Emulsifier-Free Miniemulsion Polymerization of Styrene Using a Cationic Initiator

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ABSTRACT: Polystyrene latex particles were synthesized using a method based on emulsifier-free miniemulsion polymerization under ultrasonic irradiation in the presence of 2,2′ azobis (2-amidinopropane) dihydrochloride (V-50) as a cationic ionizable water-soluble initiator and cetyl alcohol as costabilizer. The optimized conditions were obtained by using various parameters, such as the amounts of monomer and initiator, and the time and power of ultrasonic irradiation. In optimal conditions, the latex particles appeared to be about 250 nm in diameter through scanning electron microscopy (SEM). The SEM and gel permeation chromatography (GPC) analyses and monomer conversions of emulsifier-free miniemulsion polymerization were compared with those of conventional emulsifier-free emulsion polymerization using V-50 as initiator in both cases. The results showed that in the miniemulsion polymerization, the rate of polymerization (Rp) was significantly higher, and latex particles were significantly smaller than those in the conventional emulsion polymerization. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3515–3520, 2007

Key words: styrene; 2,2′ azobis (2-amidinopropane) dihydrochloride (V-50); emulsifier-free miniemulsion

INTRODUCTION

Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50–500 nm.[1,2] Miniemulsion polymerization is subject to numerous theoretical[3,4] and experimental studies.[5–8] In comparison with conventional emulsion polymerization, this method has various applications and advantages that were developed in recent years. In this method, various inorganic–organic hybrids can be produced using various inorganic nanoparticles, such as magnetite,[9,10] TiO_2[11] and SiO_2,[12] and polymers as nanocomposites. Since the progress of polymerization in miniemulsion polymerization is carried out in very small droplets called nanoreactors,[13,14] this method can be used to manufacture polymer nanoparticles[15] and nano-encpsulation of hydrophobic compounds.[16] This method also has applications in the production of high solid and viscosity control latexes[17] and it has industrial applications using amphiphatic macromolecules as surfactant to produce high solid stable latexes.[18] Many other new applications such as in polymerase chain reaction,[13] nano-emulsion production, and using them as formulations for controlled drug delivery and targeting,[19] etc, however, have been reported in the last few years.

Generally in miniemulsion polymerization, the submicrometer monomer droplets (miniemulsion droplets) are prepared by shearing a system containing monomer, water, surfactant, costabilizer, and initiator. Surfactant is used in sufficient quantity to provide the droplets with colloidal stability against coalescence and its concentration is also maintained below the critical micelle concentration (CMC) to avoid micellar nucleation.[20] A hydrophobic costabilizer (such as hexadecane as hydrophobe[8] and cetyl alcohol as costabilizer) retards the degradation by Ostwald ripening of the miniemulsion droplets[8] and the subsequent propagation reaction occurs primarily in submicrometer monomer droplets. Each of those droplets can be regarded as an individual nanophase reactor. Various surfactants and costabilizer (or hydrophobe) can be used in miniemulsion polymerization systems, which were reviewed previously.[14] It has been known that in miniemulsion polymerization, particle nucleation mechanisms are based on droplet nucleation and homogeneous nucleation. The droplet nucleation mechanism suggests that the droplets formed during the emulsification step are polymerized directly via a radical that enters these monomer droplets and reacts with the monomer present there. The homogeneous nucleation is a second possible mechanism for miniemulsion polymerization and its importance is for the so-called surfactant-free emulsion polymerization. In this case, the latex seeds are created from oligomers in the water phase, and the monomer is brought to the nucleation site by diffusion.[21]

On the other hand, in recent years, emulsion polymerization in the absence of added emulsifier has received considerable attention as a method for producing monodisperse and "clean" latexes, which are exten-

