Synthesis of Monodisperse Styrene/Methyl Methacrylate/Acrylic Acid Latex Using Surfactant-Free Emulsion Copolymerization in Air

Shengmiao Zhang,[1] Jianding Chen,[1] Mohamed Taha[2]

[1]Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
[2]Laboratoire de Rhéologie des Matières Plastiques, UMR CNRS 5223, Ingénérie des Matériaux polymères, Université Jean Monnet, Faculté des Sciences, 23 Rue de Docteur Paul Michelon, St.-Etienne Cedex 2 42023, France

ABSTRACT: Monodisperse styrene/methyl methacrylate/acrylic acid (St/MMA/AA) copolymer microspheres have been prepared with surfactant-free emulsion polymerization in air. The presence of oxygen in the system not only caused an induction period but also decreased the average particle size (D_p). However increasing AA concentration ([AA]) gave a reduction in the induction period. The FTIR and NMR analysis of the latex copolymer confirmed that the correlation of the copolymer compositions with the feed compositions was much better at the lower [AA] than at the higher levels. The AA contents of the copolymers obtained in air were much lower than those of the copolymers obtained under N_2 protection. Decreasing [AA] led to decrease in the copolymer molecular weight and broadening of the molecular weight distribution, but the particle size distribution (δ/D_p) was unaffected. In addition, the average particle diameter (D_p) was proportional to $[AA]^{-0.255}$, and increasing comonomers feed content caused linear increase of D_p, and a monodisperse sample with final solids contents up to 34.2 wt % was obtained. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1598–1605, 2009

Key words: surfactant-free emulsion polymerization; particle size distribution; molecular weight distribution; oxygen; high solids content

INTRODUCTION

Monodisperse polymer microspheres were attractive for a wide range of applications as chromatography packing materials, ion-exchange beads, coatings, calibration standards, drug delivery, and medical diagnostics.[1,2] For most of these applications, size control, narrow size distribution, and high solids content are of key importance. A rich variety of approaches have been described for producing such well-controlled polymer microspheres over several decades. The best-established and most commonly used method is emulsion polymerization. However, the presence of surfactant is a disadvantage for certain applications of emulsion polymers such as those involving instrument calibration and pore size determination. Surfactant-free emulsion polymerization is a useful approach to prepare clean monodisperse spheres.[3–6] Up to now, the preparation of monodisperse microspheres with emulsion or surfactant-free emulsion polymerization is normally performed in inert gas,[7–10] and achieved at low solids content, usually not more than 20 wt %.[11]

It has been recognized that dissolved oxygen is one of the most common impurities in real systems, which consumes radicals, and can influence the radical entry rate into the particles and micelles. In an industrial emulsion polymerization, the presence of oxygen will cause initiating induction periods and/or reacting rate retardation, both of which decrease reactor productivity and increase process cost. But in most industrial settings, it is difficult to achieve the oxygen-free levels. de Arbina et al.[12] conducted a calorimetric study in the influence of oxygen on seeded styrene emulsion polymerization. They showed that oxygen not only caused an inhibition period but also reduced the reaction rate. Cunningham et al.[13] studied the effect of oxygen on the emulsion polymerization of styrene. They suggested that the length of the induction period did not vary linearly with the initial oxygen level, and that the oxygen diffusing from the headspace was an important factor. Bruyn and coworkers[14] argued that the

retardation by oxygen in seeded emulsion polymerization of vinyl acetate resulted from a competition between the aqueous phase oligomeric radical reaction with oxygen and the inclusion of the oligomeric radicals in latex particles. Furthermore, synthesis of monodisperse latices at high solids content has arose much attraction for solids support applications.[10,15] Increasing the solids content offers advantages such as a reduction of film drying time, production, and transport costs. Mouaziz et al.[10] synthesized monodisperse microspheres using surfactant-free emulsion copolymerization of styrene (St) with methacrylic acid (MAA) under nitrogen, which yielded to solids contents of $\sim$33 wt %. Chern and Lin[16] synthesized nearly monodisperse particles (the polydispersity index of the particle size distribution $d_w/d_n \geq 1.08$) using semibatch emulsion copolymerizations of butyl acrylate and (meth-)acrylic acid at $\sim$40 wt % solids contents in inert gas.

