Popcorn-like Morphology of Poly(methyl methacrylate) Particles Formed in Dispersion Polymerization of Methyl Methacrylate

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The formation of nonspherical, popcorn-like particles in the dispersion polymerization of methyl methacrylate is reported. The essential synthesis conditions of such particles are relatively low temperature and low initiator concentration.

Many research works have been concerned with the preparation of nonspherical particles with submicron and micron size in recent years.[1–4] Most of these particles were obtained by seeded polymerization methods, such as seeded emulsion,[1] seeded dispersion,[2] and seeded precipitation polymerization.[3a] The nonspherical particles thus obtained were usually of multicomponent or one-component containing a cross-linked structure. However, we recently reported a linear nonspherical particle in a one-component system by seeded dispersion polymerization of methyl methacrylate (MMA) in the presence of poly-MMA (PMMA) seed particles. They have partial protuberances on the surface and we call them octopus-like particles.[4]

On the other hand, unseeded polymerization method is generally employed to produce the one-component particles without cross-linked structure. However, only a few works touched the production of nonspherical particles in unseeded polymerization. In 1997, Ray and Mandal[5a] reported submicron-sized, oval particles formed along with the spherical ones in the dispersion polymerization of acrylamide. Shen et al.[5b] briefly mentioned the formation of submicron-sized, egg-like PMMA particles in the dispersion polymerization of MMA about ten years ago. Nevertheless, the reason for the formation of such nonspherical particles was not explained. Unexpectedly, in our latest studies on the dispersion polymerization of MMA, we found that the nonspherical PMMA particles with popcorn-like morphology were obtained under certain polymerization conditions. Its asymmetry and larger specific surface area have potentials for new applications; however, no literature has yet described the formation of such popcorn-like particles during unseeded dispersion polymerization, as far as we know. We report the essential synthesis conditions and attempt to discuss the formation mechanism of such new class of popcorn-like particles in this paper.

A typical dispersion polymerization was carried out as follows. Prescribed amount of MMA, methanol solution of poly(vinyl pyrrolidone) (PVP K-30, weight-average molecular weight (M_w) = 40,000), and methanol solution of 2,2′-azobis(dimethylvaleronitrile) (V-65) free of oxygen were weighed into a 300-mL, Erlenmeyer flask. The total amount of the mixture was 100 g. PVP K-30 and V-65 were used as stabilizer and radical initiator, respectively. Nitrogen was bubbled through the mixture of reagents for 15 min before the flask was capped and held in a water bath. The dispersion polymerization was then carried out at a given temperature for a given time, with shaking horizontally at 135 cycles/min. The resulting polymer latex was purified, freeze-dried, and then used for scanning electron microscopy (SEM, Hitachi, S-3000N) observation and measurement of M_w as done in the previous article.[4]

Figure 1 shows the SEM micrographs of PMMA particles prepared under different polymerization temperatures and initiator concentrations. Here, the monomer conversions of MMA were adjusted to ca. 52% by changing the polymerization time. It is obvious that polymerization at 30 °C produced the popcorn-like PMMA particles with a wide size distribution (Figure 1a). Polymerization at 35 °C also produced popcorn-like PMMA particles but the size distribution of these particles is relatively narrow (Figure 1b). When the polymerization temperature

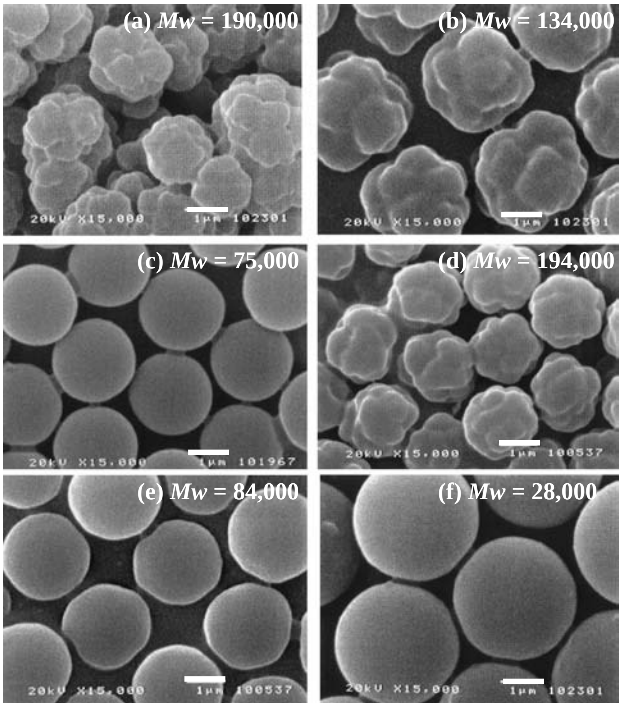

Figure 1. SEM micrographs of PMMA particles prepared by dispersion polymerization. (a), (b), and (c) are the particles obtained at a constant V-65 concentration (0.25 mol % of MMA) at different polymerization temperature and time of: (a) 30 °C/84 h, (b) 35 °C/60 h, and (c) 40 °C/48 h. (d), (e), and (f) are the particles obtained at a constant temperature (35 °C/48 h) with V-65 concentrations (mol % of MMA) of: (d) 0.125, (e) 0.5 and (f) 1.25. MMA, 2.0 g; PVP K-30, 60 wt % of MMA; Scale bar, 1 μm.

