Micron-sized, monodisperse polymer particles having reversibly transformable shapes

Masayoshi Okubo
Hideto Minami
Keisuke Morikawa

Abstract Micron-sized, monodisperse, cross-linked, hollow polymer particles having transformable shapes were produced by seeded polymerization of (divinylbenzene/vinylbiphenyl/xylene)-swollen polystyrene particles prepared utilizing the dynamic swelling method. The influence of the shell strength, which was controlled by shell thickness, cross-linking density and solvent-release temperature, on shape transformation of the hollow particles between sphere and non-sphere, respectively, based on the absorbed and release of solvent was discussed in comparison with a theoretical pressure-buckling relationship.

Keywords Dynamic swelling method · Cross-linking · Non-spherical particle · Tensile modulus · Buckling

Introduction

Recently, many researchers are studying polymer colloids of micron-sized, monodisperse polymer particles [1–5], which have been applied in the biomedical field and microelectronics. We also have prepared such particles with functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerizations of styrene with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2–l m-sized, monodisperse PS seed particles. In order to produce monodisperse polymer particles with a diameter above 5 l m, we suggested seeded polymerization utilizing a novel swelling method to make seed polymer particles absorb with a large amount of monomer, which was named “dynamic swelling method (DSM)” [9, 10].

Moreover, we developed this technique to produce micron-sized, monodisperse, cross-linked polymer particles with one hollow at the center, where hydrophobic solvent such as toluene and xylene was used for the formation of hollow structure [11–13]. In the process of the seeded polymerization for the production of the hollow polymer particles, non-spherical polymer particles with “rugby ball-like” and “red blood corpuscle-like” shapes were observed at low conversions [13]. Afterwards, the conditions to produce the “red blood corpuscle-like” [14] and “rugby ball-like” [15] polymer particles at the completion of the seeded polymerization were clarified. It was also reported that the shape of the hollow polymer particles was transformable between spherical and non-spherical shapes by absorbing/releasing of toluene [15]. In a previous article [16], the shell strength for the shape transformation was discussed with a theoretical pressure-buckling relationship proposed by Tsien [17] and Uemura and Yoshimura [18, 19].

In this article, the influence of the shell strength on the shape transformation between spheres and non-spheres will be discussed in more detail by changing the cross-linking density of the shell and solvent-release temperature.

Experimental

Materials
Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) and vinylbiphenyl (VBP) were supplied by Nippon Steel Chemical Co., Ltd., Tokyo,
Preparation of PS seed particles

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA with AIBN as initiator at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask according to the optimum conditions given in the previous article [6].

The PS particles were spherical and monodisperse; the number-average diameter and the coefficient of variation (Cv) were 1.71 μm and 2.2%, respectively, which were determined from transmission electron microscope (TEM) photographs with a Personal Image Analysis System (PIAS Co., Ltd., LA-525, Osaka, Japan).

Swelling of the seed particles with monomers and xylene utilizing DSM

The PS seed particles were dispersed in the homogeneous ethanol/water (7/3, w/w) solutions dissolving DVB, VBP, BPO and PVA and swollen with the DVB, VBP, and xylene utilizing DSM under the conditions described in Table 1.

### Table 1 Recipes for the productions of PS/P(DVB-VBP) (1/4, w/w) composite particles by seeded copolymerizations of the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>DVB/VBP (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/0</td>
</tr>
<tr>
<td>PS particlesa (mg)</td>
<td>30</td>
</tr>
<tr>
<td>DVBb (mg)</td>
<td>120.0</td>
</tr>
<tr>
<td>VBPd (mg)</td>
<td>–</td>
</tr>
<tr>
<td>Xylene (mg)</td>
<td>330</td>
</tr>
<tr>
<td>BPO (mg)</td>
<td>2.4</td>
</tr>
<tr>
<td>PVA (mg)</td>
<td>15</td>
</tr>
<tr>
<td>Ethanol (g)</td>
<td>7</td>
</tr>
<tr>
<td>Water (g)</td>
<td>43</td>
</tr>
</tbody>
</table>

a In sealed tube: 70 °C; 48 h; N2; shaking rate, 60 cycles/min (3-cm strokes)
b Dn, 1.7 μm; Cv1, 2.2%
c Purity, 96% (by catalog)
d Purity, 75% (by catalog)
e Water (40 g) was post-added at the rate of 2.66 ml/h using a microfeeder

Abbreviations: PS, polystyrene; DVB, divinylbenzene; VBP, vinylbiphenyl; P(DVB-VBP), poly(DVB-VBP), BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

Seeded polymerization

Seeded polymerizations for the dispersions of (monomers/xylene)-swollen PS particles were carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 48 h. The tubes were horizontally shaken at 60 cycles/min (3-cm strokes). The conversion was measured by gas chromatography with helium as a carrier gas. Dodecyl alcohol and 1,4-dioxane were used as standard reagent and solvent. Droplets in the dispersion were observed on a slide glass, which was covered with a cover glass, with a Nikon MICROPHOT-FXA optical microscope.

Electron microscopy

Hitachi H7100-TE and S-2500 electron microscopes were used for TEM and scanning electron microscope (SEM) observations, respectively. For the TEM samples, each emulsion was placed onto a carbon-coated grid. For the SEM samples, each emulsion was dropped onto an aluminum plate.

Preparations of PDVB and P(DVB-VBP) films

Preparations of PDVB and P(DVB-VBP) films were carried out by bulk polymerizations under the conditions listed in Table 2. The thickness of films was about 500 μm.

Tensile test

Tensile tests were carried out with tensile tester (Shimadzu, AUTOGRAPH AGS-1kND, SHIMADZU, Kyoto, Japan) at each temperature after immersing in toluene for 24 h at various temperatures. The original length of the specimen was 10 mm and the elongation rate was 1 mm/min.

### Results and discussion

Figure 1 shows optical micrographs of PS/P(DVB-VBP) (1/4, w/w) composite particles produced by seeded polymerizations PS particles swollen with DVB/VBP/xylene prepared utilizing the DSM at various weight ratios of DVB/VBP (conditions listed in Table 1). All polymerizations were completed and all particles were spherical before releasing the xylene. At the DVB/VBP ratio of 1/0, the composite particles after releasing the xylene at room temperature were still spherical and had a hollow structure (Fig. 1a). On the other hand, at the DVB/VBP ratios of 1/5 and 1/8, the composite particles were non-spherical (Fig. 1b, c). In drying process, the

### Table 2 Recipes for the preparations of PDVB and P(DVB-VBP) films by bulk polymerizations

<table>
<thead>
<tr>
<th>DVB/VBP (w/w)</th>
<th>1/0</th>
<th>1/5</th>
<th>1/8</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB (g)</td>
<td>4.0</td>
<td>0.67</td>
<td>0.44</td>
</tr>
<tr>
<td>VBP (g)</td>
<td>–</td>
<td>3.33</td>
<td>3.56</td>
</tr>
<tr>
<td>V-70 (g)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

a 30 °C; 24 h

Abbreviations: PDVB, polydivinylbenzene; V-70, 2,2’-azobisisobutyronitrile