Monodisperse glycidyl-functional polymer particles in the micron-size range by seeded polymerization

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Abstract Polymer particles having glycidyl ether groups were prepared through seeded polymerization in aqueous medium. The polystyrene seed particles were swollen with a mixture of n-butyl methacrylate, glycidyl methacrylate, ethylene glycol dimethacrylate, and benzoyl peroxide initiator. The particles produced after polymerization were characterized regarding the particle morphology and functionality. Optical microscopy and scanning electron microscopy showed that the particles are in the size range of 13–14 μm and are highly monodisperse with heterophase structures. Actually, the high content of glycidyl methacrylate in the second monomer mixture caused the particle phase to be homogeneous. This effect was explained in terms of the surface tension of each polymer phase. Moreover, the cross-linking of the seed particles had a significant effect on the final particle morphology. From the HCl–dioxane back titration method, it was found that about 20–30% of glycidyl ether groups still remained on the final particles.

Key words Composite particle · Monodisperse · Particle morphology · Surface tension · Glycidyl ether group

Introduction

Recently, great attention has been paid to micron-sized polymer particles in the fields of medical diagnostics, liquid chromatography, enzyme immobilization, and drug delivery [1–7]. Dispersion polymerization has been reported to be one of useful methods to prepare these particles. In addition to the simplicity of the process, particles in various size ranges with high monodispersity can be obtained by selecting suitable reaction conditions.

For the production of the polymer particles having special functional moieties in the micron-size range, dispersion homopolymerizations or copolymerizations have been studied by several research groups. Margel et al. [8] prepared uniform microspheres having chloromethyl groups using chloromethylstylene by dispersion polymerization in organic media. Yang et al. [9] studied the dispersion copolymerization of styrene (St) and glycidyl methacrylate (GMA) to introduce the glycidyl ether group on the particle surfaces. Dispersion copolymerization of methyl methacrylate and GMA has also been carried out by Lee and Chen [10]. They showed that the surface functionality of the glycidyl ether group was influenced by the reactivity ratio of the two monomers.

In the case of dispersion copolymerization, there are many reaction parameters, such as the initial solubility of the medium, the stabilizer concentration, and the initiator concentration. All these parameters have influence on the particle size and the size distribution of the final particles [9–13]. Therefore, the establishment of the experimental conditions is preferentially required for the high monodispersity of the particles. Moreover, particles in a size range of 10 μm or above could hardly be achieved owing to the difficulty to control the particle nucleation stage by conventional dispersion polymerization.
For particles in a size range of 10 μm or above, the methods referred to as seeded polymerization have usually been employed. In seeded polymerization, once the monodisperse seed particles are utilized, the monodispersity can be maintained throughout the procedure, including the monomer swelling and the polymerization [14–19]. Depending on the nature of the seed particles and the second monomers, a variety of monodisperse polymer particles can be produced different size (10–100 μm), matrix properties, and functionality.

In this study, by using linear and cross-linked polystyrene (PS) particles as seeds, glycidyl-functional particles within the size range of 10 μm or above were prepared through seeded polymerization in aqueous media. When cross-linked seed particles were employed in the seeded polymerization, the cross-linking of the seed particles had a significant effect on the final particle morphology [20, 21, 22]. On the basis of these results, we tried to investigate the effects of the second monomer composition as well as the cross-linking of seed particles on the final particle morphology. Also, the quantitative characterization of the glycidyl ether group was followed.

**Experimental**

**Materials**

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_n = 1.0 \times 10^3$ g mol$^{-1}$, Hyosung BASF), poly(vinylpyrrolidone) (PVP, $K_30$, $M_n = 4.0 \times 10^4$ g mol$^{-1}$, Aldrich Chemical Co.), 1-chlorododecane (CD, TCI), and 2-methoxyethanol (Kanto Chemical Co.) were used as received. Poly(vinylalcohol) (PVA, $M_n = 8.8 \times 10^3$–$9.2 \times 10^4$ g mol$^{-1}$, 87–89% hydrolyzed) was kindly supplied by Kuraray Co. The inhibitors in 2-hydroxyethyl methacrylate (HEMA, Aldrich), St (Jnsei Chemical Co.), n-butylmethacrylate (BMA, Junsei), GMA (Junsei), and ethylene glycol dimethacrylate (EGDMA, Junsei) were removed through a removing column (Aldrich). 2,2-Azobisisobutyronitrile (AIBN, Junsei) and benzoyl peroxide (BPO, Aldrich) were recrystallized from methanol.