sively used in a wide variety of industries, ranging from coatings and adhesives to biomedicine and bio-technology.[22,23] This technique has been extraordinarily useful for the preparation of model polymer colloids with narrow particle size distributions and well-characterized surface properties. In such a polymerization system, polymer particles are stabilized by ionizable initiators, hydrophilic comonomers, or ionic comonomers. For example, 2,2′ azobis (2-amidinopropane) dihydrochloride (V-50) was used as a cationic ionizable water-soluble initiator in conventional emulsifier-free polymerization of styrene to obtain monodisperse latexes by Sharifi-Sanjani et al.[22] Several mechanisms have been proposed for particle nucleation and growth during polymerization without emulsifier. It is generally agreed that the actual process depends on the water solubility of the monomer. For example, in the presence of the water-soluble initiator, potassium persulfate (KPS), it has been proposed that slightly water-soluble monomers, such as styrene, polymerizes in aqueous phase to oligomeric radicals with sulfate end groups, which are surface active and form micelles in an emulsion polymerization. However, for more water-soluble monomers, such as (meth)acrylates, the particles are formed by the precipitation of growing chains upon achievement of a critical chain length, which is 60–80 for the monomer methyl methacrylate. In both cases, subsequent polymerization would occur in monomer swollen particles.[23] Although the principle of surfactant-free miniemulsion nucleation has been mentioned theoretically,[21] there is little information about miniemulsion polymerization in the absence of emulsifier via such systems to the best of our knowledge.[24,25] We recently reported the possibility of encapsulation of magnetite nanoparticles with polystyrene via an emulsifier-free miniemulsion polymerization system using V-50 as initiator and hexadecane as hydrophobe, and also showed that in conventional emulsifier-free emulsion polymerization using this initiator encapsulation of magnetite nanoparticles did not occur.[26]

In this work, polystyrene latex particles were synthesized using emulsifier-free miniemulsion polymerization method in the presence of V-50 and the effect of various parameters were studied. The SEM (scanning electron microscopy) and gel permeation chromatography (GPC) analyses, and monomer conversions of emulsifier-free miniemulsion polymerization were compared with those of conventional emulsifier-free emulsion polymerization using V-50 as initiator in both cases.

EXPERIMENTAL

Materials

The used styrene, cetyl alcohol, and tetrahydrofuran, THF (HPLC and for synthesis grades) were purchased from Merck Chemical Co (Whitehouse Station, NJ). The

styrene was purified by distillation under vacuum (0.5% CuI used for preventing polymerization of styrene) and was stored in a dark bottle at −20°C until required. The initiator was 2,2′ azobis (2-amidinopropane) dihydrochloride that was supplied by Acros Organics Co. (Noisy LeGrand, France) as V-50. It was kept at 4°C and was used without further purification. Double distilled water and technical grade methanol were used.

Procedure

The procedure for emulsifier-free miniemulsion polymerization was carried out in a two-stage process: (1) for preparation of miniemulsion, first, 0.1 g of cetyl alcohol as costabilizer was dissolved in styrene monomer. The mixture was added to 100 mL of water containing various amounts of 2,2′ azobis (2-amidinopropane) dihydrochloride (V-50) as an initiator. Second, these mixtures were sonicated with LABSONIC®P (400 W, B. Braun, Göttingen, Germany) at various power outputs (50 and 90%) for the given times (Table I) under inert gas of N_2 while being stirred. During sonication, the temperature of the mixtures increased depending on ultrasonification duration and to prevent evaporation of mixture the sonication container was equipped with a condenser. The recipe used to prepare the water-based styrene miniemulsions is given in Table I. And (2) for polymerization of miniemulsion, the above-mentioned miniemulsions were polymerized at 70°C under mechanical stirring with half-moon shaped Teflon stirrer at 320 rpm under inert gas of N_2 in a container equipped with a condenser.

The procedure for conventional emulsifier-free emulsion polymerization was similar to the one described for emulsifier-free miniemulsion polymerization except that it does not have sonication (Experiment No. 10 in Table I). To better compare these two systems, cetyl alcohol was added to both.

After polymerizations, some polystyrene aggregates were obtained. All products were centrifuged at 2000 rpm for 5 min and then analyzed.

Characterization

Conversions of styrene monomer in polymerizations were gravimetrically measured after the samples were dried at about 60°C under vacuum to constant weight.

Size and morphology of polymer particles were investigated by scanning electron microscopy (SEM) with ZEISS DSM 960A (Oberkochen, Germany) instrument. For SEM analysis, a drop of the latexes obtained after 24 h in polymerizations was placed on the glass and dried under freeze-drying. They were then placed under vacuum, flushed with Ar, evacuated, and sputter-coated with gold.

To measure size and size distribution, a few SEM micrographs were prepared to allow reliable size

TABLE I
Recipe Used for Preparation of the Styrene–Water Miniemulsions and
Conventional Emulsion Polymerizations

Exp. no.	Styrene weight (g)	Initiator (g)	Power sonication (% output)	Sonication time (min)
1	25.0	0.100	90	4
2	15.0	0.200	90	4
3	5.0	0.220	90	4
4	5.0	0.220	90	8
5	5.0	0.220	90	12
6	5.0	0.220	90	15
7	5.0	0.220	90	20
8	5.0	0.220	50	15
9	5.0	0.220	50	20
10	5.0	0.220	–	–

measurements from each sample. A number of 200–300 latex particles were counted to calculate the d_n as number average ($\Sigma n_i d_i / \Sigma n_i$), the d_w as weight average ($\Sigma n_i d_i^4 / \Sigma n_i d_i^3$) and the DI^{-1} as inversed dispersion index (d_w/d_n) showing polydispersity of particle size, where d_i is diameter of latex particles and n_i is the number of polymer particle with d_i in diameter.[27]

Gel permeation chromatography (GPC) analyses were performed by using Agilent 1100 series (Böblingen, Germany) GPC system. For GPC analyses, the obtained latexes were dried at 60°C under vacuum, dissolved in tetrahyrofuran (THF) precipitated in large amounts of methanol and dried again. The products were dissolved in THF and injected. The mobile phase was THF with flow rate of 1 mL min^{-1}. GPC data were recorded at 30°C on a mixed organic column equipped with RI detector.

RESULTS AND DISCUSSION

Miniemulsion polymerization

Emulsifier-free miniemulsion polymerization of polystyrene (in two processes, preparation of miniemulsion, and polymerization of the miniemulsion) was investigated by the examination of various parameters, such as monomer concentration, initiator concentration, ultrasonic duration, and power sonication. To achieve miniemulsion polystyrene latex particles, we first optimized the amount of initiator and styrene in proportion to water. Details of these experiments are given in Table I. In the first two experiments, the large amount of styrene monomer and the small amount of initiator were used. The SEM micrographs of the latex particles obtained from Experiments No. 1 and 2 showed the large coagulated and amorphous particles in these experiments.

We then decreased the amount of styrene and increased initiator concentration to raise the concentration of oligomeric radicals with cationic end groups, which are surface active and act like a surfac-