However, relatively few works have been done on the issue of oxygen effects on surfactant-free emulsion polymerization, and few indeed have actually synthesized monodisperse polymer microspheres using high solids content surfactant-free emulsion polymerization in air.

The monodisperse P(styrene-methyl methacrylate-acrylic acid) (P(St-MMA-AA)) microspheres have been prepared with surfactant-free copolymerization of St, MMA, and AA under inert gas protection previously.[8,11] The particle size, copolymer composition, and surface group of this type microspheres can be tailored.[8,11] The products can be used to fabricate colloidal crystallization,[17] and to prepare nanocomposite microspheres etc.[18] With intention of making the laboratory and the industrial preparation of the monodisperse microspheres easily, in this work the P(St-MMA-AA) microspheres were prepared with surfactant-free emulsion copolymerization in air. The effect of the atmosphere and reaction parameters on the surfactant-free emulsion copolymerization for synthesis of high solids content monodisperse polymer microspheres were studied. In addition, it has been confirmed that the copolymer microspheres obtained in this work could be effective in achieving stable high internal phase emulsions and their subsequent conversion to porous polymers.[19]

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were purchased from Linfeng Chemical reagent, Shanghai, China. They were distilled and stored at 4°C, when not used immediately. Ammonium persulfate (APS) (Linfeng Chemical reagent, Shanghai, China. +98%) was recrystallized twice in deionized water before use. Hydroquinone (Aldrich, +99%) was used as received without further purification. Water was freshly deionized.
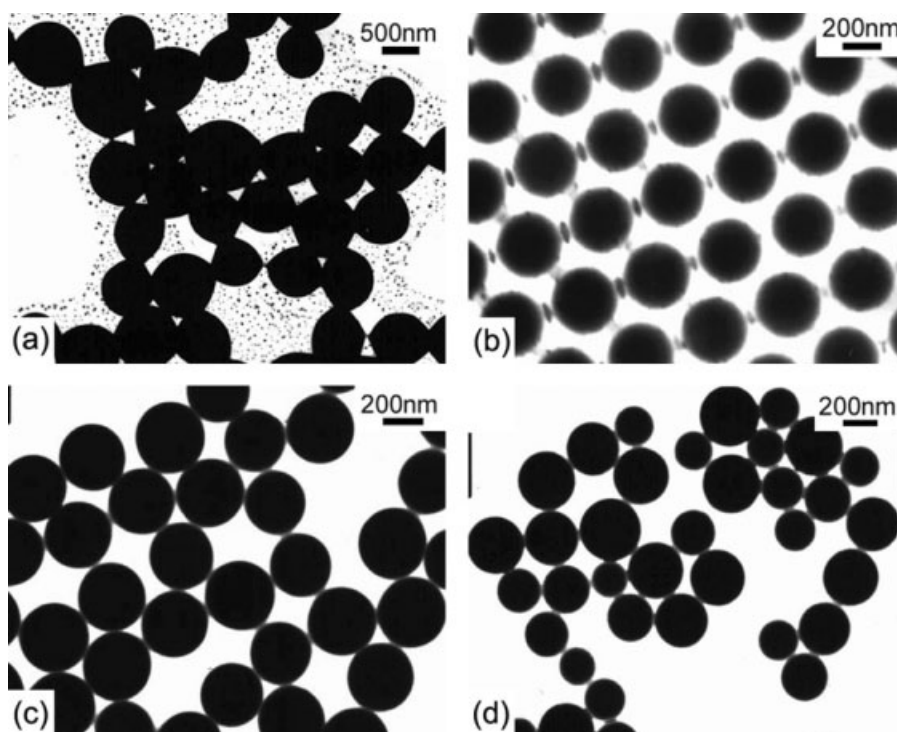
Surfactant-free emulsion polymerization

The polymerizations were carried out as follows when conducted in air: appropriate deionized water containing APS of 7.0×10^{-3} M was firstly fed in a four-necked jacketed glass reactor (250 mL) with an overhead leaf-shaped stirrer paddle and a condenser. Thermal regulation was obtained by circulating appropriately thermostatic hot water through the reactor jacket. Then appropriate mass of each monomer (St, MMA, and AA) was added to target the monomer feed content [M] (wt %) of the desired latex. The mixture was stirred steadily at 200 rpm and left at a given reaction temperature for 12 h. It was then rapidly cooled to room temperature.

