiated by APS. The polymerization ranged surfactant concentration, initiator concentration and monomer ratio at a total monomer concentration of 0.3 M. An increase in MMA mole fraction in the copolymerization (X_{MMA}) increased the number of polymer particles, while the particle dispersion was destabilized at $X_{\text{MMA}} \geq 2/3$. The polymerizations conducted for $X_{\text{MMA}} = 0.5$ at APS concentrations of 10 and 20 mM indicated that the latter APS concentration allowed the favorable results of large N_p and small C_v . The CMC of SOS was reduced to 0.085 mM by the addition of APS at the high concentration of 20 mM. SOS concentration was ranged across the CMC in emulsion polymerization at the APS concentration of 20 mM for $X_{\text{MMA}} = 0$ and 0.5. In the both cases of X_{MMA} , monodisperse polymer nanoparticles could be produced at surfactant concentrations well above the CMC, which is a distinctive feature different from conventional emulsion polymerization producing polydisperse particles at surfactant concentrations above CMC. The present results imply that the low CMC enables the production of large number of polymer particles in the presence of micelles even at low surfactant concentrations and the completion of particle **generation** in a very early stage of the polymerization. The reaction conditions of $X_{\text{MMA}} = 0.5$ and 1 mM SOS prepared monodisperse polymer particles with d_v as small as 33 nm.

Acknowledgement

This research was mainly supported by the Ministry of Education, Culture, Sports, Science and Technology (JSPS KAKENHI Grant No. 25600001). This research was partially supported by the Adaptable and Seamless Technology transfer Program through target driven R&D (A-STEP) from Japan Science and Technology Agency, JST (Grant No. AS262Z02259M).

Figure Captions

Table Averaged diameters (d_v), coefficients of variation of particle size distribution (C_v), polydispersity index (d_w/d_n), hydrodynamic diameters (d_{DLS}), polydispersity index (PDI_{DLS}) calculated from DLS measurement, the final numbers of particles (N_p), **polymer yields and solid contents (SC)** in polymerizations in the presence of SOS.

Figure 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.

Figure 2 (a) SEM image of polymer nanoparticles prepared in the emulsion polymerization of MMA ($X_{MMA} = 1.0$). (b) Averaged diameters (d_v) and coefficients of variation of particle size distribution (C_v) plotted against MMA molar composition in monomer (St + MMA). The concentrations of monomer, SOS and APS were 0.3 M, 0.1 mM and 20 mM, respectively.

Figure 3 TEM images of polymer nanoparticles prepared by emulsion polymerization of St in the SOS concentration range of 0.025 - 1.0 mM. The concentrations of St and APS were 0.3 M and 20 mM, respectively. Each scale bar shows 200 nm.

Figure 4 TEM images of polymer nanoparticles prepared by emulsion copolymerization of St and MMA ($X_{\text{MMA}} = 0.5$) in the SOS concentration range of 0.05 - 1.0 mM. The concentrations of St, MMA and APS were 0.15 M, 0.15 M and 20 mM, respectively. Each scale bar shows 100 nm.

Figure 5 The number of particles, N_p , plotted against surfactant concentration, C_s . Closed triangle shows results in the emulsion polymerization of St in the presence of SOS. Closed and open circles show results in the emulsion copolymerization ($X_{\text{MMA}} = 0.5$) in the presence of SOS and SDS, respectively. Monomer and APS concentrations were 0.3 M and 20 mM, respectively.

Figure 6 Coefficient of variation, C_v , plotted against surfactant concentration, C_s . Closed triangle shows results in the emulsion polymerization of St in the presence of SOS. Closed and open circles show results in the emulsion copolymerization ($X_{\text{MMA}} = 0.5$) in the presence of SOS and SDS, respectively. Monomer and APS concentrations were 0.3 M and 20 mM, respectively.

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Graphical Abstract

Emulsion copolymerization of St and MMA

with a low CMC surfactant

Sodium Octadecyl Sulfate (SOS)
(CMC = 0.085 mM)

APS, 70 °C

[Surfactant] < 0.04 wt%

Sub-50 nm monodisperse lattices

[SOS] = 0.4 mM

$d_v = 48$ nm

$C_v = 6.5$ %

[SOS] = 1.0 mM

$d_v = 33$ nm

$C_v = 9.2$ %

Table

Table Averaged diameters (d_v), coefficients of variation of particle size distribution (C_v), polydispersity index (d_w/d_n), hydrodynamic diameters (d_{DLS}), polydispersity index (PDI_{DLS}) calculated from DLS measurement, the final numbers of particles (N_p), polymer yields, and solid contents (SC) in polymerizations in the presence of SOS.

