Nonspherical and Octopus-like Poly(methyl methacrylate) Particles Prepared by Seeded Dispersion Polymerization

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Nonspherical and octopus-like particles were prepared for the first time in one-component system by seeded dispersion polymerization of methyl methacrylate (MMA) on spherical and micron-sized polyMMA (PMMA) seed particles. The essential synthesis conditions and formation mechanism were discussed.

Nonspherical morphology is one of the functional properties of micron-sized, monodisperse polymer particles. Seeded dispersion polymerization is appropriate for producing micron-sized, monodisperse polymer particles with a spherical shape resulting from a minimization of the surface energy.[1] However, Okubo et al. have recently reported a variety of particles with nonspherical morphologies, e.g., egg-like,[2] snowman-like,[3,4] and confetti-like[4] shapes, from seeded dispersion polymerization. These anomalous particles have aroused interest widely and the formation mechanisms have also been elucidated by the authors.

All the polymer particles mentioned above were in multi-component (composite) system or one-component system in which the seed particles contained a crosslinked structure. In this article, we report for the first time the preparation of nonspherical particles in one-component system with no crosslinked structure by the seeded dispersion polymerization of methyl methacrylate (MMA) in the presence of polyMMA (PMMA) seed particles. The obtained particles have partial protuberance on particle surface. Similarly shaped particles were reported by Okubo et al. in seeded emulsion copolymerization and named as octopus-like particles.[5] The anisotropy of the particles make them applicable to photonic devices and diagnosis reagents.[6,7]

The PMMA seed particles ($Dn = 3.44\,\mu m$, $M_w = 147{,}000$) used in this study was prepared by a normal dispersion polymerization technique. The seed particles were spherical and had a good monodispersity ($Cv = 2.59\%$), as shown in Figure 2a. A typical experimental procedure of seeded polymerization was as follows. Prescribed amount of PMMA seed particles, MMA monomer, methanol solution of polyvinylpyrrolidone (PVP K-30, $M_w = 40{,}000$) stabilizer, methanol solution of 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65) initiator, and methanol were weighted into a 300-mL Erlenmeyer flask in which the total amount of the mixture was 100 g. After the purge with nitrogen, the flask was capped and kept in an ice-water bath for 24 h with shaking gently. The seeded dispersion polymerization was then carried out in a 30 °C water bath with shaking horizontally at 135 cycles/min. The polymerization was stopped at various time intervals by cooling in the ice-water bath. The obtained dispersion was centrifuged at 3000 rpm for 2 min, the supernatant decanted, and the white sediment redispersed in a 0.025% methanol solution of PVP K-30. This centrifugation–decantation–redispersion operation was repeated for at least 4 times to remove the soluble impurities in the PMMA dispersions. The purified dispersion was vacuum-dried and subjected to scanning electron microscopy (SEM) and gel permeation chromatography (GPC). The particle surface morphology was observed by SEM (Hitachi, S-3000N) after sputter-coating with gold (200 Å). The weight-average molecular weight (M_w) was measured by GPC with using a TOSOH TSK_{gel} GMH_{HR}-M column and a differential refractometer RI-8020. Tetrahydrofuran (THF) was used as eluent and polystyrene standards were used for calibration. The monomer conversion was determined by gravimetry.

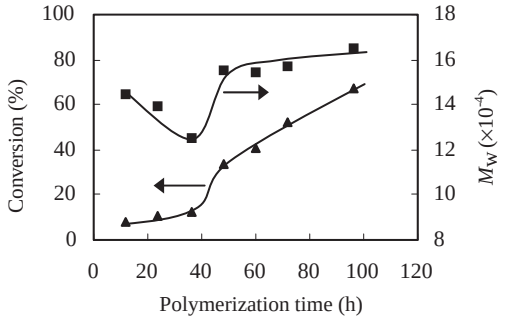

Figure 1. Plots of molecular weight and monomer conversion versus polymerization time for seeded dispersion polymerization of MMA on PMMA seed particles. PMMA seed: 0.286 g, MMA: 2 g, PVP K-30: 0.05 g, V-65: 0.25 mol % on MMA, temperature: 30 °C.

Figure 1 shows the monomer conversion and molecular weight of PMMA particles as a function of polymerization time. The conversion–time curve was nearly S-shaped. It is obvious that the polymerization rate was extremely slow at early stage but increased abruptly at about 40 h, after which the polymerization rate slowed down again. The molecular weight (M_w) of the PMMA particles was lower than that of PMMA seed particles ($M_w = 147{,}000$) at early stage and became higher after an abrupt increase around 40 h. Though the observed molecular weight is the average of the seed polymer and the newly formed polymer in seeded polymerization, it can be inferred that at the initial stage, the molecular weight of the newly formed polymer must be much lower than that of the seed polymer and became higher at the latter stage. These results suggest that a significant gel effect occurred during the seeded dispersion polymerization.