For experiments conducted under nitrogen, nitrogen was bubbled through the mixture of reagents for 1 h before elevating the temperature, and the nitrogen blanket was maintained throughout the polymerization.

Characterization

The induction period and comonomers conversion were determined by gravimetric method. A latex sample was withdrawn from the reactor every 10 min after the emulsion was heated to the given polymerization temperature. The sample was poured with hydroquinone solution to stop the polymerization, and the polymer solution was precipitated with acetone. The precipitated polymer was washed with an ethanol and water mixture, and dried by vacuum to constant weight.[20] The time the polymer was firstly precipitated was considered as the induction period. Conversion and the solids content of the latex were calculated from the [M] and polymer weight obtained. A sample of each latex was centrifuged at 4000 rpm for 40 min after the polymerization was completed, and then washed with distilled water. After repetition of this, the particles were dried 48 h in a vacuum oven at 60°C. FTIR spectral of the sample was recorded on an Infrared Spectrophotometer (Nicolet 5700). The ^{1}H-NMR spectra of the polymer sample were recorded with a 500 MHz high resolution NMR spectrometer (AVANCE 500) using deuterated chloroform as solvent. The composition of the latex copolymer was obtained by the FTIR and ^{1}H-NMR spectral. The molecular weight of the latex copolymer was detected by a multidetectors size exclusion chromatography (SEC) equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector (Waters 515, Wyatt Technology Corporation). SEC

Figure 1 TEM photographs of the latices obtained with surfactant-free emulsion copolymerization of St, MMA, and AA (mass ratio of St : MMA : AA = 95.4 : 4 : 0.6) at different polymerization temperature in air. (a) 60°C, (b) 70°C, (c) 80°C, and (d) 90°C.

was performed using THF as eluent at 35°C with a flow rate of 1 mL/min in crosslinked styrene-divinyl benzene copolymer gel columns (MZ-Gel SD Plus 10E6Å 5 μm 10E 5Å 10E3Å).

The particle size (D_p) and morphology of the polymer microspheres were characterized by transmission electron microscopy (TEM, JEM-1200EX II). The polydispersity of particle size was expressed as the quotient of the standard deviation (δ) of D_p values. The less the value of δ/D_p, the more narrow will be the size distribution.

RESULTS AND DISCUSSION

The influences of oxygen and temperature on the copolymerization

Previous studies on the surfactant-free emulsion copolymerization of St and hydrophilic comonomers under inert gas indicated that the particle morphology, size, and size distribution were greatly influenced by polymerization temperature and hydrophilic comonomers concentration.[6,21]
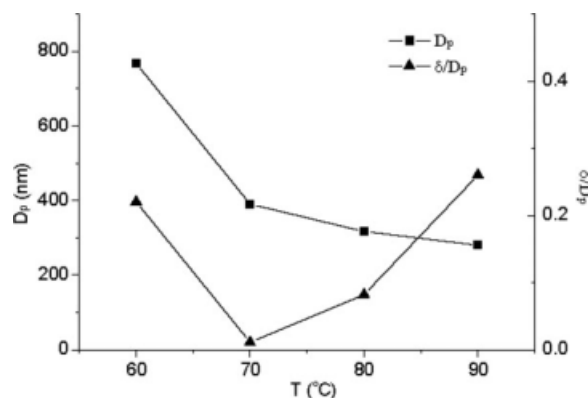
In this work, the P(St-MMA-AA) microspheres (Fig. 1) were obtained with surfactant-free emulsion copolymerization of St, MMA, and AA in air. The copolymerizations were run with temperature varied in the range of 60–90°C. As expected, increasing reaction temperature from 60 to 70°C significantly increased the conversion of the monomers at the end of the polymerization from 78.44 to 93.32%,

further elevating the reaction temperature from 70 to 80 and 90°C, the conversion of monomers increased slightly from 93.32 to 95.42 and 96.35%, respectively (Fig. 2). The evolutions of average particle size and size distribution with reaction temperature are shown in Figure 3.

