Preparation of Raspberry-like Poly(methyl methacrylate) Particles by Seeded Dispersion Polymerization

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ABSTRACT: The facile preparation of nonspherical raspberry-like poly(methyl methacrylate) (PMMA) particles by seeded dispersion polymerization of methyl methacrylate (MMA) on micron-sized PMMA seed particles was described. Various polymerization parameters influencing the particle morphology, as well as the polymerization kinetic and morphological stability, were investigated in detail. It was found that the following polymerization conditions were necessary to prepare this kind of nonspherical particles: a relatively low temperature, an appropriate ratio of seed/MMA, an initiator with a relatively low decomposition rate, and a relatively low initiator concentration. These particles showed very good morphological stability at room temperature, but they changed to the spherical ones when heat treated at 60°C in methanol solution of MMA. The experimental results suggest that the prepared PMMA particles were kinetically favored and the localized polymerization of the MMA monomer on PMMA seed particle surface was responsible for the formation of the raspberry-like particles. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 501–508, 2011

Key words: nonspherical particles; seeded dispersion polymerization; colloids; polymer synthesis and characterization; morphology

INTRODUCTION

Most nonspherical polymer particles reported in literature are of multicomponent[1–6] or one component in the form of a crosslinked network.[7–10] These particles are usually prepared by seeded polymerization technique, such as seeded emulsion, seeded dispersion, and seeded precipitation polymerization. The formation of nonspherical morphology is generally based on the phase separation induced by the incompatibility of constituent polymers or by the crosslinked structure.

Is it feasible to prepare the nonspherical polymer particles of one component without crosslinked structure? Over the last few decades, several research groups have used viscoelastic deformation to transform the linear polymer particles from spherical to ellipsoidal shape.[11–15] In this method, monodisperse spherical polymer particles were first dispersed in an elastic matrix. The matrix is then stretched at a temperature higher than the glass transition temperature of the polymer particles. As a result, the softened polymer particles deformed in the elongated matrix film and became ellipsoids. On the other hand, Xia and coworkers[16] used an approach based on geometrical confinement to assemble spherical colloids into discrete clusters with well-controlled shapes, dimensions, and structures. Particles were physically trapped in cylindrical holes and joined together by subsequent annealing. A variety of polygonal or polyhedral clusters have been fabricated via this approach, including dimers, triangles, squares, hexagons, and so on.

Obviously, whether the viscoelastic deformation or geometrical confinement was a physical method and only worked for fabricating small quantities of nonspherical polymer particles. For large-scale fabrication of nonspherical polymer particles, the development of the technology based on polymerization process is expected. However, there are only a few studies available in literature. Zhao and coworkers[17] recently reported the synthesis of nonspherical particles by seeded polymerization technique. The surface of polystyrene (PS) microspheres was first partially modified after self-assembling into colloidal crystal. These PS particles were used as seeds in a subsequent polymerization of styrene monomer. The polymerization preferentially occurred on the chemically modified area. Finally, PS particles with protruding edges were formed. This method provides

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TABLE I
The Standard Recipe for the Preparation of PMMA Seed Particles by Dispersion Polymerization at 57°C for 12 h

Ingredients	Amounts (g)
MMA	10.0
AIBN	0.1
PVP	8.0
Methanol	81.9

an excellent route to the synthesis of nonspherical particles by seeded polymerization. However, the prerequisite of this method is the successful modification of seed particles, which is usually not very easy for most cases.

In a previous paper,[18] we reported a direct preparation of nonspherical popcorn-like poly(methyl methacrylate) (PMMA) particles by dispersion polymerization of methyl methacrylate (MMA) at relatively low temperature and relatively low initiator concentration. More interestingly, in a seeded dispersion polymerization of MMA on the micron-sized PMMA seed particles,[19] octopus-like PMMA particles, which have partial protuberance on particle surface, were unexpectedly obtained. No additional modification of the seed particles was required in this polymerization process. In further investigation of this polymerization system, we found that another kind of nonspherical PMMA particles possessing a raspberry-like morphology could also be prepared under certain conditions. The details with respect to the formation of these particles are given in this article.

EXPERIMENTAL

Materials

MMA monomer was purified by distillation under reduced pressure in a nitrogen atmosphere. The initiators, 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65) and 2,2′-azobisisobutyronitrile (AIBN) were purified by recrystallization from methanol shortly before use. Another initiator, benzoyl peroxide (BPO) was purified by recrystallization from chloroform. The stabilizer polyvinylpyrrolidone (PVP) (K-30, M_w = 40,000) and the dispersion medium methanol were used as received. BPO was obtained from Sigma–Aldrich, St. Louis, MO, and all other reagents were supplied by Wako Pure Chemical Industries.

Dispersion polymerization of MMA

The micron-sized PMMA seed particles were prepared by the dispersion polymerization of MMA monomer in methanol using PVP as the stabilizer and AIBN as the initiator. The standard recipe was given in Table I. For a typical procedure, all ingredients were weighed into a 300-mL Erlenmeyer flask and bubbled with nitrogen for at least 30 min after a homogeneous solution formed. Then, the flask was capped and placed in a 57°C water bath for 12 h with shaking horizontally at 135 cycles per minute. After the polymerization, the resulted PMMA seed latex was centrifuged at 3000 rpm for 2 min, the supernatant decanted, and the white sediment redispersed in a fresh methanol. This centrifugation–decantation–redispersion operation was repeated for at least four times to remove the soluble impurities.

Seeded dispersion polymerization of MMA in the presence of PMMA seed particles

The standard recipe for the seeded dispersion polymerization of MMA on PMMA seed particles was summarized in Table II. A typical experimental procedure was as follows. The prescribed amount of the PMMA seed particles, MMA monomer, PVP stabilizer, AIBN (V-65 or BPO) initiator, and methanol were weighed into a 300-mL Erlenmeyer flask in which the total amount of the mixture was 100 g. After the purge with nitrogen for at least 30 min, the flask was capped and kept in an ice water bath for 24 h with shaking gently. Then, the seeded dispersion polymerization was carried out at a given temperature for a given time with shaking horizontally at 135 cycles per minute. The polymerization was stopped at various time intervals by cooling the flask in the ice water bath. The monomer conversion was determined gravimetrically.

Characterization

The surface morphology of the prepared PMMA particles was observed by scanning electron microscopy (SEM, Hitachi *S*-3000N, and JEOL JSM-5300) after sputter coating with gold (200 Å). The M_w of the particles was measured by gel permeation chromatography (GPC) using a TOSOH column (TSK_{gel} GMH_{HR}-M) and a differential refractometer (RI-

TABLE II
The Standard Recipe for the Seeded Dispersion Polymerization of MMA on PMMA Seed Particles

Ingredients	Amounts (g)
PMMA seed particles	0.25–1.0
MMA	2.0[a]
AIBN (BPO, V-65)	0.0062–0.0328[b]
PVP	0.05[c]
Methanol	96.94–97.69[d]

[a] 2.0 wt % based on the total charge.
[b] 0.125–1.0 mol % based on the MMA monomer.
[c] 0.05 wt % based on the total charge.
[d] The amount was adjusted so that the total charge was 100 g.

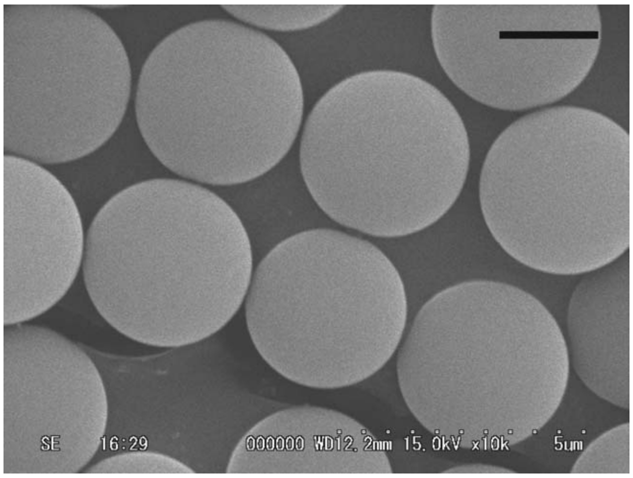

Figure 1 SEM micrograph of the PMMA seed particles. Scale bar (black) = 2 μm.

8020). Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using five linear PS samples ($M_w = 4.74 \times 10^2$–7.75×10^5, $M_w/M_n = 1.01$–1.20).

RESULTS AND DISCUSSION

PMMA seed particles

PMMA seed particles were prepared by dispersion polymerization under the conditions listed in Table I. No obvious coagulation of the particles was observed during the polymerization. The final monomer conversion was about 95%. A typical SEM micrograph of the PMMA seed particles was shown in Figure 1. As is clear from Figure 1, the prepared seed particles were perfectly spherical. The particles had a number-average diameter (D_n) of 3.44 μm with a very good monodispersity (C_v = 2.59%). The M_w of the seed particles, determined from GPC analysis, was about 1.47×10^5.