tant.[23] These oligomeric radicals are created by heat and shearing during ultrasonication.[26] These oligomeric radicals drive the homogeneous nucleation mechanism ahead, and increasing the oligomeric radicals concentration that promotes this mechanism. In Experiment No. 3, after sonication for 4 min at 90% output (400 W), the temperature increased to around 51°C and two phases were obtained; one phase was an organic transparent layer over the other opaque aqueous phase that had slightly dispersed organic emulsion. Then, this miniemulsion was polymerized at 70°C and the organic transparent layer gradually disappeared during polymerization after several hours. SEM, Figure 1(a), for this experiment showed that there was a wide range of particle sizes for latex below and above 500 nm (100 nm to 1.2 μm) in diameter of which the number average (d_n), the weight average (d_w), and the inversed dispersion index (DI^{-1}) as polydispersity of particle size are shown in Table II. As SEM micrograph, Figure 1(a), and the data of Table II show DI^{-1} showing size polydispersity is large for this experiment and this is a result of two mechanisms due to inadequate amount of the oligomeric radicals with surface activity in this experiment due to inadequate duration of sonication. The first mechanism is conventional emulsifier-free emulsion polymerization that acts for organic layer obtained after sonication and produces polymer particles above 500 nm (up to 1.2 μm) in diameter. The second mechanism is for emulsifier-free miniemulsion that produces polymer particles between 200 and 500 nm in diameter and acts for the aqueous phase obtained after sonication.[26] So, the duration of sonication was increased to raise the efficiency of initiator as the source of the oligomeric radicals with surface activity in the beginning of the polymerization process and in Experiment No. 4, the sample was sonicated for 8 min. After sonication for 8 min in this experiment, the temperature increased up to 72°C and organic transparent layer and opaque aqueous phase were also obtained similar to Experiment No. 3 with the difference that the amount of the
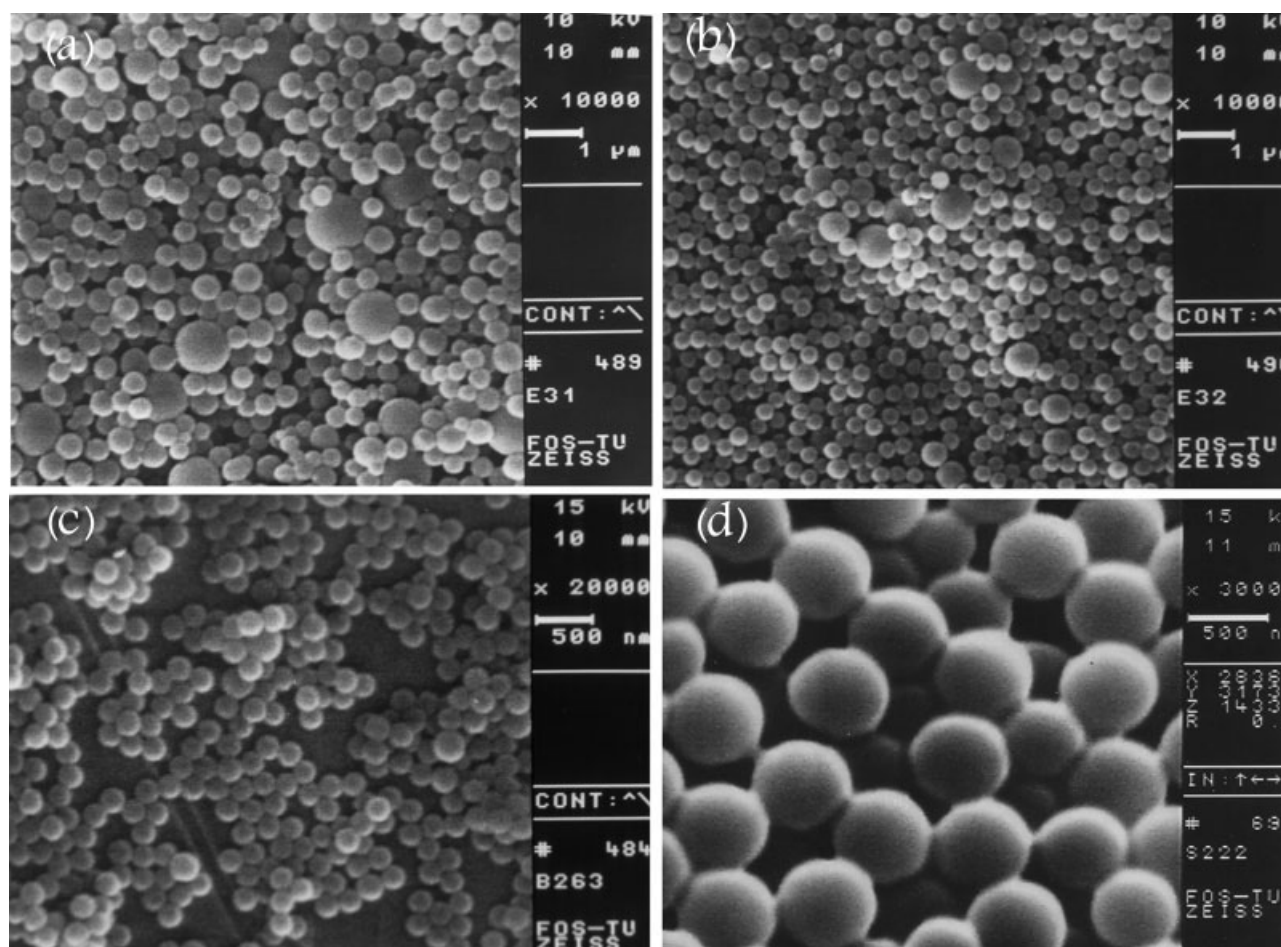
Figure 1 SEM micrographs of the latex particles obtained from experiments with difference sonication time, (a) 4, (b) 8, (c) 12, and (d) 0 min at power outputs of 90%.

organic layer in Experiment No. 4 was less than that in Experiment No. 3. Analysis of latex obtained after the polymerization of this product by SEM, Figure 1(b), showed that there was a wide range of particle sizes for latex from 200 nm to 1.1 μm like Experiment No. 3 of which the d_n, the d_w and the DI^{-1} are also shown in Table II. Comparison of SEM micrograph and amount of DI^{-1} of Experiment No. 3, Figure 1(a) and Table II, with SEM micrograph and amount of DI^{-1} of Experiment No. 4, Figure 1(b) and Table II, shows that the number of polymer particles above 500

TABLE II
Number Averages (d_n), Weight Averages (d_w)
and Inversed Dispersion Indexes (DI^{-1}) for Miniemulsion
and Emulsion Polymerizations

Exp. no.	d_n (nm)	d_w (nm)	DI^{-1}
3	521	770	1.478
4	394	527	1.338
5	253	260	1.028
8	469	610	1.301
9	269	274	1.019
10	634	645	1.017

nm in diameter and the size distribution of particles (DI^{-1}) in Experiment No. 4 are smaller than those in Experiment No. 3 because of the increasing amount of concentration of the oligomeric radicals with surface activity. This makes miniemulsion better due to increasing sonication time.

