

Surface Modification of Monodisperse-Crosslinked Polymeric Microspheres Using a Redox Initiation System

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ABSTRACT: The surface modification of monodisperse-crosslinked polymeric microspheres was carried out by introducing hydroxyl groups on the surface and utilizing the redox initiation system. The emulsions of the second monomer mixture were swollen into the monodisperse PS seed particles. The hydroxyl groups were introduced by hydrolysis of the acetate groups on the surface of microspheres. Ceric ammonium sulfate in sulfuric acid solution was employed to graft the acrylic monomer onto the polymeric microspheres. The surface characteristics of the surface-modified particles were confirmed by FTIR, SEM, and TGA

measurements. From the FE-TEM image, a uniform coating layer was confirmed on the surface of microsphere. In DSC analysis, only an exothermal peak appeared when high content of DVB was used in the seeded polymerization, while, T_g s emerged after hydrolysis and graft polymerization using the low content of DVB in the second monomer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1349–1356, 2006

Key words: surface modification; polymeric microspheres; seeded polymerization; hydrolysis; graft polymerization

INTRODUCTION

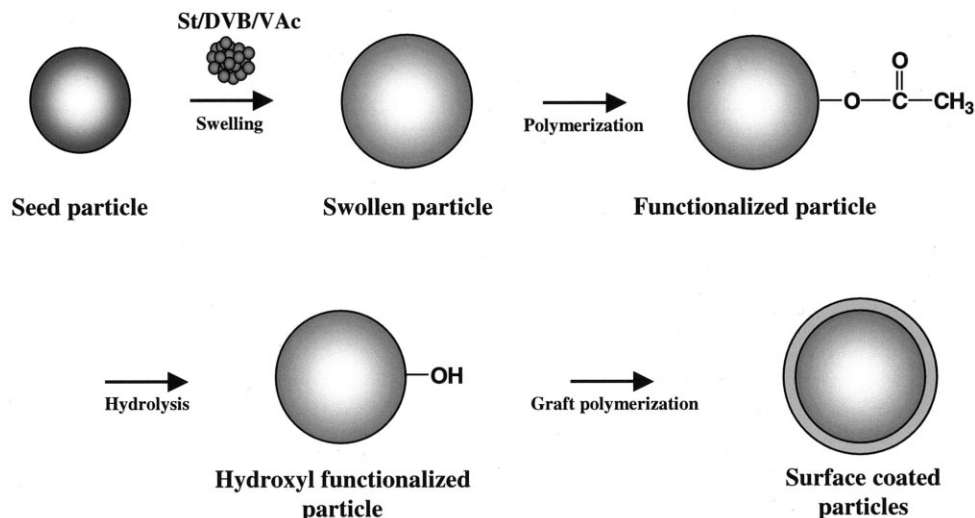
Monodisperse-crosslinked polymeric microspheres have been applied in a number of industrial fields because of their requirements of high dimensional stability and durability.¹ Therefore, considerable efforts both in the academic and the industry have concentrated on the preparation of highly monodisperse-crosslinked polymeric microspheres. The dispersion polymerization and seeding method are generally employed to produce monodisperse polymer particles in the micrometer range. However, the crosslinking of the particles by the dispersion polymerization is accompanied by serious problems, such as a broad size distribution, odd shape, or coagulum, despite of a small amount of crosslinker.^{2–4} Highly monodisperse-crosslinked polymeric microspheres can be obtained by swelling the second monomer into the seed particles and consecutive polymerization.^{1,5–7} The polymer particles made by the seeded polymerization have high monodispersity, high crosslinking density and heat-resistance property, and easy to tailor the diameter of the final polymer particles.