It is now well established in surfactant-free emulsion polymerization using water-soluble initiator, as it was done in this study, water is the initial locus of reaction.[4,5,22–25] These initiation reactions supply
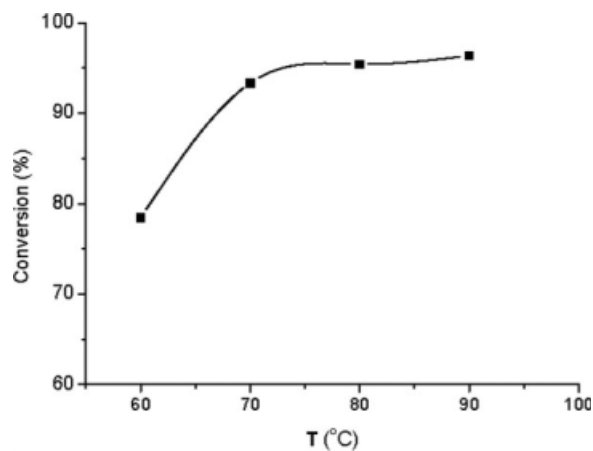
Figure 2 Influence of polymerization temperature on comonomers conversion in the surfactant-free emulsion copolymerization of St, MMA, and AA in air. The comonomers feed contents were 16.7 wt %.

Figure 3 Influence of polymerization temperature on the particle size and its distribution of the copolymer particles obtained with surfactant-free emulsion copolymerization of St, MMA, and AA in air. The comonomers feed contents were 16.7 wt %.

oligomeric radicals to the growing particles or micelles. Reaction in micelles leads to polymeric chains and consequently to particles, whereas reaction in the bulk monomer phase leads to coagulum. The presence of oxygen during polymerization in the different phases (water, micelles, and monomer bulk) leads to polymerization termination, and thus to induction and retardation.[12,26,27] Seen that oxygen concentration in the different constituents of the system depends of temperature, an evolution of all reactions involving oxygen also changes with temperature. In addition, initiator adsorption at the monomer and the micelles surface also change with temperature. The evolution of all these parameters results in the phenomenon observed of particles.

As seen in Figures 1 and 3, increasing reaction temperature from 60 to 70°C led to decrease in the average particles size (D_p) and narrowed the particle size distribution. Further increasing the temperature

up to 80 and 90°C also resulted in a decrease of D_p, however the particles were no longer monodisperse due to monomer bulk phase polymerization.

As measured from the TEM images, the presence of oxygen in the system caused decrease in the D_p (Table I). This observation is consistent with the findings and predictions of Huo et al.[28] Oxygen is often treated as a water-soluble impurity, whereas it is in fact also oil-soluble.[28] The oxygen inside the organic phase acted as oil-soluble inhibitor, and retard the particle growth rate at the reaction beginning, thereby prolonging the nucleation period and resulting in a greater number of particles. Although the D_p of the copolymer partilces was affected by the oxygen in the system significantly, the effect of the oxygen on the particle size distribution could be neglected (Table I), which means that monodisperse copolymer microspheres can be prepared in air.

The influences of [AA] on the copolymerization and microspheres

To study the effect of water-soluble monomer on the copolymerization and microspheres, the surfactant-free emulsion copolymerizations of St, MMA, and AA were run with variations of AA feed concentration [AA] (Table I). Gravimetric analysis of the polymerizations indicated that no obvious induction periods were found in all range of [AA] for the reactions realized under N_2 protection. However, when the polymerizations were carried out in air, the induction periods were observed. As shown in Table I, increasing [AA] gave a reduction in the induction period. This result is similar to that of emulsion polymerization reported by Krishnan et al.[29] AA is much more hydrophilic than St, increasing [AA] results in increase of the monomer concentration in the aqueous phase, which causes increase of initiator

TABLE I
Surfactant-Free Emulsion Copolymerization of St, MMA, and AA[a]

Comonomer feed/(wt %)				Copolymer compositions/(wt %)[b]							Induction
St	MMA	AA	Atmosphere	St	MMA	AA	$M_w \times 10^{-5c}$	M_w/M_n[d]	D_p[e]/(nm)	δ/D_p[f]	period[g]/(min)
86.0	4.0	10.0	Air	92.27	2.96	4.77	2.45	1.95	208	0.021	≤ 10
91.0	4.0	5.0	Air	92.00	3.85	4.15	1.23	3.18	238	0.016	$10 \leq t \leq 20$
95.4	4.0	0.6	Air	95.06	4.40	0.54	1.02	6.85	390	0.020	$20 \leq t \leq 30$
86.0	4.0	10.0	N_2	90.80	1.18	8.02	7.40	1.74	250	0.026	≤ 10
91.0	4.0	5.0	N_2	92.67	2.45	4.88	2.73	2.55	306	0.014	≤ 10
95.4	4.0	0.6	N_2	95.84	3.34	0.82	1.78	5.08	460	0.034	≤ 10