was increased to 40 °C, the projections disappeared and the normal spherical PMMA particles were formed ($Dn = 1.2\,\mu m$, $Cv = 3.4\%$) (Figure 1c). The latter three SEM micrographs in Figure 1 show the influence on the particle morphology of the initiator concentration in the range of 0.125–1.25 mol %. When the initiator concentration was decreased from 0.25 mol % (Figure 1b) to 0.125 mol % (Figure 1d), the morphology of the resulted PMMA particles scarcely changed and the popcorn-like particles were obtained with a relatively small size. However, increasing initiator concentration to 0.5 mol % led to the formation of the slightly distorted spherical PMMA particles (Figure 1e). Further increasing initiator concentration up to 1.25 mol % gave the regular spherical PMMA particles ($Dn = 3.22\,\mu m$, $Cv = 6.5\%$) (Figure 1f).

The above experimental results indicate that it is necessary to conduct the dispersion polymerization at the relatively low temperature and low initiator concentration in order to prepare the popcorn-like PMMA particles. On the other hand, lower polymerization temperature, and lower initiator concentration resulted in relatively high molecular weight, as is clear from the M_w data shown in Figure 1. This seems to be a common conclusion in radical-induced dispersion polymerization.[6] Longer polymer chains have a lower diffusivity; moreover, polymer particles composed of longer polymer chains have a higher internal viscosity. Accordingly, after the nucleation stage in the dispersion polymerization, the newly generated oligomeric radicals in continuous phase were expected to be nearly fixed when captured by the existing particles (i.e., secondary particles or stable particles). These oligomeric radicals separately underwent subsequent propagation by adsorbing the monomer from the polymer phase and/or continuous phase. As a result, the popcorn-like particle, which looks like an aggregate of several small particles, was formed during the polymerization.

Figure 2 shows the evolution of particle morphology during the process of MMA dispersion polymerization. It is evident that polymerization at monomer conversion of 12.7% had yielded the initial popcorn-like PMMA particles on which some tiny projections are observable (Figure 2a). The size of the projections as well as the molecular weight gradually increased up as the polymerization proceeded to 52% conversion (Figures 2b, 2c, and 1d). This observation supports the formation mechanism proposed above.

From these investigations, the popcorn-like PMMA particles were obviously formed in a kinetically controlled system. Such particles can be easily changed to the thermodynamically favored ones by solvent or heat treatment.[7] In our experiment, dipping the freeze-dried popcorn-like PMMA particles into hot methanol solution of MMA (2 wt %) at 60 °C for 8 h followed by removal of methanol solution produced the nearly spherical particles. It is proposed that the relatively high temperature and the swelling of monomer decreased the intraparticle viscosity and thus enhanced the mobility of polymer chains, which facilitated the final formation of the thermodynamically stable particles. This also suggests that maintaining the high viscosity within the growing particles is essential to prepare the popcorn-like particles in the dispersion polymerization of MMA.

The results of the present studies reveal another character of the conventional dispersion polymerization of MMA which allows a facile control of particle morphology in the one-component system. However, more detailed research should be done to extend this approach to other one-component systems, e.g., polystyrene.

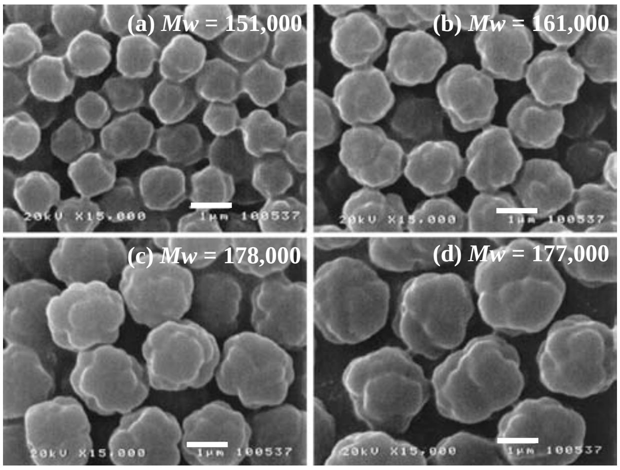

Figure 2. SEM micrographs of PMMA particles prepared by dispersion polymerization at monomer conversions of: (a) 12.7%, (b) 18.5%, (c) 37.3%, and (d) 76.7%. MMA, 2.0 g; PVP K-30, 60 wt % of MMA; V-65, 0.125 mol % of MMA; temperature, 35 °C; Scale bar, 1 µm.

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