In the recent day, polymeric microspheres require additional properties for the specific application fields maintaining their dimensional stability and durability. In detail, an adhesion property of the ball-type spacer in liquid crystal display (LCD) is required to prevent drop down by the gravity.^{8,9} Furthermore, the dispersion ability of hydrophobic microspheres in the hydrophilic medium for the paint industry, and the biocompatibility of polymer particles in a blood for the medical treatments are also requested. Although the surface modification of polymer particles using reactive microgel,^{10,11} core-shell structure,¹² or copolymerization¹³ had been reported, however, they were limited in nanosize and noncrosslinked polymer particles. For the surface modification of crosslinked polymer particles, the chemical initiation (redox system)¹⁴ or high-energy radiation (ultraviolet, plasma, physical, or chemical vapor deposition) methods^{15,16} are available. Among them, the redox system by transition metal ions has been found to be effective in oxidizing the hydroxyl group on the polymer surface.¹⁴

In the present study, the surface modification of the monodisperse-crosslinked polymeric microspheres was performed by utilizing hydroxyl groups on the surface and the redox initiation system. Styrene (St), divinylbenzene (DVB), and vinyl acetate (VAc) were chosen as the second monomer in the seeded polymerization, and swollen into the PS seed particles. The acetate groups induced on the surface of particles were hydrolyzed to alcoholic groups in methanol solution with NaOH. The hydroxyl functional groups on

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Scheme 1 The representations of the seeded polymerization, saponification, and surface graft polymerization.

the polymeric microspheres were initiated by ceric ammonium sulfate (CAS) in sulfuric acid solution, then grafted by acrylic monomers (MMA and BMA).

The morphology of polymer particles was monitored by optical and scanning electron microscope, and the surface characteristics of microspheres were examined by using transmission electron microscope, FTIR, and thermal analysis.

EXPERIMENTAL

Materials

Polypropylene diacrylate (PPGDA, crosslinker) was synthesized by the reaction of polypropylene glycol (PPG, $M_w = 2.0 \times 10^4$ g/mol, Polyol) with acryloyl chloride (AC, Sigma) in tetrahydrofuran (THF, Mallinckrodt).¹⁷ Styrene (St, Kanto), azobis(isobutyronitrile) (AIBN, Junsei), polyvinylpyrrolidone (PVP K-30, $M_w = 4.0 \times 10^4$ g/mol, Sigma), aerosol-OT (AOT, Sigma), and ethanol (Carlo) were all reagent grades. Methyl methacrylate (MMA) and butyl methacrylate (BMA) were purchased from Junsei Chemicals. Divinylbenzene (DVB, Fluka), vinyl acetate (VAc, Junsei), benzoyl peroxide (BPO, Junsei), sodium lauryl sulfate (SLS, Yakuri), sodium hydroxide (NaOH, Yakuri), methanol (J. T. Baker), ceric ammonium sulfate (CAS, Aldrich), and sulfuric acid (Yakuri) were also used without further purification.

PS seed particles crosslinked with PPGDA

The crosslinked-PS seed particles were produced by the dispersion polymerization. AOT (0.4 g), PVP (1.8 g), and ethanol 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), and AIBN (0.125 g) mixture were 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.

Hydroxyl functionalized polymeric microspheres

Polymeric microspheres containing hydroxyl functional groups on the surface were prepared by the seeded polymerization and the saponification procedure. The PS seed particles were redispersed in 0.25 wt % SLS water/EtOH (5/1, g/g) solution by sonification. The emulsions of the second monomer mixture (St/DVB/VAc) via ultrasonic homogenizer in 0.25 wt % SLS water/EtOH (5/1, g/g) solution were poured into the reactor. The swelling was continued until emulsion droplets disappeared completely at 30°C. The swollen particles were stabilized with 5% PVP aqueous solution, and polymerized at 80°C for 10 h. The particles were washed repeatedly with water and dried in vacuum oven. Then, saponification of the acetate groups on the surface of microspheres was carried out. The dried polymer particles were dispersed in methanol, and 30% NaOH aqueous solution was added. The mixture was stirred for 8 h at 50°C. The hydroxyl-functionalized microspheres were obtained by filtering and repeated washing with DDI water. Schematic representation of seeded polymerization and saponification procedure is shown in Scheme 1. A standard recipe of seeded polymerization and saponification procedure is summarized in Table I.

TABLE I
Standard Recipe of the Seeded Polymerization and the Saponification Procedure

Stage	Ingredient	Quantity
Seeded polymerization ^a	PS seed particles	0.10 g
	SE solution ^b	40.00 g
	Styrene	0.50/3.00 g
	Divinylbenzene	3.00/0.50 g
	Vinyl acetate	1.50 g
	Benzoyl peroxide	0.07 g
	SE solution ^b	21.00 g
	PVP solution ^c	40.00 g
Saponification ^d	Acetate-functionalized particles	2.00 g
	MeOH	80.00 mL
	NaOH solution ^e	2.00 mL

^a 80°C, 10 h, 125 rpm.