Figure 2 shows SEM micrographs of PMMA seed particles and PMMA particles prepared by seeded dispersion polymerization at different polymerization times. It is evident that the spherical PMMA seed particles (Figure 2a) changed to octopus-like

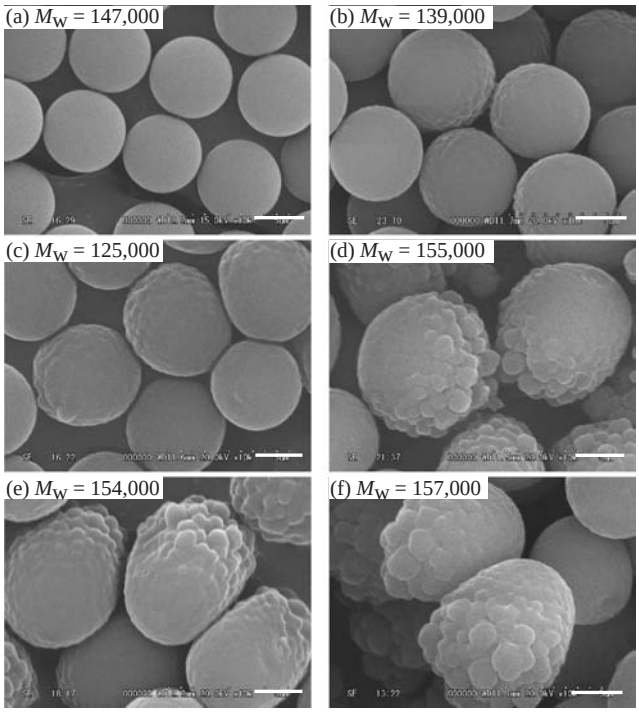

Figure 2. SEM micrographs of PMMA particles prepared by seeded dispersion polymerization of MMA on PMMA seed particles at polymerization times of: (a) 0 h (PMMA particles), (b) 12 h, (c) 36 h, (d) 48 h, (e) 60 h, and (f) 72 h. PMMA seed: 0.286 g, MMA: 2 g, PVP K-30: 0.05 g, V-65: 0.25 mol % on MMA, temperature: 30 °C. Scale bar: 2 μm.

particles when the seeded dispersion polymerization was carried out for about 60 h (Figure 2e) or longer (Figure 2f). At polymerization time of 12 h, a slightly uneven structure was observable on the half surface of PMMA particles. The uneven structure became more remarkable at polymerization time of 36 h. A pronounced growth of the uneven structure to many protuberances was observed at polymerization time of 48 h (Figure 2d), probably due to the gel effect shown in Figure 1. As the polymerization further proceeded, the protuberances grew and the octopus-like PMMA particles were finally obtained.

It is proposed that the formation of the octopus-like PMMA particles was mainly a result of the extremely low reaction rate at initial polymerization stage. The low polymerization rate resulted in a limited amount of oligomeric radicals in continuous phase. These oligomeric radicals gathered and localized on the partial surface of particles when captured by the large amount of PMMA seed particles. The captured oligomeric radicals formed a new domain which adsorbed MMA monomer preferentially from the continuous phase due to the relatively low molecular weight compared to the PMMA seed particles. Therefore, the seeded polymerization took place predominantly within the new domain and eventually octopus-like particles were formed.

Figure 3 shows the influence of initiator (V-65) concentration on the surface morphology of PMMA particles prepared by seeded dispersion polymerization. No noticeable difference in particle surface morphology was observed as the initiator concentration was increased from 0.125 to 0.5 mol % (Figure 3a, Figure 2e, and Figure 3b). However, increasing initiator concentration up to 0.75 mol % led to the formation of egg-like particles together with much coagulum. It is thus concluded that using initiator at a relatively low concentration is essential to prepare the octopus-like PMMA particles. It is also apparent from Figure 3 that the increase of initiator concentration resulted in a decrease of molecular weight of PMMA particles. This seems to be a general observation in dispersion polymerization.[8]

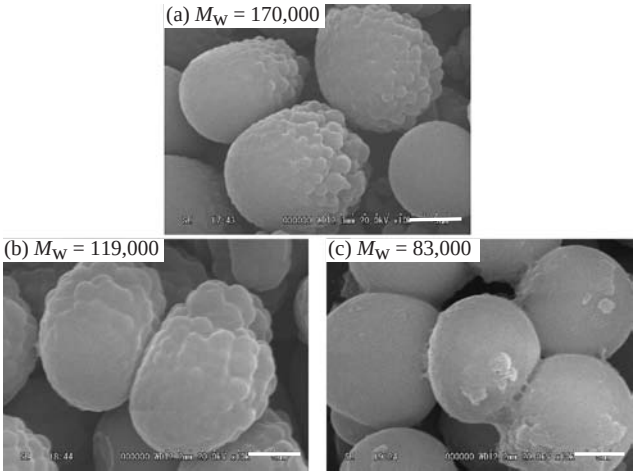

Figure 3. SEM micrographs of PMMA particles prepared by seeded dispersion polymerization of MMA on PMMA seed particles at initiator (V-65) concentrations (mol % on MMA) of: (a) 0.125, (b) 0.5, and (c) 0.75. PMMA seed: 0.286 g, MMA: 2 g, PVP K-30: 0.05 g, temperature: 30 °C, polymerization time: 60 h. Scale bar: 2 μm.

Finally, it should be noted that, to prepare the nonspherical and octopus-like PMMA particles by the seeded dispersion polymerization, it is necessary to perform the polymerization not only at relatively low initiator concentration but also at relatively low polymerization temperature (30 °C). When elevating the temperature to 35 °C, raspberry-like PMMA particles resulted. Further elevating the temperature to 40 °C or higher, the normal spherical PMMA particles were obtained. The detailed studies on the fabrication of PMMA particles with various surface morphologies by using this technique are forthcoming.

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