Kinetic study of the seeded dispersion polymerization

The seeded dispersion polymerization of MMA monomer on the PMMA seed particles was carried out under various conditions. The representative monomer conversion and molecular weight of the obtained PMMA particles were given in Figure 2 as a function of polymerization time. As shown in Figure 2, the monomer conversion–time curve was nearly *S*-shaped. The polymerization rate was extremely slow at early stage. The monomer conversion was only about 2.1% at the polymerization time of 12 h. However, the polymerization rate increased abruptly at about 15 h. The monomer conversion attained up to about 27.0% at 36 h, after which the polymerization rate slowed down again. The M_w was slightly lower than that of the seed polymer at the initial polymerization stage but became higher after the abrupt increase in the monomer conversion around 15 h. Although the observed molecular weight is the average of the seed polymer and the newly formed polymer in seeded polymerization, it can be inferred qualitatively that, at the initial stage, the molecular weight of the newly formed polymer must be lower than that of the seed polymer and became much higher at the latter stage. These results indicate that a significant gel effect occurred during the seeded dispersion polymerization.

Evolution of raspberry-like PMMA particles during the seeded dispersion polymerization

The seeded dispersion polymerization of MMA on PMMA seed particles, the kinetic data of which had been shown in Figure 2, eventually led to the formation of raspberry-like PMMA particles. The evolution of such particles during the seeded dispersion polymerization was given in Figure 3. It is obvious that the PMMA particles still maintained their sphericity at the monomer conversion of 2.1%, although the particle size increased to some extent [Fig. 3(a)]. At the monomer conversion of 16.4%, a lot of nanoprojections appeared on the whole particle surface. As a result, the PMMA particles with slightly rough surface were generated [Fig. 3(b)]. As the polymerization further proceeded, the uneven structure became more and more remarkable [Fig. 3(c)]. Finally, at the monomer conversion of 35.1% or higher, well-defined raspberry-like PMMA particles were formed [Fig. 3(d,e)]. From these results, we can see that the unsmooth surface of the PMMA

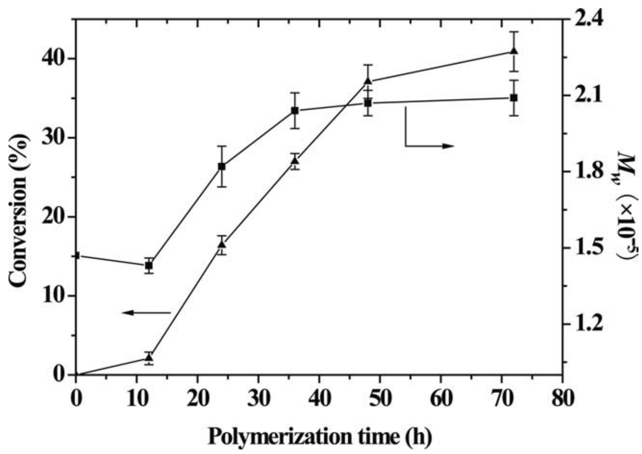

Figure 2 Plots of monomer conversion and M_w versus polymerization time for the seeded dispersion polymerization of MMA on PMMA seed particles. The data were the average values of three repeated experiments and the error bars represented the standard deviation. Polymerization conditions: temperature = 40°C, PMMA seed = 0.286 g, MMA = 2 g, PVP = 0.05 g, and AIBN = 0.25 mol % based on MMA.