[a] 16.7 wt % comonomer feed content, polymerized at 70°C.
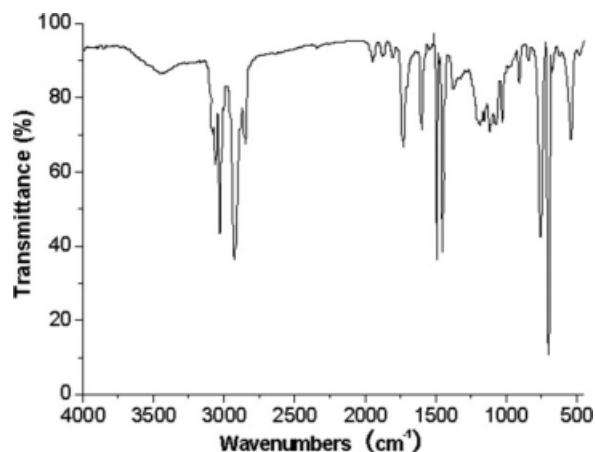[b] Determined from ^{1}H NMR analysis.
[c] The weight average molecular weight, determined by SEC.
[d] M_n is the number average molecular weight, which determined by SEC.
[e] Average particle diameter measured by TEM.
[f] Particle size polydispersity index, calculated from the TEM images.
[g] Determined by gravimetric method.

Figure 4 FTIR spectra of latex copolymer sample made by surfactant-free emulsion polymerization of St, MMA, and AA (mass ratio of 91 : 4 : 5) in air at 70°C.

efficiency[30] and thus raises oligomeric radical concentration at early stage of the polymerization.[31] So the oxygen initially dissolved in the aqueous phase was more rapidly consumed at the beginning of the polymerization,[14] and therefore the induction period was reduced.

FTIR spectra of these latex polymers (typically shown in Fig. 4) provided confirmatory evidence for the incorporation of each of St, MMA, and AA comonomers. The latex copolymer composition was estimated from ^{1}H-NMR, and the results for a series of copolymer latices that obtained in air or under N_2 protection are given in Table I. The correlation with the feed compositions of the latex copolymer prepared in air was much better at the lower [AA] than at the higher levels. NMR derived data showed that the AA contents in the copolymer were always lower than the feed values. In addition, it was also found that the AA contents of the copolymers prepared in air were much lower than that of the copolymers obtained with equivalent condition but under N_2 protection. The presence of oxygen in the aqueous phase at the beginning of the polymerization consumed a part of the AA, which led to water-soluble oligomeric formation, and lowered the contents of AA in the resulting copolymers.[14]

As mentioned above, oxygen is not only water-soluble but also oil-soluble, the oxygen reside in the oil phase inhibit the growth of radicals within the particles, and thus caused a decrease of the copolymer molecular weight, and broadened the molecular weight distribution, as shown in SEC analysis (Table I). Lower average molecular weight and broader molecular weight distribution of the latex copolymer may be beneficial to tailoring the morphology of the copolymer particles.[32,33] It was also found increasing AA feed contents resulted in an increase of the molecular weight of the latex copolymers obtained

either in air or under N_2 protection (Table I). Increasing AA amount lowered the entrance rate of oligomeric radicals (formed in aqueous phase) into the latex particles, and therefore lowered the termination rate,[34] which increased the average molecular weight of the resulting copolymer.

With intention of tailoring size of the P(St-MMA-AA) microspheres, the copolymerizations with [M] of 16.7 wt % were carried out at different [AA] (in the range of 0.1–12.5 wt % relative to total comonomers) at 70°C in air. Unlike the particle size first increases to a maximum at a critical [AA], and then decreases with further increasing [AA] in the semi-batch surfactant-free emulsion polymerization.[16] Figure 5 shows that the average particle size decreased significantly with an increase of [AA]. This can be explained as follows: with increasing of AA concentration, the hydrophilic oligomeric concentration increased in the early stage of the polymerization, which led to a larger number of micelles, and consequently to a larger number of particles. For a constant mass fraction of polymer, this result led to a reduction of the average particle size.