Run	St	MMA	SOS	d_v	C_v	d_w/d_n	d_{DLS}	PDI_{DLS}	N_p	Yield	SC
	[M]	[M]	[mM]	[nm]	[%]	[-]	[nm]	[-]	[m ⁻³]	[%]	[wt%]
1	0.3	-	0.025	218	1.9	1.001	221	0.114	4.45×10^{18}	89	3.12
2	0.3	-	0.05	165	2.0	1.001	185	0.021	1.01×10^{19}	88	3.10
3	0.3	-	0.1	105	2.6	1.002	116	0.013	4.01×10^{19}	89	3.12
4	0.3	-	0.15	74	8.9	1.023	81	0.018	1.05×10^{20}	82	2.93
5	0.3	-	0.2	67	8.4	1.019	75	0.014	1.59×10^{20}	91	3.18
6	0.3	-	0.4	58	12.3	1.042	64	0.011	2.42×10^{20}	92	3.21
7	0.3	-	1.0	46	13.1	1.047	50	0.082	4.22×10^{20}	99	3.48
8	0.2	0.1	0.1	75	2.8	1.002	82	0.009	1.17×10^{20}	95	3.29
9	0.1	0.2	0.1	60	4.1	1.005	Coagulation	-	-	-	-
10	0	0.3	0.1	-	-	-	Coagulation	-	-	-	-
11	0.15	0.15	0.05	74	3.4	1.004	110	0.066	1.02×10^{20}	80	2.83
12	0.15	0.15	0.1	64	3.8	1.004	80	0.007	1.80×10^{20}	94	3.20
13	0.15	0.15	0.15	56	4.5	1.006	71	0.011	2.70×10^{20}	92	3.17
14	0.15	0.15	0.2	51	4.6	1.007	63	0.011	3.28×10^{20}	87	3.02
15	0.15	0.15	0.4	48	6.5	1.013	57	0.028	4.26×10^{20}	92	3.17
16	0.15	0.15	1.0	33	9.2	1.026	43	0.069	1.34×10^{21}	97	3.35
17	0.15	0.15	2.0	33	12.1	1.041	37	0.054	1.15×10^{21}	87	3.08

The polymerizations were conducted at the APS concentration of 20 mM and 70 °C.

Figure 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

Figure 2 (a) SEM image of polymer nanoparticles prepared in the emulsion polymerization of MMA ($X_{\text{MMA}} = 1.0$). (b) Averaged diameters (d_v) and coefficients of variation of particle size distribution (C_v) plotted against MMA molar composition in monomer (St + MMA). The concentrations of monomer, SOS and APS were 0.3 M, 0.1 mM and 20 mM, respectively.

Figure 3 TEM images of polymer nanoparticles prepared by emulsion polymerization of St in the SOS concentration range of 0.025 - 1.0 mM. The concentrations of St and APS were 0.3 M and 20 mM, respectively. Each scale bar shows 200 nm.

Figure 4 TEM images of polymer nanoparticles prepared by emulsion copolymerization of St and MMA ($X_{\text{MMA}} = 0.5$) in the SOS concentration range of 0.05 - 1.0 mM. The concentrations of St, MMA and APS were 0.15 M, 0.15 M and 20 mM, respectively. Each scale bar shows 100 nm.

Figure 5 The number of particles, N_p , plotted against surfactant concentration, C_s . Closed triangle shows results in the emulsion polymerization of St in the presence of SOS. Closed and open circles show results in the emulsion copolymerization ($X_{MMA} = 0.5$) in the presence of SOS and SDS, respectively. Monomer and APS concentrations were 0.3 M and 20 mM, respectively.

Figure 6 Coefficient of variation, C_v , plotted against surfactant concentration, C_s . Closed triangle shows results in the emulsion polymerization of St in the presence of SOS. Closed and open circles show results in the emulsion copolymerization ($X_{MMA} = 0.5$) in the presence of SOS and SDS, respectively. Monomer and APS concentrations were 0.3 M and 20 mM, respectively.