

Note

PREPARATION OF MICRON-SIZED NONSPHERICAL POLYSTYRENE/POLY(STYRENE-*co*-ETHYLENEGLYCOL DIMETHACRYLATE) PARTICLES BY SEEDED SOAP-FREE EMULSION POLYMERIZATION*

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Abstract Micron-sized nonspherical polymer particles having different morphologies were synthesized by seeded soap-free emulsion polymerization of styrene (St) and ethyleneglycol dimethacrylate (EGDMA, used as a crosslinker) on spherical, linear polystyrene (PS) seed particles. The morphology of the resulting PS/poly(St-*co*-EGDMA) particles was dependent on the crosslinker concentration and polymerization temperature.

Keywords: Nonspherical; Polymer particles; Seeded soap-free emulsion polymerization; Crosslinking.

INTRODUCTION

Polymer particles prepared by the traditional emulsion or dispersion polymerization are always perfectly spherical as a result of the minimization of surface tension^[1, 2]. For this reason, it is difficult to synthesize polymer particles with nonspherical^[3–7] shape by these methods. However, the case becomes different when a crosslinked network is introduced into the particle in a seeded polymerization process. If the elastic stress of the crosslinked network dominates the surface tension, phase separation between the newly formed polymer and original polymer will occur during polymerization. This results in uniform nonspherical polymer particles under some conditions. For example, in the seeded soap-free emulsion polymerization, various nonspherical particles have been prepared by using crosslinked seed particles^[1, 2, 8–10]. These nonspherical particles include doublets, triplets, raspberry-like particles, popcorn-like particles, and so on. In addition, it is also possible to prepare nonspherical particles in the seeded soap-free emulsion polymerization by crosslinking the second-stage polymer, as first reported in our previous paper^[11]. Submicron-sized poly(methyl methacrylate)/poly(styrene-*co*-divinylbenzene) particles which have multiple dents on particle surface have been successfully synthesized. The surface morphology of the resultant particles was greatly affected by the parameters such as polymerization temperature, the addition mode of the second-stage monomers, the molecular weight of seed particles, and so on.

On the other hand, both elastic stress and surface tension are dependent upon the size of particles. Then, is it feasible to prepare the nonspherical particles of a larger size by crosslinking the second-stage polymer in the seeded soap-free emulsion polymerization? Here we report the synthesis of polystyrene/poly(styrene-*co*-

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ethyleneglycol dimethacrylate) [PS/P(St-co-EGDMA)] particles which have a micron-sized range and a variety of nonspherical morphologies by this method. Micron-sized linear PS seed particles were first synthesized by dispersion polymerization. Then, seeded soap-free emulsion polymerization of St and EGDMA (used as a crosslinker) monomers was performed on the PS seed particles. The effects of crosslinker concentration and polymerization temperature on the morphology of the resulting PS/P(St-co-EGDMA) particles, as well as the morphological evolution of these particles were investigated in detail.

EXPERIMENTAL

Materials

Unless otherwise stated, the reagents used in this study were purchased from Sinopharm Chemical Reagent Co., Ltd. St and EGDMA (Fluka) were distilled under reduced pressure. Potassium persulfate (KPS) was recrystallized from water, and 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Ethanol, methanol, aerosol T (AOT), sodium dodecyl sulfate (SDS), tetrahydrofuran (THF) and polyvinylpyrrolidone (PVP, $M_w = 40000$) were all analytical grade and used without further purification. Double-distilled water was used in all experiments.

Synthesis

The linear PS seed particles were synthesized by dispersion polymerization using 30.0 g St as monomer, 0.3 g AIBN as initiator, 1.8 g PVP as stabilizer, 0.5 g AOT as co-stabilizer, 67.4 g ethanol as solvent. All the ingredients were charged into a 250 mL three-necked flask under stirring of 300 r/min followed by the purge of nitrogen for 30 min. Then the polymerization was carried out at 70°C for 24 h. After the polymerization, the obtained dispersion was centrifuged at 3000 r/min for 5 min, the supernatant decanted, and the white sediment redispersed in ethanol. This centrifugation-decantation-redispersion operation was repeated three times and finally the resulted PS seed particles were dispersed in water.

The synthesis of PS/P(St-co-EGDMA) particles by seeded soap-free emulsion polymerization was as follows. To a 500 mL three-necked flask, 18.0 mL PS seed latex (containing 1.0 g solid polymer), 0.2 g PVP, 0.05 g KPS and 140 mL water were added. Meanwhile, a monomer emulsion was prepared in a 100 mL beaker containing 3.0 g St, prescribed amount of EGDMA, 0.03 g SDS (0.002 mol/L, a concentration lower than CMC) and 50 mL water. The monomer emulsion was then charged into the above flask under stirring of 300 r/min and the nitrogen was bubbled through for 30 min. The seeded soap-free emulsion polymerization was initiated by immersing the flask into the water bath thermostated at the given temperature for 6 h. During the polymerization, reaction mixture of about 2 mL was sampled at different times to determine the monomer conversion and to observe the morphological evolution.

Characterization

The surface morphology of the as-polymerized PS seed and PS/P(St-co-EGDMA) particles was observed by scanning electron microscopy (SEM, S-3400N, Hitachi) after freeze-drying and sputter-coating with gold. The dispersion of PS seed particles and the particles sampled during the seeded soap-free emulsion polymerization were also observed directly by optical microscopy (OM, BT-1600, Bettersize Instruments LTD.). A drop of particle dispersion was placed on a slide glass and covered with a cover glass. To avoid the possible deformation caused by the pressing of cover glass, a spacer (*ca.* 100 μm in thickness) was set between the slide and cover glass. All the specimens were observed at a magnification of 640. The monomer conversion was determined by gas chromatography (GC, 3420A, BFRL Analytical Instrument Co., Ltd.). The temperatures of the column, the injector and the flame ionization detector were 200°C, 230°C and 170°C, respectively.

RESULTS AND DISCUSSION

The linear PS seed particles were prepared by dispersion polymerization under the conditions described above. SEM observation showed that the obtained PS particles had spherical shape with a smooth surface (Fig. 1a). The particles had a number-average diameter (D_n) of 3.13 μm with a relatively good monodispersity ($C_v = 7.8\%$).

The seeded soap-free emulsion polymerizations of St with different concentrations of EGDMA were performed in the presence of these spherical PS seed particles at a temperature of 55°C. The typical SEM micrographs of the synthesized PS/P(St-co-EGDMA) particles were shown in Figs. 1(b)–1(f). When no EGDMA was added, the resulted particles were perfectly spherical (Fig. 1b) and the particle size increased obviously compared to that of PS seed particles (Fig. 1a). However, when 1.7% (wt%, based on St, the same hereinafter) EGDMA was added in the seeded soap-free emulsion polymerization, a few small dents were formed on the surface of PS/P(St-co-EGDMA) particles (Fig. 1c). The size of these dents was about 500 nm in diameter. When 5.0%, 8.3% and 11.6% EGDMA were added, the similar dented PS/P(St-co-EGDMA) particles were observed (Figs. 1d–1f). The size and depth of the dents increased as the EGDMA concentration increased. Especially, as the EGDMA concentration was increased to 11.6%, the obtained PS/P(St-co-EGDMA) particles were significantly distorted with irregular dents on their surface (Fig. 1f). These results showed that, by introducing the crosslinked network into the second-stage polymer, it is possible to prepare the micron-sized nonspherical particles in seeded soap-free emulsion polymerization. In addition, the morphology of these particles was dependent on the concentration of the crosslinker used.