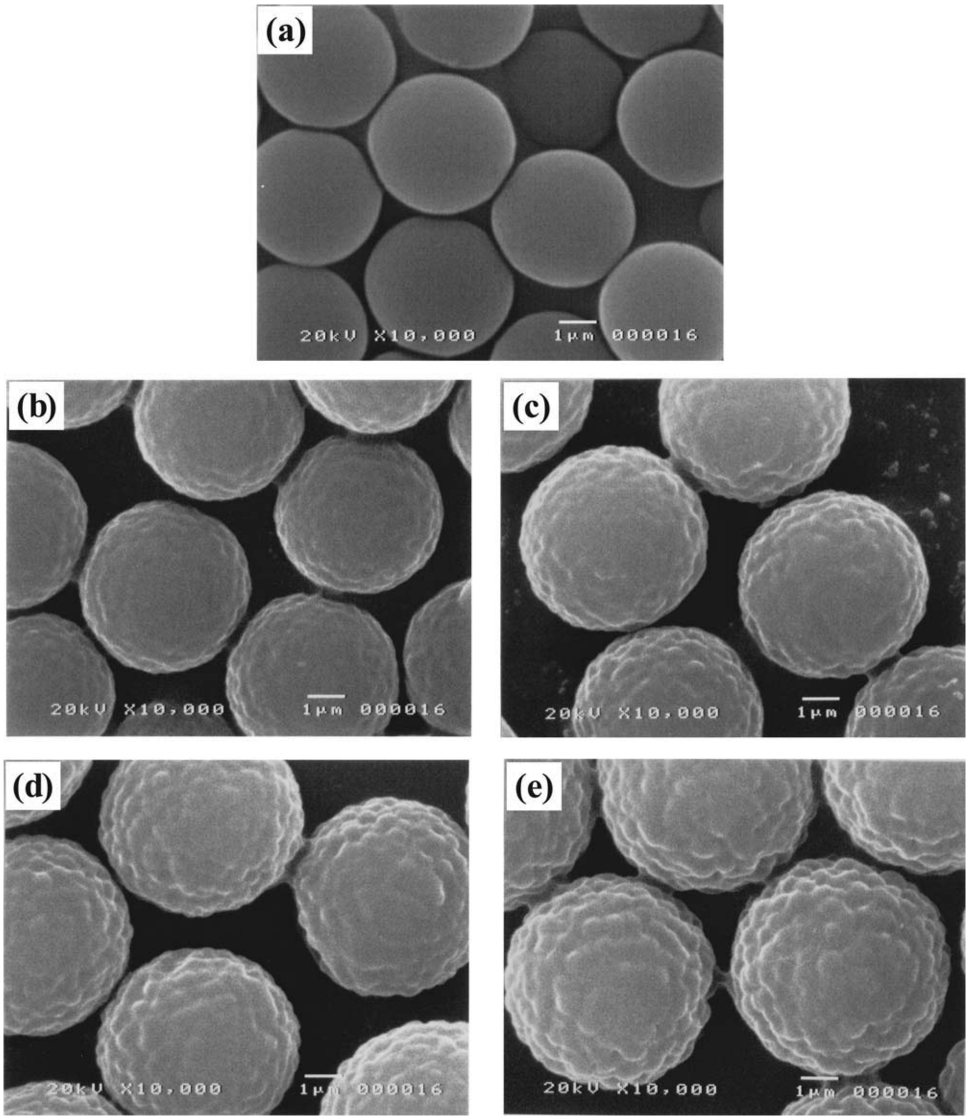

Figure 3 SEM micrographs of the PMMA particles obtained by seeded dispersion polymerization of MMA on PMMA seed particles at different monomer conversions: (a) 2.1%, (b) 16.4%, (c) 27.0%, (d) 35.1%, and (e) 40.9%. Polymerization conditions: temperature = 40°C, PMMA seed = 0.286 g, MMA = 2 g, PVP = 0.05 g, and AIBN = 0.25 mol % based on MMA.

particles began to form at the time when the polymerization rate, as well as the molecular weight, increased sharply, as shown in Figure 2. It is well known in the radical polymerization that the gel effect results in the abrupt increase of polymerization rate and molecular weight. The gel effect is mainly due to the increase of the viscosity in the polymerization loci. Thus, the relatively high intraparticle viscosity is probably responsible for the formation of raspberry-like PMMA particles during the seeded dispersion polymerization.

Influence of the initiator type and initiator concentration

Three kinds of oil-soluble initiators, BPO, AIBN, and V-65, were used to initiate the seeded dispersion polymerization of MMA. The decomposition rate constants (k_d) in toluene solvent are 1.1×10^{-5} s^{-1} for BPO (measured at 70.3°C), 4.0×10^{-5} s^{-1} for AIBN (measured at 70°C), and 1.9×10^{-4} s^{-1} for V-65 (measure at 68°C).[20] Thus, their thermal decomposition rate is in the order of BPO < AIBN < V-65.