Interestingly, with [AA] increasing in the range of 0.1 to 10.0 wt %, the polymer microspheres stayed highly monodispersity (the δ/D_p of each sample was less than 0.04) and good spherical symmetry [Fig. 6(a–e)]. Moreover, an empirical relationship between the D_p and [AA] of eq. (1) was obtained, which meant that the particle size of copolymer microspheres prepared in this work could be controlled easily by varying hydrophilic comonomer concentration.

$$D_p = 360 \times [AA]^{-0.255} \qquad (1)$$

The copolymer latex with [AA] of 12.5 wt % was also prepared, nevertheless it was not monodisperse
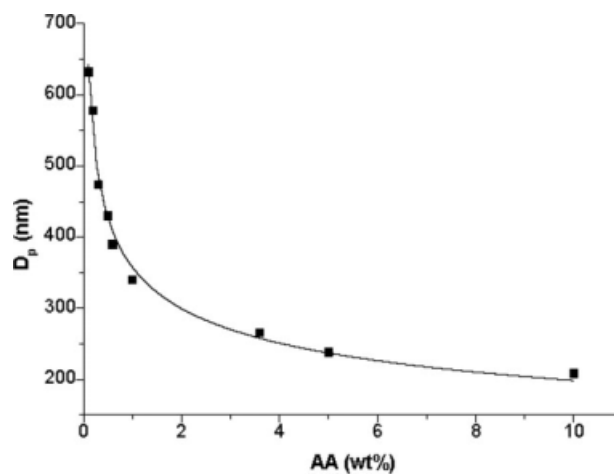
Figure 5 Variations of latex particle size with wt % of AA, relative to total comonomers, in surfactant-free emulsion copolymerization of St, MMA, and AA at 16.7 wt % comonomers feed content.
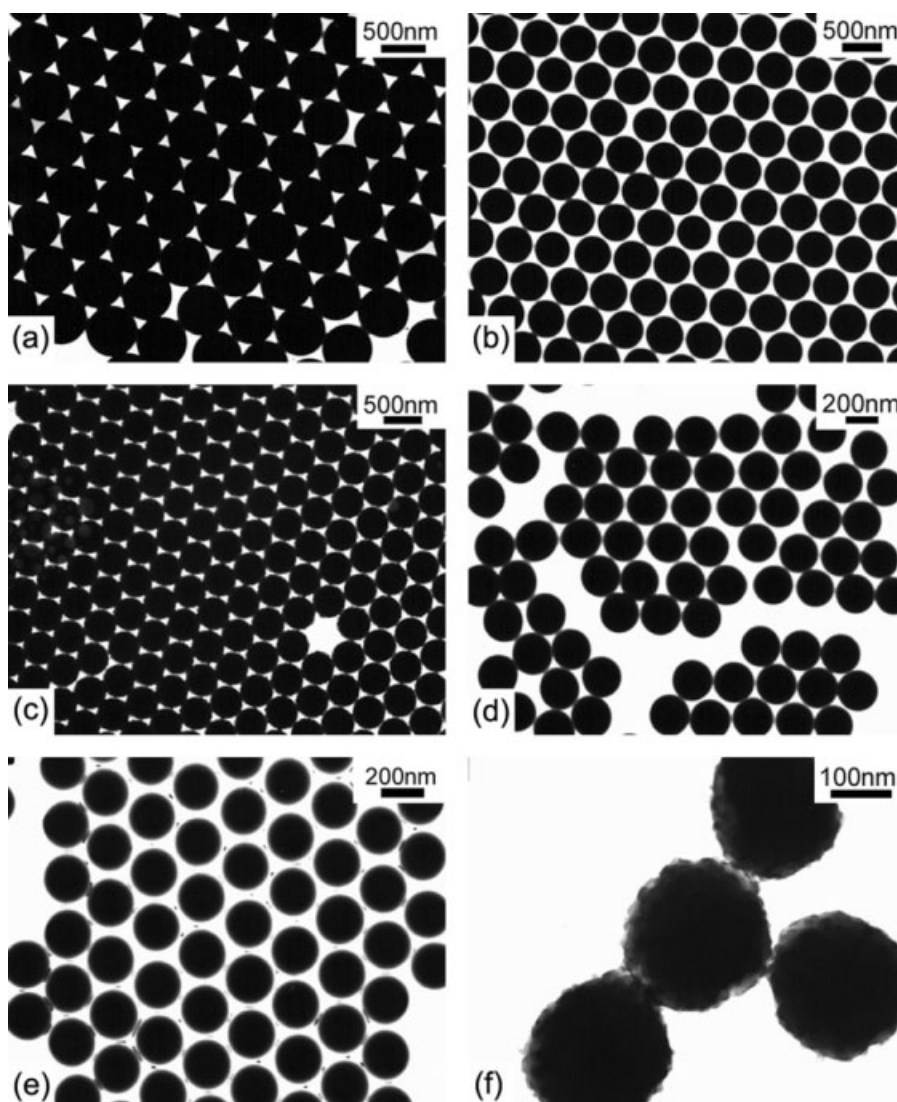
Figure 6 TEM photographs of the latex particles obtained with variations of AA feed concentration in air at 70°C. The comonomers feed contents were 16.7 wt %. The AA feed content [AA] and polydispersity index (δ/D_p) of the particle size of the samples: (a) [AA] = 0.2 wt %, δ/D_p = 0.032; (b) [AA] = 0.3 wt %, δ/D_p = 0.016; (c) [AA] = 0.5 wt %, δ/D_p = 0.011; (d) [AA] = 5.0 wt %, δ/D_p = 0.016; (e) [AA] = 10.0 wt %, δ/D_p = 0.021; (f) [AA] = 12.5 wt %, δ/D_p = 0.080.