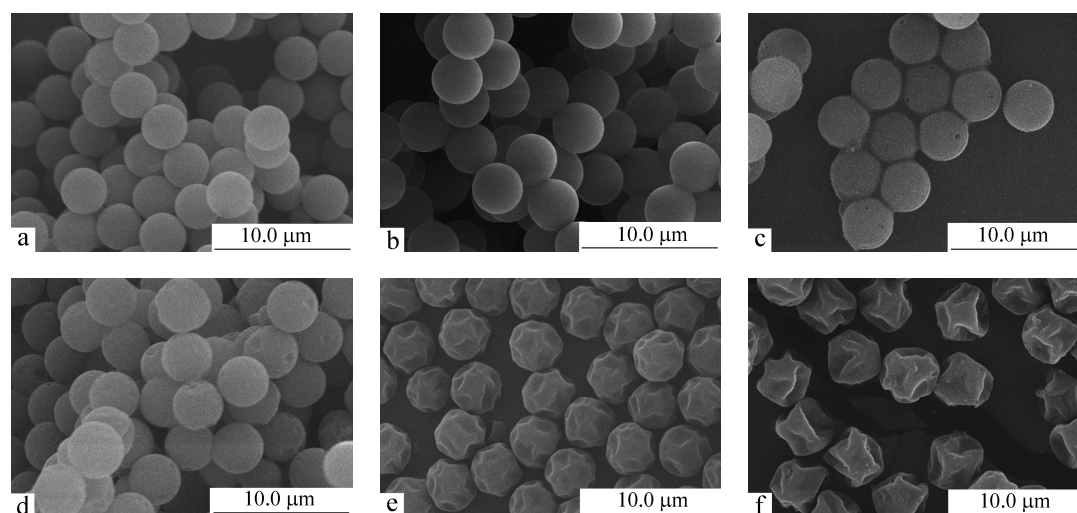


Fig. 1 SEM micrographs of PS seed particles (a), and PS/P(St-co-EGDMA) particles prepared by seed soap-free emulsion polymerization using EGDMA concentrations (wt%, based on St) of (b) 0%, (c) 1.7%, (d) 5.0%, (e) 8.3% and (f) 11.6%
Polymerization temperature: 55°C

The change of St monomer conversion with the polymerization time during the seeded soap-free emulsion polymerization was investigated. Figure 2 shows a representative result. It is evident that the monomer conversion-time curve was nearly S-shaped. The polymerization rate was extremely slow at early stage. The monomer conversion was only about 5% at the polymerization time of 120 min. However, the polymerization rate increased abruptly at about 150 min and the monomer conversion attained up to about 80% at 225 min, after which the polymerization rate slowed down again. The final monomer conversion was about 86%. This suggests that a typical gel effect occurred during the seeded soap-free emulsion polymerization.

Figure 3 shows OM micrographs of PS seed particles and PS/P(St-co-EGDMA) particles sampled during the seeded soap-free emulsion polymerization at different polymerization times. At the beginning stage of polymerization, the shape of the resultant particles was spherical and the particle size was much larger than PS seed particles due to the swelling by the second-stage monomers (Figs. 3a, 3b). As the polymerization proceeded to about 60, 120 and 150 min, the particle size tended to gradually decrease but the shape remained nearly

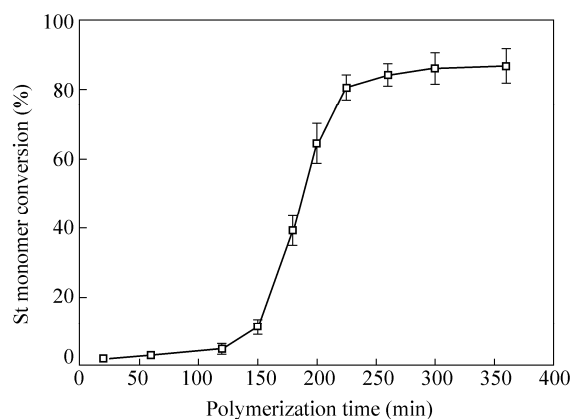


Fig. 2 Plot of St monomer conversion versus polymerization time for the seeded soap-free emulsion polymerization
EGDMA concentration: 11.6%; Polymerization temperature: 55°C

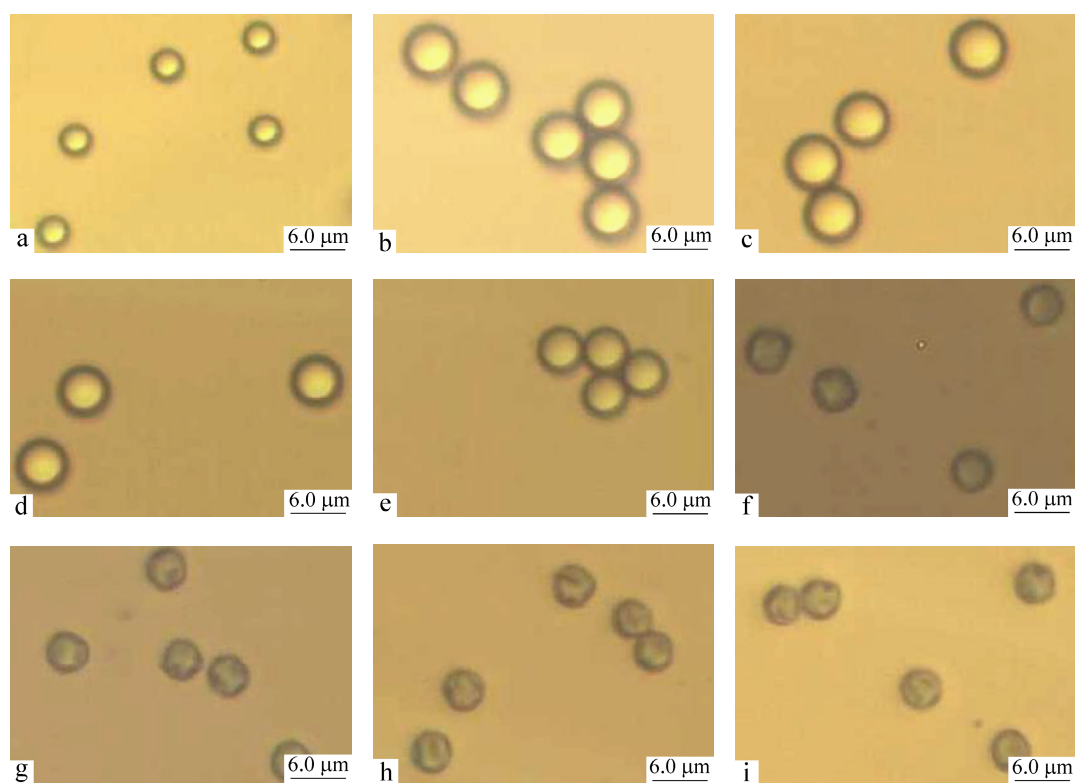


Fig. 3 OM micrographs of PS seed particles (a) and PS/P(St-co-EGDMA) particles prepared by seed soap-free emulsion polymerization at different polymerization times: (b) 20 min, (c) 60 min, (d) 120 min, (e) 150 min, (f) 180 min, (g) 200 min, (h) 225 min and (i) 360 min
EGDMA concentration: 11.6%; Polymerization temperature: 55°C

unchanged (Figs. 3c, 3d, 3e). However, at the polymerization time of 180 min, the particles became slightly deformed (Fig. 3f). The deformation of the particles became more remarkable at 200 min (Fig. 3g). As the polymerization further proceeded, the PS/P(St-co-EGDMA) particles with significantly distorted shape were finally formed (Figs. 3h, 3i). On the other hand, the solubility experiment^[11] of the resulted particles in THF (a good solvent for PS) showed that a 3D network had effectively formed at the polymerization time of 120 min.

The PS network further developed around the original PS seed particles as the polymerization progressed. The formed PS network swelled by absorbing the unreacted monomers and then contracted to relax the polymer chains^[9, 10]. However, the uneven crosslinking structure of the PS network provoked phase separation of monomers (and possibly linear PS) from the densest parts of the network into the regions where mixing is still thermodynamically favorable^[12]. Eventually, PS/P(St-co-EGDMA) particles with highly dented surface resulted as the monomer conversion increased.

All the seeded soap-free emulsion polymerizations described above were carried out at a temperature of 55°C. It was found that the polymerization temperature in the seeded soap-free emulsion polymerization also influenced the morphology of the resulted PS/P(St-co-EGDMA) particles. Figure 4 shows SEM micrographs of PS/P(St-co-EGDMA) particles prepared by seeded soap-free emulsion polymerization at 50°C and 70°C. It is evident that the polymerization at lower temperature produced PS/P(St-co-EGDMA) particles with much deeper indentations on the surface. The particles prepared at 50°C look like a kind of military helmet (Fig. 4a). In general, the lower the polymerization temperature, the slower the polymerization rate and the higher the intraparticle viscosity. However, whether these differences relate to the morphological difference observed above remained unknown at present.

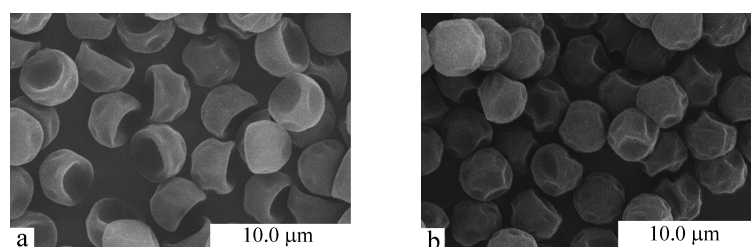


Fig. 4 SEM micrographs of PS/P(St-co-EGDMA) particles prepared by seeded soap-free emulsion polymerization at difference polymerization temperatures: (a) 50°C and (b) 70°C EGDMA concentration: 11.6%

CONCLUSIONS

We showed in this study that the seeded soap-free emulsion polymerization is a useful means to prepare micron-sized nonspherical polymer particles by introducing crosslinked network into the second-stage polymer. Nonspherical PS/P(St-co-EGDMA) particles having various morphologies have been successfully prepared by varying the crosslinker concentration and the polymerization temperature.

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