^b EtOH/water = 1/5 (w/w), 0.25 wt % SLS solution.

^c 5% PVP aqueous solution.

^d 50°C, 8 h, 125 rpm.

^e 30% NaOH aqueous solution.

TABLE II
Standard Recipe for the Surface Graft Polymerization of Microspheres^a

Ingredient	Quantity (g)
OH seed particles	0.20
H ₂ SO ₄ solution ^b	40.0
Acrylic monomer ^c	0.20
H ₂ SO ₄ solution	5.00
Ceric ammonium sulfate ^d	0.10
H ₂ SO ₄ solution	5.00

^a 45°C, 4 h, 250 rpm.

^b 0.188 mol/L.

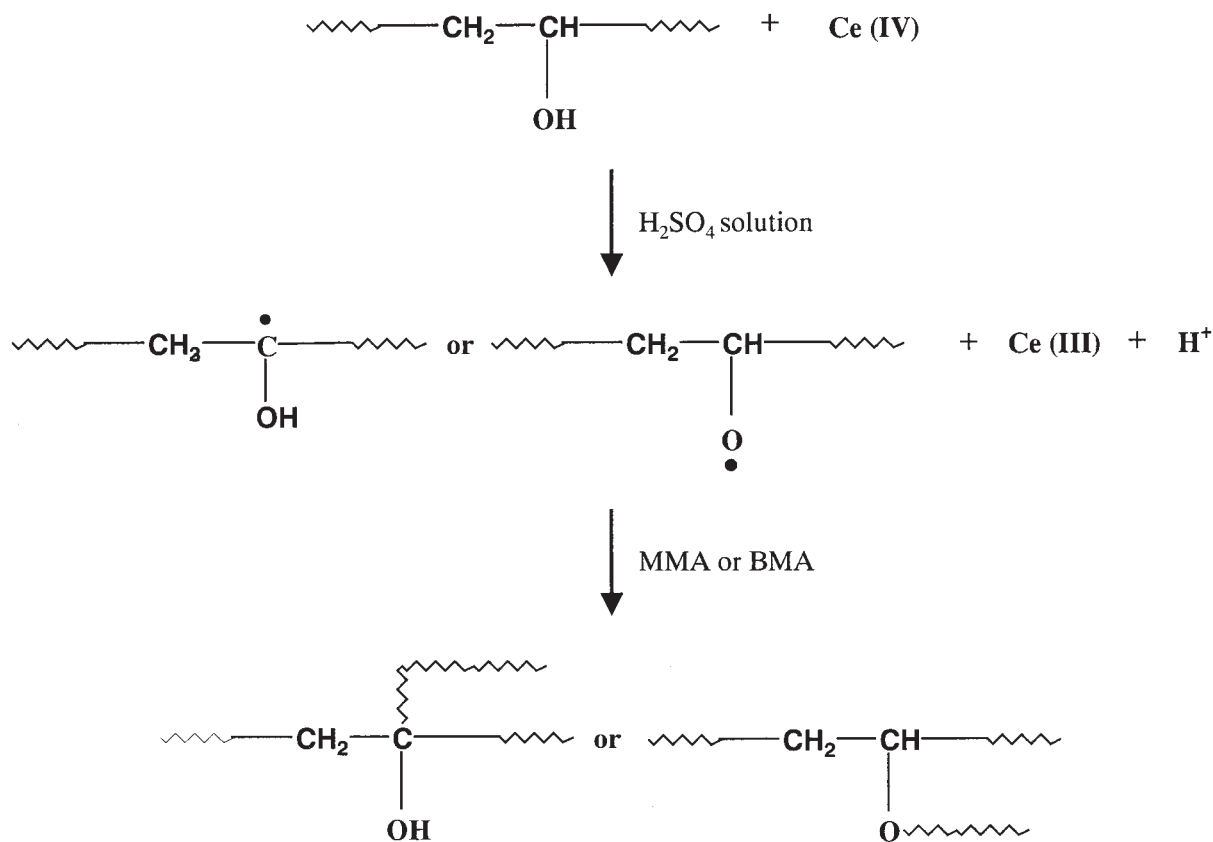
^c Methyl methacrylate or buthyl methacrylate.