(δ/D_p = 0.08), and had irregular morphology [Fig. 6(f)]. The D_p of these copolymer particles was 230 nm which was larger than that (189 nm) estimated from eq. (1). The possible interpretation for the phenomenon was that with increasing [AA], the hydrophilic molecular segments of the resulting copolymer increased, and these segments trended to gather in the surface of the particles, which made the particles swollen by water easily, thus coalescence occurred when the collision of the particles happened.

Effect of comonomers feed content

Because monodisperse microspheres with diameter range of 208–632 nm (Fig. 5) using surfactant-free emulsion copolymerization of St/MMA/AA have been prepared with variations in [AA] at 16.7 wt % [M] in air, it is of interest to assess whether this type microspheres could be obtained with a narrow particle size distribution at higher [M] without inert gas protection. Thereby, the latices were prepared, respectively, at 20.0, 28.6, 33.3, and 35.0 wt % [M], each sample with [AA] of 5.0 wt % relative to total comonomers. All of these copolymer particles were proved to be monodisperse and good spherical symmetry (Fig. 7), with the final solids contents to be 18.8, 27.2, 32.0, and 34.2 wt %, respectively. However, the polymerization at higher [M], for example, 36.0 wt % was failed, because much coagulum was formed.

On the other hand, a linear relationship emerged this time in the variation of particle size with [M]
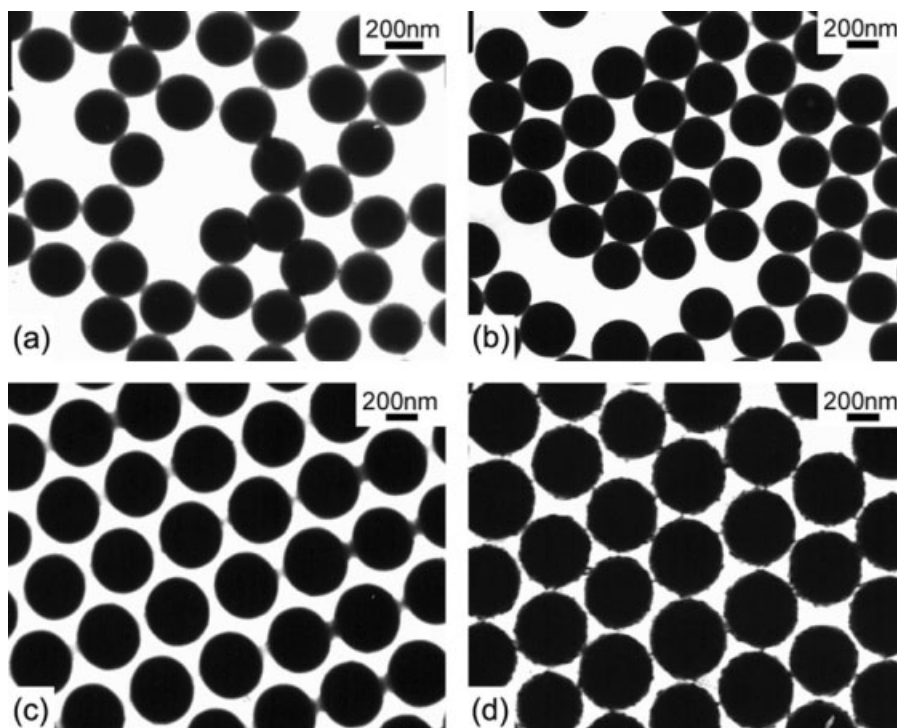
Figure 7 TEM photographs of the latex particles obtained at 70°C in air. The comonomers feed content [M] and polydispersity index (δ/D_p) of the particle size of the samples: (a) [M] = 20.0 wt %, δ/D_p = 0.021; (b) [M] = 28.6 wt %, δ/D_p = 0.025; (c) [M] = 33.3 wt %, δ/D_p = 0.030; and (d) [M] = 35.0 wt %, δ/D_p = 0.046.

