Preparation of micron-sized, monodispersed, anomalous polymer particles by utilizing the solvent-absorbing/releasing method

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Abstract About 2-μm-sized polystyrene (PS) particles having uneven surfaces were prepared by a post-treatment in which toluene-swollen PS particles were thrown into a methanol bath to release toluene therefrom rapidly. The post-treatment was named the “solvent-absorbing/releasing method”. The PS particle had large dents at the surface. The size of the dents was changed by the conditions of the posttreatment.

Key words Anomalous shape · Micron-sized, monodispersed particle · Solvent

Introduction

Polymer particles produced by emulsion polymerization are normally spherical because they minimize the interfacial free energy between the particle and the aqueous medium; however, in a series of our investigations on the production of sub-micron-sized composite polymer particles by seeded emulsion polymerization, various anomalous polymer particles have been produced [1–9].

On the other hand, recently, many researchers studying polymer colloids have been concentrating their attention on the production of micron-sized, monodispersed polymer particles [10–13] which have been applied in the biomedical field, microelectronics, etc. We have been producing micron-sized, monodispersed polymer particles having functional groups such as chloromethyl [14] and vinyl groups [15, 16] by seeded dispersion copolymerizations of styrene (S) with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2-μm-sized, monodispersed polystyrene (PS) particles as seeds. However, it was difficult to produce monodispersed particles of more than 5-μm size even by dispersion polymerization and seeded dispersion polymerization. In order to produce monodispersed polymer particles having diameters above 5 μm, seeded polymerization utilizing a new type of swelling method of seed polymer particles with a large amount of monomer which was named “the dynamic swelling method” was suggested [17, 18]. In previous work [19, 20], this technique was developed to produce micron-sized, monodispersed polymer particles having one hollow in the inside, and the formation mechanism of the hollow structure was proposed [21]. Moreover, anomalous polymer particles having “rugby-ball-like” and “red-blood-corpuscle-like” shapes were observed at low conversions of the seeded polymerization for the production of hollow polymer particles [21, 22]. Control of the particle shape should be one of the functionalization of polymer particle [23].

In this study, the formation of micron-sized, monodispersed, anomalous polymer particles by a posttreatment is proposed.
Experimental

Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(acrylic acid) used as a colloidal stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [14]. The other ingredients were of reagent grade and were used as received.

Preparation of anomalous PS particles by posttreatment

Hydrophobic solvent was emulsified in an ethanol/water (2/3, v/v) medium dissolving sodium dodecyl sulfate by an ultrasonic homogenizer (US-300T, Nihonseiki) at 0 °C for 10 min. The prepared solvent emulsion was mixed with the ethanol aqueous dispersion of PS particles produced by dispersion polymerization of S under the conditions listed in Table 1. The mixture was stirred at room temperature with a magnetic stirrer at 200 rpm for 2.5 h. The mixture (about 10 g) was sprayed into an excess of methanol in a bath (200 ml) under stirring at 500 rpm with a nebulizer with a nozzle diameter of 0.39 mm equipped with an air pump (air pump: pressure, 0.12 kgf/cm²; flow, 32 l/min) to release the solvent from the swollen PS particles rapidly. The PS particles and the swollen particles were observed with a Nikon MICROPHOT-FXA optical microscope, a Hitachi H-7100 TEM transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM).

Table 1 Production of micron-sized, monodispersed polystyrene (PS) particles by dispersion polymerization. N2; 70 °C; 24 h; stirring rate, 60 rpm

<table>
<thead>
<tr>
<th>Ingredients</th>
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<tbody>
<tr>
<td>Styrene</td>
<td>30 g</td>
</tr>
<tr>
<td>2,2′-Azobis(isobutyronitrile)</td>
<td>540.5 mg</td>
</tr>
<tr>
<td>Poly(acrylic acid)</td>
<td>3.6 g</td>
</tr>
<tr>
<td>Ethanol</td>
<td>205.5 g</td>
</tr>
<tr>
<td>Water</td>
<td>60 g</td>
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</tbody>
</table>

Measurement of the solubility of the solvent in the bath

Toluene (1 g) or decalin (3 g) respectively, was, added to a methanol/water or a methanol bath (10 g) in glass cylindrical reactors and these reactors were left at 30 °C for several hours. The amounts of the solvents dissolving in the baths were measured by gas chromatography (Shimadzu, GC-18APFsc).

Measurement of the dissolving rate of toluene in the bath

Toluene (50 mg) dissolving small amount of oil blue dye was added into the bath (50 g) in a glass cylindrical reactor (diameter, 40 mm) without stirring. The time for the toluene droplets to disappear was measured at room temperature.

Turbidity measurement

A nonsolvent (methanol, ethanol or 2-propanol) for PS was slowly dropped into a 0.1 wt% PS toluene solution (8 g). The transmittance of the solution at various contents of the nonsolvent was measured at room temperature with a photoelectric photometer (Tokyo Koden, Co., model 7) at 470 nm.

Results and discussion

An optical micrograph, a TEM photograph and a SEM photograph of PS particles produced by the dispersion polymerization of S in an ethanol/water (7/3, w/w) medium with AIBN initiator at 70 °C for 24 h under the conditions listed in Table 1 according to the optimum conditions in a previous article [14] are shown in Fig. 1. The particles were spherical and homogeneous in the inside, and the size of particles was monodisperse: the number-average diameter and the coefficient of variation determined from the TEM photograph were 1.6 μm and 3.7%, respectively. The weight-average molecular weight of PS, which was measured by gel permeation chromatography with calibration obtained using PS standards with tetrahydrofuran as the eluent, was 2.0 × 10⁶.

An optical micrograph of toluene-swollen PS particles (PS/toluene: 1/10, w/w) is shown in Fig. 2a. The swollen particles were prepared by mixing an ethanol aqueous dispersion of the toluene droplets and the PS particles under the conditions listed in Table 2.