**Synthesis of urethane acrylate cross-linker**

TDI was poured into a four-necked glass reactor equipped with a stirrer, a reflux condenser, and thermocouples, and nitrogen (purity, 99.9%) was inlet for 10 min to eliminate the residual moisture. Then, TDI, PTMG, and HEMA were reacted stepwise with a reaction molar ratio of 2:1:2. During the reaction, the end point of the urethane reaction was found by the amine back titration method [23]. Other detailed reaction procedures and the molecular structure of urethane acrylate (UA) can be found in our previous works [20–22].

**PS seeds by dispersion polymerization**

St, UA, AIBN, PVP, 2-methoxyethanol, and ethanol were weighed into 50-ml glass vials. After sealing under a nitrogen atmosphere, the vials were submerged in a thermostatted water bath and tumbled with a rotation speed of 40 rpm at 70 ± 0.1°C for 24 h. The particles obtained were centrifuged for 10 min at 6,000 rpm. The supernatant was then decanted and the remaining precipitate was repeatedly washed by four centrifugations and dried under vacuum at ambient temperature. All the ingredients used are summarized in Table 1.

**Two-staged monomer swelling and polymerization**

Two-staged swelling and polymerization were also carried out in the four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. The PS seed particles (0.1 g) redispersed in 0.25% sodium lauryl sulfate (SLS) aqueous solution (40 g) by 10 min sonication were swollen with CD (0.2 g) emulsified by ultrasonic homogenizing in 0.25% SLS aqueous solution (10 g) at 30°C for 10 h. The stirring speed was fixed at 200 rpm throughout the process. After complete disappearance of the CD droplets, 100 g 0.25% SLS solution was added. Then, the mixture of monomers (BMA, GMA, EGDMDA) and BPO (1 wt% of the total monomers) was emulsified by the same method as CD and poured into the reactor. The swelling was continued for another 6 h at 30°C. The swollen particles were reacted with PVA aqueous solution of which the concentration was fixed at 1% of the total amount (250 g). The polymerization that can take place in the aqueous phase was inhibited by adding copper chloride (0.01 g) [24]. After removal of air with N2, the polymerization was carried out at 70°C for 10 h. The conversions were determined with a gravimetric method. After the sampling of 10 g reactants from the reactor in vials, 1% of hydroquinone solution was added into the vials and the reaction was quenched in ice-water. The conversion reached at 92% after 8 h from the onset of the temperature. The particles obtained were repeatedly washed by decantation in water and ethanol and were dried under vacuum at ambient temperature.

**Characterizations**

The swollen particles and the polymer particles produced were monitored using an optical microscope (OM, Nikon Microphoto Fax). The particles were also observed using a scanning electron microscope (SEM, JSM-6300, Jeol). The mean diameter and the particle size distribution (PSD) were determined by counting at least 100 individuals from SEM photographs and the average was taken.

The morphology of selected samples was examined by transmission electron microscopy (TEM) after preferentially staining the PS seed domains with RuO4 vapor for 24 h. Then, the particles were embedded in epoxy resin and cured overnight at 60°C. The samples embedded were sectioned with an ultramicrotome (LKB, Bromma). To investigate the change in the surface tension of the copolymer, poly(BMA-co-GMA) copolymer film was prepared.

Table 1 The standard recipe for the dispersion polymerization of styrene and urethane acrylate. (70°C; 24 h; 10 wt% of monomer concentration based on total weight)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>1.00</td>
</tr>
<tr>
<td>Urethane acrylate</td>
<td>0 or 0.03</td>
</tr>
<tr>
<td>Poly(vinylpyrrolidone) K-30</td>
<td>0.18</td>
</tr>
<tr>
<td>Aerosol Ot*</td>
<td>0.04</td>
</tr>
<tr>
<td>2,2-Azobisisobutyronitrile</td>
<td>0.01</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
<td>4.39</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.39</td>
</tr>
</tbody>
</table>

*Costabilizer: di-2-ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid)