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Surface modification of monodisperse hydroxyl functionalized polymeric microspheres using ceric ammonium nitrate

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Abstract

The surface modification of monodisperse hydroxyl functionalized polymeric microspheres was carried out by utilizing a redox initiation system. Styrene, divinylbenzene and hydroxyethyl methacrylate were used as the second monomer in the seeded polymerization. An excessive amount of the second monomer emulsion was swollen into the polystyrene (PS) seed particles completely by controlling the medium solvency and swelling temperature. The hydroxyl functional groups were radicalized by the ceric ammonium nitrate in nitric acid solution, and the methyl methacrylate was reacted uniformly on the surface of microspheres. From the SEM, and FE-TEM measurements, highly monodisperse microspheres having a smooth surface, and polymethylmethacrylate (PMMA) coating layer were observed, respectively. The surface characteristics of the PS seed particles, hydroxyl functionalized and surface-modified polymeric microspheres were confirmed by utilizing FT-IR, XPS and thermal analysis.

Keywords: Surface modification; Monodisperse functionalized polymeric microspheres; Seeded polymerization; Ceric ammonium nitrate; PMMA grafting

1. Introduction

Monodisperse and highly crosslinked polymeric microspheres were useful in a wide range of chemical applications including the standard kit, a catalyst, chromatography, supporter, or the ball-type spacer in the liquid crystal display (LCD) because of their dimensional stability and durability [1,2]. The polymer particles can be prepared by using the heterogeneous polymerization techniques such as suspension, emulsion, dispersion and precipitation polymerization [3]. Suspension polymerization is a useful technique for making crosslinked polymer beads, but the size distribution of beads is too broad [4,5]. Therefore, an additional classification process must be followed to obtain the monodispersity. Spherical latex particles synthesized by the emulsion polymerization tend to fall in the nanometer size range [6], and a rough surface and a porous structure of polymer particles are obtained by using the

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precipitation polymerization [7,8]. The crosslinking of polymer particles by the dispersion polymerization is accompanied by a broad size distribution, odd shape or coagulum, despite of a small amount of crosslinker [9–11].

The heterogeneous polymerization techniques have the limitations for the preparation of monodisperse and highly crosslinked particles [12]. Monodisperse and highly crosslinked polymeric microspheres can be achieved by swelling the second monomer into the seed particles and consecutive polymerization. The seeded polymerization was extensively investigated by Ugelstad et al. [1,13,14] as an activated swelling procedure (ASP), El-Aasser et al. [2,15,16] as a successive seeded polymerization, Okubo and Nakagawa [17] as a dynamic swelling method (DSM), and others [18,19]. Once the monodisperse seed particles are utilized, the monodispersity of microspheres can be maintained during the seeded polymerization. Another merit of seeded polymerization is that the diameter, the matrix property or the functionality of polymer microspheres are easily manipulated by the nature of seed particles and the composition of the second monomer. In our earlier works [20–22], the monodisperse polymer particles having high crosslinking density and functionality were produced by using the seeded polymerization.

In the recent day, the additional requirements of polymeric microspheres rise up for the specific application fields maintaining their monodispersity and high crosslinking density. For instance, an adhesive property of the ball-type LCD spacer is needed to prevent drop down by the gravity in the LCD [23,24]. Besides, the dispersion ability of hydrophobic microspheres in a hydrophilic medium, and the biocompatibility of polymer particles in a blood are also requested in the paint industry, and the medical treatments, respectively. The additional properties of polymeric microspheres can be provided by the surface modification utilizing the chemical modification [25], or the high energy radiation (ultraviolet, plasma, physical or chemical vapor deposition) methods [26,27]. Especially, the redox system by transition metal ions has been found to be effective in oxidizing the functional groups on the surface without changing the original properties of polymeric microspheres [25].

In the present study, the surface modification of monodisperse and highly crosslinked polymeric microspheres was performed by introducing hydroxyl groups on the surface, and utilizing the redox initiation system. Styrene (St), divinylbenzene (DVB) and hydroxyethyl methacrylate (HEMA) were chosen as the second monomer in the seeded polymerization, and swollen into the PS seed particles. The hydroxyl groups on the surface were initiated by ceric ammonium nitrate (CAN) in the nitric acid solution, then methyl methacrylate (MMA) was reacted on the microspheres uniformly. The morphologies of polymer particles were monitored by an optical, scanning and transmission electron microscope. The thermal analysis of surface-modified polymeric microspheres was also carried out.

2. Experimental

2.1. Materials

Styrene (St, Kanto), methyl methacrylate (MMA, Junsei), azobis(isobutyronitrile) (AIBN, Junsei), polyvinylpyrrolidone (PVP, $M_w = 4.0 \times 10^4$ g/mol, Sigma), aerosol-OT (AOT, Sigma) and ethanol (Carlo) were all reagent grades. Divinylbenzene (DVB, Fluka), 2-hydroxyethyl methacrylate (HEMA, Aldrich), sodium lauryl sulfate (SLS, Yakuri), ceric ammonium nitrate (CAN, Aldrich) and nitric acid (Aldrich) were also used without further purification.

2.2. PS seed particles crosslinked with PPGDA

Polypropylene diacrylate (PPGDA, crosslinker) was synthesized by the reaction of polypropylene glycol (PPG, $M_w = 2.0 \times 10^3$ g/mol, Polyol) with acryloyl chloride (AC, Sigma Chemicals) in tetrahydrofuran (THF, Mallinckrodt) [28]. The crosslinked PS seed particles were produced by the dispersion polymerization. AOT (0.2 g), PVP (1.8 g) and ethanol (85 g) were weighed into a 250 ml four-necked round flask equipped with a reflux condenser, nitrogen inlet apparatus and a mechanical stirrer. Then St (10 g), PPGDA (2.5 g), AIBN (0.125 g) mixture was poured into the reactor at room temperature. After 30 min of vigorous stirring, the homogeneous mixture was reacted at 70 °C for 24 h with 40 rpm stirring. The product was purified three times through centrifugation at 2500 rpm for 10 min, and washed with ethanol to remove the surface-anchored PVP molecules. Final particles were dried at room temperature.

2.3. Hydroxyl functionalized polymeric microspheres

Polymer particles containing hydroxyl functional groups were prepared by the seeded polymerization. The PS seed particles were redispersed in 0.25 wt% SLS of EtOH/water (1/5, g/g) solution (SE solution) by sonification. The emulsion of the second monomer mixture (St/DVB/HEMA) in a SE solution was poured into the reactor. The swelling was continued at 30 °C until emulsion droplets disappeared completely. The swollen particles were stabilized with 5% PVP aqueous solution, and polymerized at 70 °C for 10 h. The particles washed repeatedly with water and dried in vacuum oven. A standard recipe of the seeded polymerization was summarized in Table 1.