After 12 min of sonication in Experiment No. 5, the temperature increased up to 83°C and one aqueous phase without organic layer was obtained. Polymerization of this miniemulsion produced polystyrene latex particles below 500 nm (at about 250 nm) in diameter. Figure 1(c) is SEM micrograph for latex obtained in Experiment No. 5 which rather has monodisperse polymer nanoparticles about 250 nm in diameter with the DI^{-1} close to unit, Table II, and dose not have latex particles above 500 nm in diameter (formed by conventional emulsion mechanism). The effect of further lengthening of sonication time up to 15 min in which the temperature was 83°C after sonication, in Experiment No. 6, was not significant on size and morphology of latex particles, but lengthening of sonication time up to 20 min caused the dispersion to agglomerate in Experiment No. 7.

Comparison of miniemulsion and emulsion polymerizations

We attempted to compare the results of SEM and GPC analyses and the polymerization rate of emulsifier-free miniemulsion polymerization with those of conventional emulsifier-free emulsion polymerization method using V-50 as initiator in both cases. The details of conventional emulsion polymerization are also given in Table I (Experiment No. 10). Figure 1(d) is SEM micrograph for latex produced in Experiment No. 10. As this figure shows, the size of the latex particles was about 650 nm in diameter that was significantly larger than that in emulsifier-free miniemulsion polymerization [Fig. 1(c)]. The d_n, d_w, and DI^{-1} are also shown in Table II for this experiment (Exp. No. 10).

It also showed that the rates of polymerization of monomer in these polymerization systems are significantly different. Figure 2 shows the time evolution of conversions for the emulsifier-free miniemulsion polymerization, like Experiment No. 6 (in detail), and conventional emulsifier-free emulsion polymerization, like Experiment No. 10 (in detail). This time evolution was considered only for the second stage (polymerization) of process. As Figure 2 shows, the rate of polymerization of monomer in miniemulsion polymerization is significantly higher than that of conventional emulsion polymerization and the monomer conversion of this system reaches up to 87% after 4 h, while it reaches up to about this conversion (86%) after 14 h in conventional emulsion polymerization using V-50 in both cases, respectively. This result is comparable with results of other researchers[7] who studied miniemulsion and emulsion polymerization systems in the presence of initially added emulsifier and as they showed, the rate of polymerization of monomer is
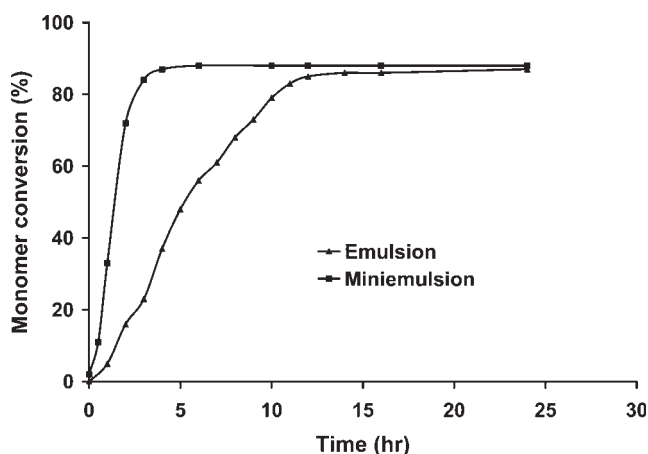
TABLE III
GPC Data of Polymers Obtained from Emulsifier-Free Miniemulsion and Emulsion Polymerizations

Exp. type	M_n (10^{-4} g mol^{-1})	M_w (10^{-5} g mol^{-1})	M_w/M_n
Miniemulsion	3.9	1.8	4.61
Emulsion	2.6	1.7	6.54

directly proportional to the number of particles formed, according to the well-known polymerization rate equation:

$$R_p = k_p[M]_p N_p n / N_A$$

Where k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the polymer particles, n is the average number of radicals per particle, N_p is the number of polymer particles, and N_A is the Avogadro's number. If n and $[M]_p$ are constant, the rate of polymerization reaction is mainly determined by the number of polymer particles.