^d 3.16×10^{-3} mol/L, with dropping funnel.

Graft polymerization of acrylic monomer using hydroxyl functional groups

Hydroxyl-functionalized microspheres were dispersed in sulfuric acid solution. The acrylic monomer

(MMA or BMA) in the sulfuric acid solution was poured into the reactor. Nitrogen atmosphere was maintained throughout the reaction period. An amount of ceric ammonium sulfate in sulfuric acid solution was added slowly. Then, the graft polymerization was carried out at 45°C for 4 h. The schematic representation and reaction mechanism of the surface graft polymerization by ceric ions were represented in Schemes 1 and 2, respectively. The surface-modified microspheres were filtered and washed with DDI water repeatedly. The recipe of the graft polymerization was illustrated in Table II.



Scheme 2 The mechanism of surface graft polymerization by using ceric ammonium sulfate initiator.

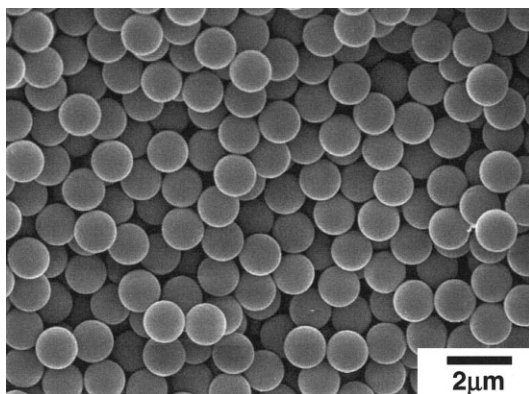


Figure 1 SEM photograph of the seed particle comprised of styrene and PPGDA via dispersion polymerization.

Characterization

Swelling procedure and morphology of polymeric microspheres were monitored by optical microscope (OM, Olympus BH-2) and scanning electron microscope (SEM, JSM-6330F JEOL). About a hundred individual particle diameters were measured from SEM photographs, the average was taken, and their polydispersity index (PDI) was calculated. The existence of hydroxyl group and acrylic monomer grafted on the surface of polymer particles was confirmed by using fourier transform infrared spectroscopy (FTIR, Nicolet, Magna IR-550) and transmission electron microscope (FE-TEM, JEM 2100F, JEOL). Thermal stability and glass-transition temperature (T_g) of surface-modified polymeric microspheres were determined by using a thermogravimetric analysis (TGA, TA Instruments) and a differential scanning calorimeter (DSC, DSC-7, Perkin-Elmer), respectively.

RESULTS AND DISCUSSION

Monodisperse-crosslinked polymeric microspheres

The monodispersity of seed particles is one of the key factors to prepare the monodisperse polymeric microspheres in the seeded polymerization. To obtain highly monodisperse seed particles, the dispersion polymerization was carried out. Moreover, 2 wt % of macrocrosslinker (PPGDA) was copolymerized to supply monomer swellability of the seed particles. Because polystyrene is a well-known rigid and stiff material, copolymerization of PPGDA having flexible backbone with styrene was used for a complete swelling of the second monomer into the seed particles and to prevent the morphological change after polymerization.¹⁷ Figure 1 shows the SEM photograph of monodisperse-crosslinked PS particles by dispersion polymerization. The PS particles have high monodispersity (polydispersity index (PDI) = 1.01, 1.10 μm), smooth surface, and spherical shape.

For the preparation of the polymeric microspheres having high durability and functional groups, the amount of the second monomer mixture was fixed to fifty-fold based on the weight of seed particles used. By adjusting solvency of medium (water/EtOH = 5/1) and swelling temperature (30°C), a large amount of the second monomer emulsion was completely swollen into the seed particles. Figure 2(a) shows that the seed particles dispersed separately well in the medium. Also, the small size of the emulsions was not shown in the medium [Fig. 2(b)], which means the complete swelling of the second monomers into the seed particles. After polymerization, the monomer conversion of 86% was obtained using a gravimetric method.

Hydroxyl functional groups on the microspheres

Polyvinyl acetate is an important material in the industrial fields to produce polyvinyl alcohol by the hydrolysis. The incorporation of hydroxyl functional groups on the polymeric microspheres was achieved by utilizing the same method used in our earlier work.¹⁸ The acetate groups on the surface of microspheres were converted to hydroxyl groups through

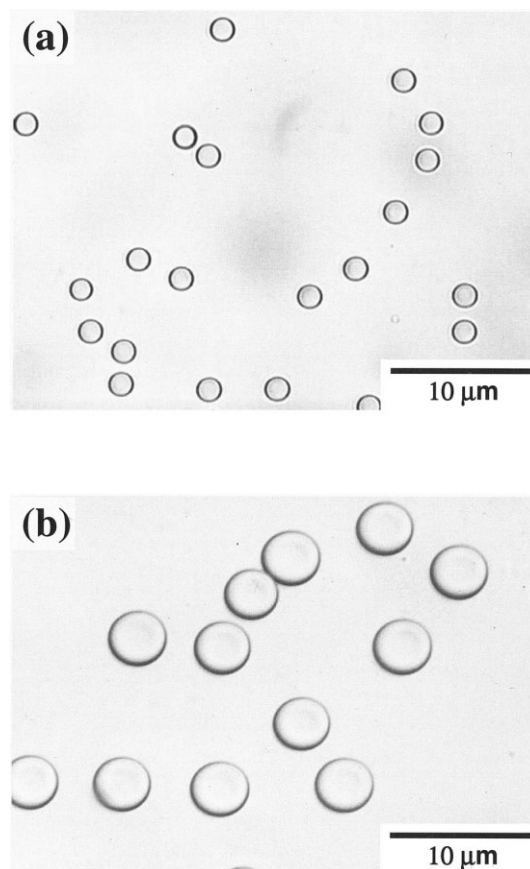


Figure 2 OM photographs of seed particles dispersed in medium (a) and 2nd monomer swollen particles (b).

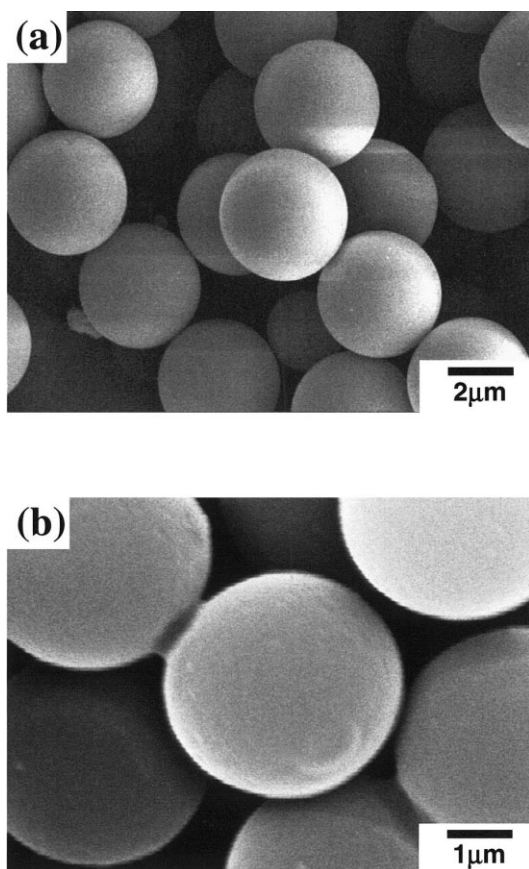


Figure 3 SEM photographs of polymeric microspheres having hydroxyl groups on the surface (a) and after graft polymerization (b).

the saponification procedure in methanol. The SEM photograph of polymeric microspheres containing hydroxyl groups on the surface was depicted in Figure 3(a). The diameter of polymer particles is $3.43 \mu\text{m}$. Although relatively large amount of crosslinker (DVB) was swollen into the seed particles, high monodispersity ($\text{PDI} = 1.01$), smooth surface, and spherical shape of polymeric microspheres were maintained even after polymerization.

After the seeded polymerization and the saponification procedure, hydroxyl groups were introduced on the surface of microspheres. The incorporation of the hydroxyl groups onto the surfaces of polymeric microspheres was confirmed by FTIR spectroscopy. Figures 4(a) and 4(b) show the FTIR spectra of poly-(DVB-co-VAc) microspheres before and after the saponification procedure, respectively. From the generation of the typical alcoholic absorption band in the region of $3600\text{--}3100\text{cm}^{-1}$ after the saponification procedure, it is obvious that the surfaces of the microspheres were functionalized with the hydroxyl groups. In addition, there was no evidence of morphological changes in the microspheres as a result of the incorporation of the hydroxyl groups onto the polymeric microspheres as shown in SEM images.

Surface graft polymerization using redox initiator and hydroxyl groups

The basic concept of the surface graft polymerization is that the redox reaction of transition metal ions generated the free radicals on the hydroxyl groups and initiated, as represented in Scheme 2. Ceric ammonium sulfate with sulfuric acid, which is chosen in this work, is a well-known redox initiator system for surface grafting of acrylic monomer, resulting in fast reaction and good yield. MMA and BMA were selected as coating material on the surface of monodisperse-crosslinked polymeric microspheres. By using the different T_g of surface coating materials, adhesive property would be added to polymeric microspheres maintaining their own dimensional stability and durability. The reaction conditions for the surface initiation of the hydroxyl-functionalized polymeric microspheres were determined by our preliminary experiments, and summarized in Table II.

Surface-modified polymeric microspheres were investigated by SEM and FTIR analysis to evaluate the existence of acrylic monomer on the surface of microspheres. After the surface graft polymerization [Fig. 3(b)], the diameter of microspheres slightly increased ($3.52 \mu\text{m}$), and relatively rough surface was observed maintaining the monodispersity. In FTIR measurement, a broad OH peak around $3600\text{--}3100 \text{cm}^{-1}$ [Fig. 4(b)] was diminished and new peak was observed at 1730cm^{-1} [Fig. 4(c)] after the graft polymerization. It is suggested that the hydroxyl groups were initiated by ceric ion and grafted by the coating material, and the new absorption band of carbonyl bond in acrylic monomer

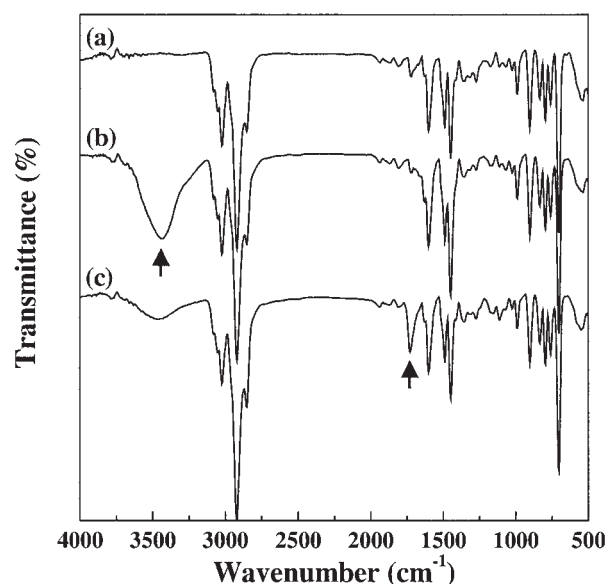


Figure 4 FTIR spectra of the seed particles (a), hydroxyl functionalized- (b), and surface-modified polymeric microspheres (with BMA) (c).

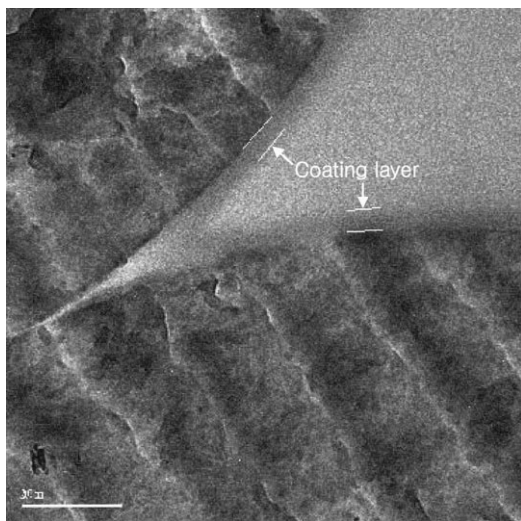


Figure 5 FE-TEM photograph of the PMMA-grafted polymeric microspheres.

(MMA, BMA) was detected. In addition, uniform coating layer was confirmed in the FE-TEM image of surface-modified polymeric microspheres (Fig. 5). From the results, we conclude that acrylic monomers were uniformly coated on the surface of polymeric microspheres sustaining their monodispersity and morphology.

Thermal analysis of surface modified polymeric microspheres

In Figure 6(a), T_g of PS seed particles is detected around 108°C; however, only an exothermal peak appeared in a range of 150–160°C, and no T_g was detected with respect to the hydroxyl-functionalized [Fig. 6(b)] and the surface-modified [Fig. 6(c)] polymeric microspheres when BMA was used as a coating material. Similar result was obtained in case of MMA surface coating. The appearance of the exothermal peak should be explained by a reaction of residual double bond in the polydivinylbenzene. Ma and co-workers¹⁹ proposed that when high content of DVB was homo-polymerized or copolymerized with other monomers, some second double bonds should be kept free of polymerization in the formed polymers and no T_g of polymer was shown.

The surface modification of microspheres by using the difference of T_g was difficult to confirm because of high DVB content; therefore, thermal stability of microspheres was examined by using TGA. Figure 7 and Table III show the TG curves and the thermal decomposition temperature (T_d) of seed, hydroxyl-functionalized- and surface-modified polymeric microspheres, respectively. The hydroxyl-functionalized and surface-modified microspheres have higher T_d and the residue than these of

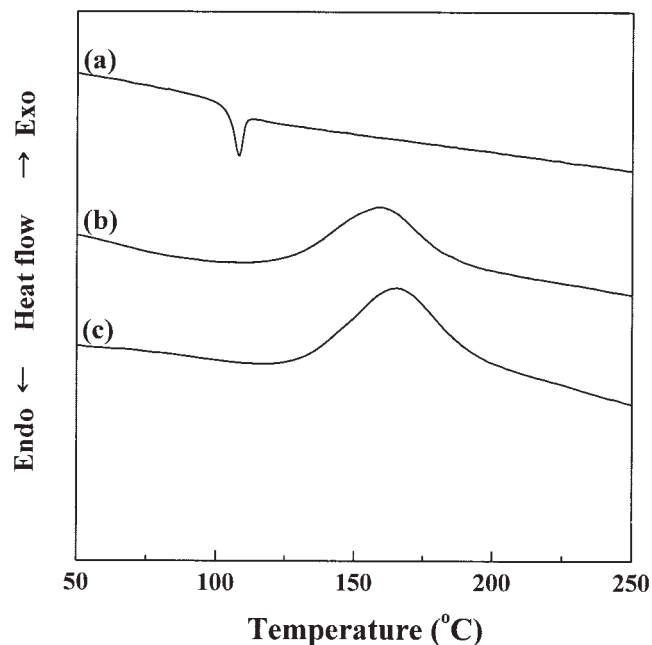


Figure 6 DSC curves of the seed particles (a), hydroxyl functionalized- (b), and BMA-coated polymeric microsphere (c), with 60% of DVB content in 2nd monomer.

the seed particles due to the high crosslinking structure by DVB in the microspheres. Although the residue of the hydroxyl functionalized and surface-modified microspheres are almost the same, interestingly, the hydroxyl functionalized and BMA-

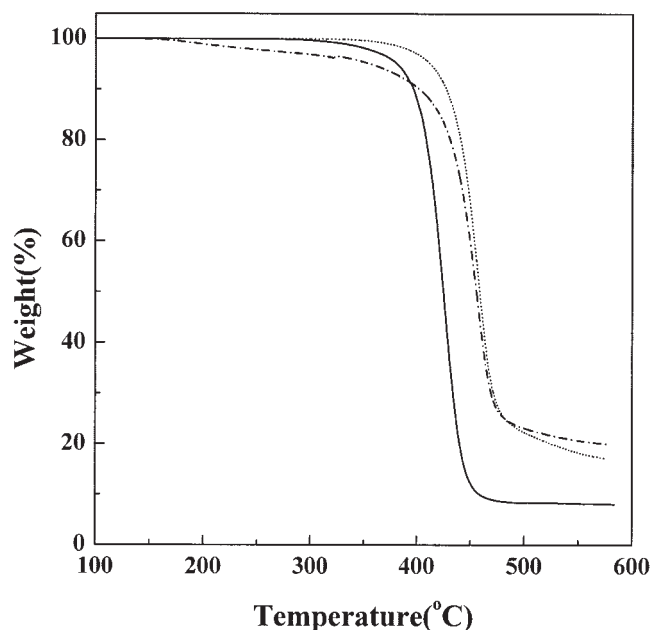


Figure 7 TG curves of the seed (solid line), hydroxyl functionalized (dotted line) and surface-modified polymeric microspheres (dash dotted line) with BMA.

TABLE III
Thermal Stability of Seed, Hydroxyl-Functionalized-, and Surface-Modified Polymeric Microspheres^a

Produced particles	Coating materials	T_d^b (°C)	Residual quantity (%)
Seed particles	—	422.6	8.08
OH-functionalized microspheres	—	461.1	17.17
Surface-modified microsphere	MMA	456.8	21.05
Surface-modified microsphere	BMA	454.3	20.91

^a 45°C, 4 h, 250 rpm.

^b Thermal decomposition temperature.

coated microspheres firstly decomposed around 400°C and 150°C, respectively. It is expected that the surface-coated materials, which have lower thermal stability than that of DVB, caused this phenomenon.

Higher content of DVB in polymeric microspheres resulted in no endothermic peak (T_g) in DSC measurement; therefore, the DVB content was controlled in the seeded polymerization to confirm the T_g . Figure 8 shows the DSC curves of polymeric microspheres containing hydroxyl functional groups and PMMA coated on the surface. When the content of DVB was decreased to 10% based on the second monomer weight, T_g of hydroxyl-functionalized microspheres emerged at 132°C, which is higher than that of the seed particles (108°C), and continuously appeared even after the MMA grafting. Also an endothermic peak newly appeared at 111°C after the graft polymerization, which means MMA was grafted on the surface of micro-

spheres. To conclude, the surface modification of monodisperse-crosslinked polymeric microspheres could be performed by initiating the hydroxyl group on the surface, and it could be applied in industrial fields for providing additional property in microspheres usefully.

CONCLUSIONS

The surface modification of monodisperse-crosslinked polymeric microspheres was carried out by using hydroxyl functional groups and grafting acrylic monomers on the surface of microspheres. VAc was incorporated as the second monomer in seeded polymerization, and transformed to hydroxyl groups by the saponification method. In DSC measurement, only an exothermic peak appeared because of high content of DVB. The surface modification of microspheres was confirmed by TEM and TA analysis. Moreover, when low content of DVB was used in microspheres, T_g of hydroxyl-functionalized- and surface-modified polymeric microspheres emerged in DSC measurement. From the results, it would be concluded that the surface modification of monodisperse-crosslinked polymeric microspheres was achieved successfully. By using this technique, additional property could be provided efficiently to the monodisperse-crosslinked polymeric microspheres maintaining their own property.

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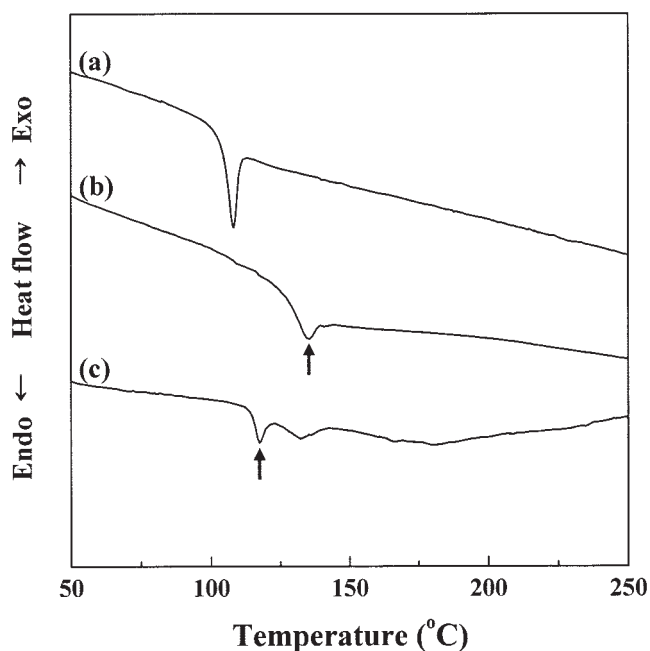


Figure 8 DSC curves of the seed particles (a), hydroxyl functionalized (b), and MMA coated (c) polymeric microspheres with 10% of DVB content in the second monomer.

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