The seeded dispersion polymerization of MMA on PMMA seed particles was conducted using these initiators at 40°C. The initiator concentrations were varied over a range of 0.125–1.0 mol % based on the MMA monomer. Although the initiator type and concentration were varied as specified, the other parameters were left the same. Figure 4 showed SEM micrographs of the PMMA particles obtained from these polymerizations. At all initiator concentrations investigated, BPO produced raspberry-like PMMA particles without noticeable difference in particle surface [Fig. 4(a–c)]. In contrast, for AIBN initiator,

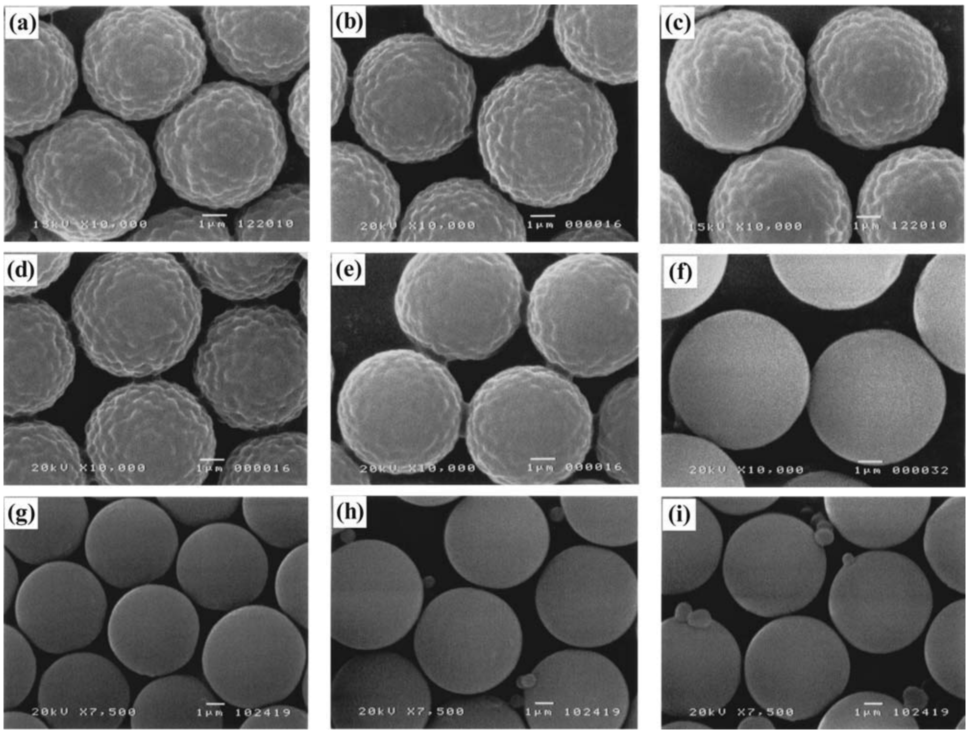

Figure 4 SEM micrographs of the PMMA particles obtained by seeded dispersion polymerization of MMA on PMMA seed particles using different initiators at different concentrations: (a) BPO, 0.25 mol %, (b) BPO, 0.5 mol %, (c) BPO, 1.0 mol %; (d) AIBN, 0.25 mol %, (e) AIBN, 0.5 mol %, (f) AIBN, 1.0 mol %; (g) V-65, 0.125 mol %, (h) V-65, 0.25 mol %, (i) V-65, 0.5 mol %. Polymerization conditions: temperature = 40°C, PMMA seed = 0.286 g, MMA = 2 g, PVP = 0.05 g, and monomer conversion = 41% ± 5%.

the increase in initiator concentration led to a continuous change in particle surface morphology. At the concentration of 0.25 mol %, raspberry-like PMMA particles were observed [Fig. 4(d)]; at the concentration of 0.5 mol %, the surface roughness of the PMMA particles remarkably decreased [Fig. 4(e)]; further increasing the concentration to 1.0 mol % resulted in the normal spherical PMMA particles with featureless surface [Fig. 4(f)]. On the other hand, all polymerizations using V-65 initiator generated the spherical PMMA particles with smooth surface even decreasing the concentration to 0.125 mol % [Fig. 4(g–i)]. Moreover, at the relatively high concentrations of 0.25 and 0.5 mol %, a number of new particles with much smaller size were inevitably formed [Fig. 4(h,i)].

The above results suggest that, in the seeded dispersion polymerization of MMA on PMMA seed particles, the initiator type and concentration had a great effect on the particle morphology. It seems likely that, the slower the decomposition rate of initiator, and the lower the initiator concentration, the easier was the formation of raspberry-like PMMA particles.

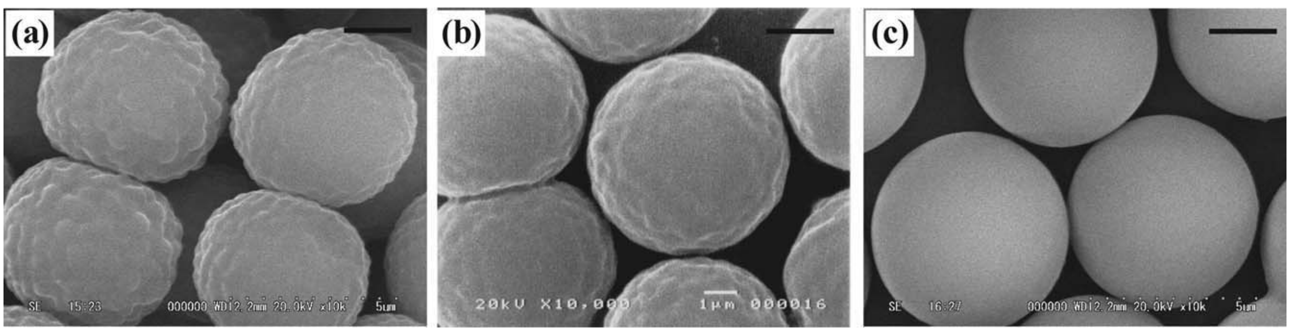

Figure 5 SEM micrographs of the PMMA particles obtained by seeded dispersion polymerization of MMA on PMMA seed particles at 35°C using V-65 initiator at different concentrations: (a) 0.125 mol %, (b) 0.25 mol %, and (c) 0.5 mol %. Scale bar (black) = 2 μm. Polymerization conditions: PMMA seed = 0.286 g, MMA = 2 g, PVP = 0.05 g, and monomer conversion = 40% ± 5%.

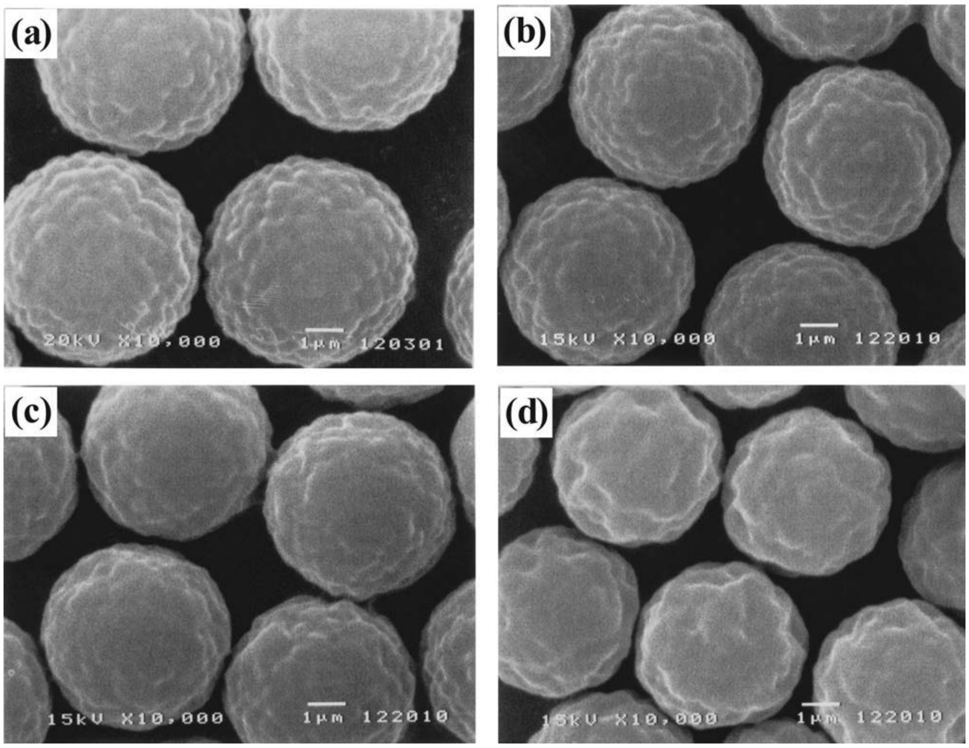

Figure 6 SEM micrographs of the PMMA particles obtained by seeded dispersion polymerization of MMA on PMMA seed particles at different contents of PMMA seed particles: (a) 0.25 g, (b) 0.4 g, (c) 0.5 g, and (d) 1.0 g. Polymerization conditions: temperature = 40°C, MMA = 2 g, PVP = 0.05 g, and AIBN = 0.25 mol % based on MMA, monomer conversion 47% ± 2%.

Influence of the polymerization temperature

Although the seeded dispersion polymerization of MMA on PMMA seed particles at 40°C using V-65 initiator produced the spherical PMMA particles, decreasing temperature to some extent allowed for the preparation of raspberry-like PMMA particles at certain initiator concentration. In this set of experiments, the polymerization temperature was lowered from 40 to 35°C, while maintaining other conditions, the same as those shown in Figure 4(g–i). The SEM micrographs of the resulting PMMA particles were shown in Figure 5. At the initiator concentration of 0.125 mol %, the raspberry-like PMMA particles were obtained but the particle shape was slightly distorted [Fig. 5(a)]. Increasing the initiator concentration to 0.25 mol % decreased the roughness of the particle surface [Fig. 5(b)]. Further increasing the initiator concentration to 0.5 mol % led to the formation of regular spherical PMMA particles [Fig. 5(c)].

We have also performed this set of polymerizations at even much lower temperature 30°C using V-65 initiator. To our surprise, the resulting PMMA particles had an octopus-like morphology, of which the preparation was detailed in our previous paper.[19] On the other hand, a series of seeded dispersion polymerizations using AIBN and BPO initiators were carried out at relatively high temperature of 45 and 50°C as well. All these polymerizations produced the normal spherical PMMA particles along with many smaller ones, similar to those shown in Figure 4(h,i). These results indicate that the polymerization temperature greatly influenced the surface morphology of the PMMA particles in seeded dispersion polymerization of MMA on PMMA seed particles, whether an initiator with high or low decomposition rate was used.

Influence of the content of PMMA seed particles

The seeded dispersion polymerization of MMA in the presence of PMMA seed particles at various contents was carried out in this set of polymerizations. Except for the content of PMMA seed particles, the amount of MMA monomer and all other parameters were held constant. AIBN was used as initiator. The monomer conversion was adjusted to be 47% ± 2% by changing the polymerization time. SEM micrographs of the resulting PMMA particles were shown in Figure 6. At seed contents of 0.25, 0.4, and 0.5 g (the seed/monomer ratios were correspondingly 1 : 8, 1 : 5, and 1 : 4), raspberry-like PMMA particles without dramatic difference in particle surface were obtained [Fig. 6(a–c)]. The morphologies were very similar to the case adding 0.286 g PMMA seed

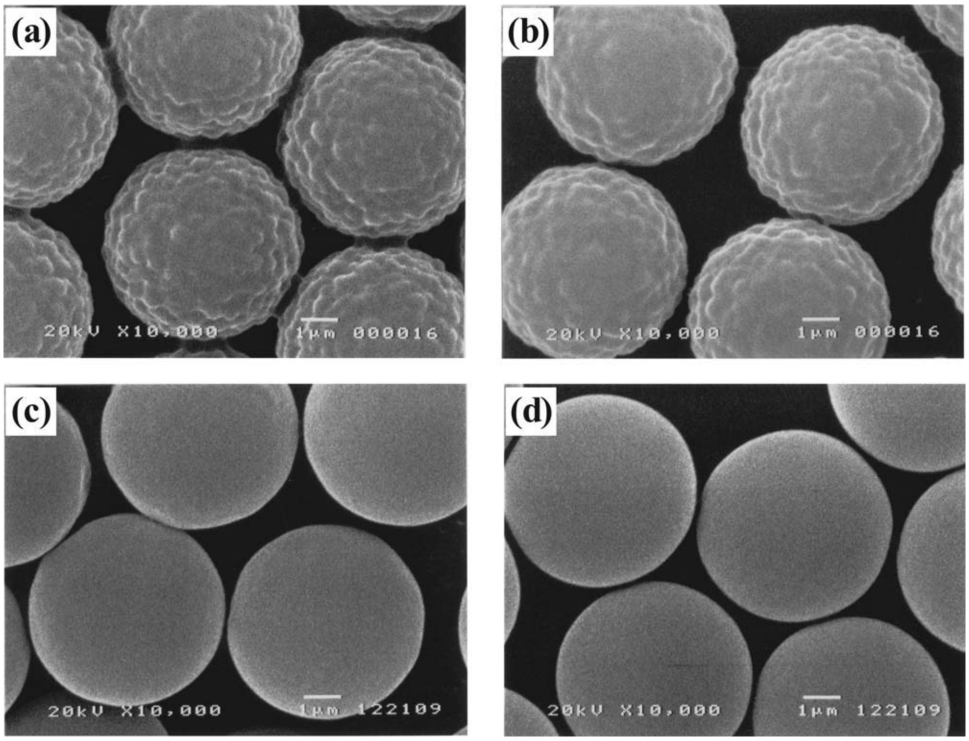

Figure 7 SEM micrographs of the raspberry-like PMMA particles after different treatments: (a) after a storage for 13 months in methanol at room temperature, (b) after ultrasonication at about 15°C for 8 h, (c) after heat treatment in 60°C methanol for 8 h, and (d) after heat treatment in 60°C methanol solution of MMA (2 wt %) for 8 h.