GPC data for miniemulsion (like Experiment No. 6) were compared with those of emulsion polymerization (like Experiment No. 10). The samples at about 86% monomer conversion, i.e., polymerization in 4 h and 14 h for miniemulsion and conventional emulsion, respectively, were analyzed. The GPC data for these systems are given in Table III. The results showed a significant increase in the number-average molecular weight (M_n) and a slight increase in the weight-average molecular weight (M_w), and as a result, the molecular weight distribution (M_w/M_n) decreased in miniemulsion in comparison with conventional emulsion under the same conditions except for the sonication time. These results were probably due to monodisperse and small size of particles in miniemulsion system.

Figure 2 The time variation of overall conversion for emulsifier-free miniemulsion polymerization, like Experiment No. 6 (in detail), and the conventional emulsion polymerization, like Experiment No. 10 (in detail).

Effect of sonication power in miniemulsion polymerization

At last, we investigated the effect of sonication power. In Experiment No. 8, polymerization of the miniemulsion obtained after sonication at 50% output (400 W) for 15 min produced a latex having some latex particles above 500 nm (up to 900 nm) showed by SEM analysis due to lower power of sonication and thus lower concentration of oligomeric radicals. SEM micrograph of latex particles for this experiment is shown in Figure 3(a). Thus, the sonication duration was increased up to 20 min in Experiment No. 9. SEM analysis, Figure 3(b), shows that this experiment gave latex particles at about 200–400 nm in diameter after polymerization of the miniemulsion. The d_n, d_w, and DI^{-1} of these two experiments (Exp. No. 8 and 9) are also shown in Table II.
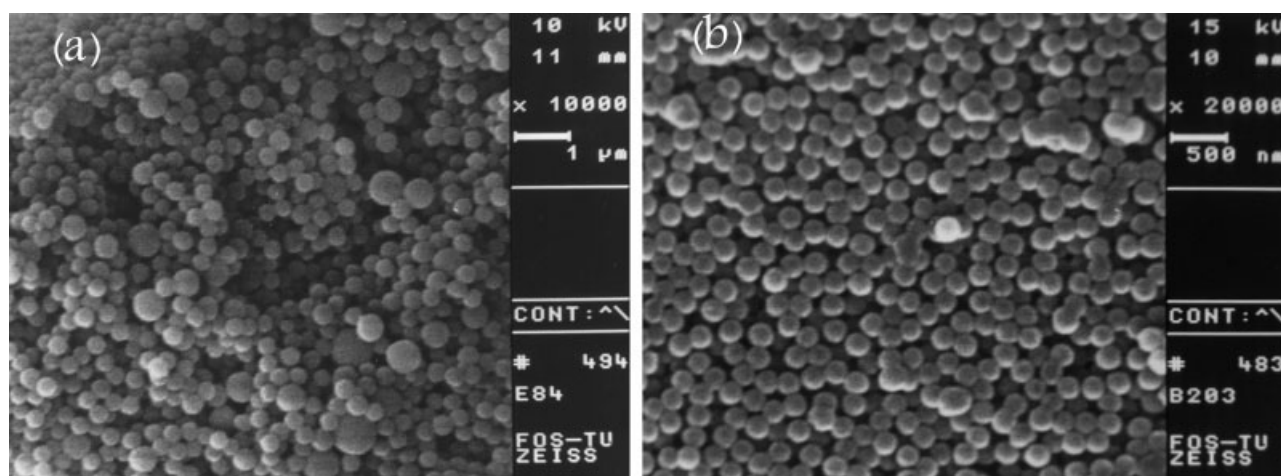
Figure 3 SEM micrographs of the latex particles obtained from experiments with difference sonication time, (a) 15 and (b) 20 min at power outputs of 50%.

CONCLUSIONS

It was shown that latex polystyrene nanoparticles at about 250 nm in diameter can be achieved by a new method based on emulsifier-free miniemulsion using a cationic ionizable water-soluble initiator and ultrasound waves to shear. It was also shown that sonication time and the overall amounts of monomer and initiator played key roles in controlling particle size and distribution. In short sonication time, there were two mechanisms, that is, emulsifier-free miniemulsion and conventional emulsifier-free emulsion polymerizations. So latex particles were produced in a wide range from 100 nm up to about 1.2 microns in diameter. Sonication for 12–15 min proved to be optimal for creating polystyrene nanoparticles with about 250 nm in diameter. Comparison of this method with conventional emulsifier-free emulsion polymerization under the same conditions showed that this method produced the latex particles with smaller particles size, narrower molecular weight distribution and higher number-average molecular weight and weight-average molecular weight. It was found that the rate of polymerization (R_p) in miniemulsion polymerization was significantly higher than that in conventional emulsion due to increasing the particles number.

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