(Fig. 8). These data yields an empirical relationship for the diameter, D_p of

$$D_p = 8.4 \times [M] + 100 \qquad (2)$$

This empirical relationship between D_p and [M] was also confirmed by the polymerization at lower [M] in this method. For example, the D_p of copolymer particles obtained with [M] of 10.0 wt % was 180 nm approaching to 184 nm that evaluated by eq. (2).
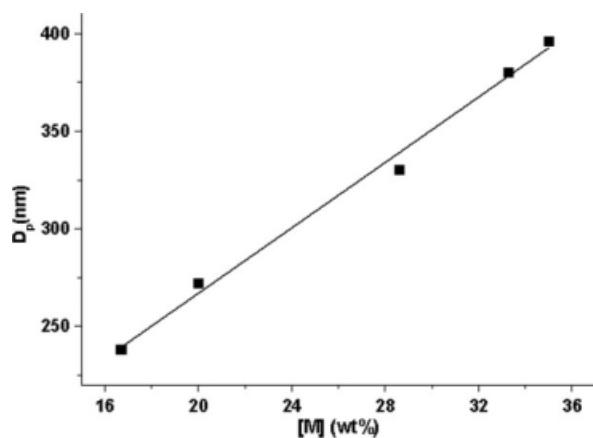
Figure 8 Variations of latex particle size with comonomers feed contents [M] in surfactant-free emulsion copolymerization of St, MMA, and AA at 70°C without inert gas protection.

CONCLUSIONS

High solids content surfactant-free emulsion copolymerizations with St, MMA, and AA as comonomers have been carried out in one-step batch process without inert gas protection. The effects of comonomers feed concentration [M], AA concentration [AA], and polymerization temperature on the copolymerization process were studied.

It was found that the presence of oxygen in the system caused the induction period, and decreased the average particle size of the copolymer latices due to the prolonged nucleation period. Increasing polymerization temperature or increasing [AA] gave a reduction in the induction period. The FTIR and NMR analysis of the latex copolymer obtained in air confirmed that St, MMA, and AA have been incorporated in the latex copolymers. The correlation of the latex copolymer compositions with the feed compositions was much better at the lower [AA] than at the higher levels, with the composition of AA contents always being less than the feed values. It was also found that the AA contents of the copolymers prepared in air were much less than that of the copolymers obtained under N_2 protection. Decreasing [AA] resulted in decrease in average molecular weight of the copolymer and broadening of the molecular weight distribution, with the SEC derived data for the average molecular weight and molecular weight distribution always being less and broader

than that obtained under purge, respectively, but the particle size distribution (δ/D_p) was unaffected (all of δ/D_p of the copolymer microspheres ≤ 0.04).

Moreover, investigation from TEM images indicated that the D_p was proportional to $[AA]^{-0.255}$ at [M] of 16.7 wt % at 70°C. To obtain high solids content monodisperse polymer microspheres, the copolymerization with [M] varied in the range of 16.7–35.0 wt % have been explored successfully, which caused the microspheres diameter increased linearly. And the final solids content up to 34.2 wt % monodisperse microspheres emulsion was obtained.

The ability to synthesize particle size controlled monodisperse microspheres at high solids content in such a simple one-step batch procedure without any inert gas protection makes both the laboratory and the industry preparation of microspheres with narrow size distribution easily, and provides a convenient source of concentrated monodisperse microspheres for exploitation in solid support applications.

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