particles, as shown in Figure 4(d). In contrast, at seed content of 1.0 g (seed/monomer = 1 : 2), the number of protuberance on the resultant PMMA particle surface decreased significantly, resulting in the so-called confetti-like morphology [Fig. 6(d)].

Morphological stability of the raspberry-like PMMA particles

The raspberry-like PMMA particles shown in Figure 4(d) were used to examine their morphological stability toward the various post-treatments. It was found that the particle morphology remained nearly unchanged in methanol at room temperature even after a storage time as long as 13 months [Fig. 7(a)]. Subjecting the particles to the intense ultrasonic irradiation (38 kHz) at 15°C for 8 h also resulted in no appreciable change in particle surface [Fig. 7(b)]. However, after dipping the PMMA particles into methanol at 60°C for 8 h, the particle surface became almost smooth [Fig. 7(c)]. In addition, treatment with hot methanol solution of MMA (2 wt %, 60°C) for 8 h transformed the raspberry-like particles into spherical ones perfectly [Fig. 7(d)]. These results suggest that the formation of raspberry-like PMMA particles in the seeded dispersion polymerization was kinetically controlled. In the heat treatment by hot methanol or methanol solution of MMA, the relatively high temperature and the swelling of MMA decreased the intraparticle viscosity and hence enhanced the mobility of polymer chains, which facilitated the formation of the thermodynamically stable particles.[21] As a result, the spherical PMMA particles, which have the minimum interfacial free energy, were finally developed.

Formation mechanism of the raspberry-like PMMA particles

On the basis of the present experimental data, it is still difficult to exactly elucidate how the raspberry-like PMMA particles were formed during the seeded dispersion polymerization of MMA in the presence of PMMA seed particles. However, it is proposed that the localized polymerization on particle surface played an important role in the formation of such particles, similar to that of the popcorn-like and octopus-like PMMA particles.[18,19] The oligomeric radicals, generated in continuous phase, were first captured by the whole surface of existing PMMA seed particles. The captured oligomeric radicals formed new domains and underwent subsequent propagation separately by adsorbing MMA monomer from the continuous phase. As a result, the particles having a number of protuberances on the surface were eventually formed.

During this formation process, the high viscosity within the growing particles appears to be important to fabricate the raspberry-like particles, as shown in

Figure 3. This is probably because the high intraparticle viscosity restricted the mobility of the oligomeric or polymeric chains, hence, facilitating the formation of kinetically controlled particle morphology. Another important aspect to fabricate the raspberry-like particles is the low generation rate of oligomeric radicals[22] during the seeded dispersion polymerization. Accordingly, it is necessary to conduct polymerization using the initiator with a relatively low decomposition rate at a relatively low concentration, as well as to conduct polymerization at a relatively low temperature, as shown in Figures 4 and 5. Finally, a reasonable seed/monomer ratio is also important. When the seed content was increased to a certain extent, the total surface area of seed particles increased and the amount of adsorbed oligomeric radicals per unit area correspondingly decreased. As a result, the number of the protuberance decreased but the size increased, resulting in the confetti-like particles instead of raspberry-like ones, as shown in Figure 6.

CONCLUSIONS

This study demonstrated the facile preparation of raspberry-like PMMA particles by seeded dispersion polymerization of MMA in the presence of PMMA seed particles. It was found that, to prepare this kind of particles, it was necessary to perform the seeded polymerization under such conditions as using the initiator having a relatively low decomposition rate, at a relatively low initiator concentration, at a relatively low temperature, and at an appropriate ratio of seed to MMA monomer. The prepared raspberry-like particles were kinetically favored and could be changed to the thermodynamically favored spherical ones by hot solvent treatment. The unique surface morphology of these raspberry-like particles makes them potentially applicable in the self-assembly of photonic crystals with high complexity,[14] in the fabrication of superhydrophobic surface,[23] and in the studies of suspension rheology,[24] light scattering,[25] and random close packing[9] of nonspherical particles.

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