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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 chloromethylstyrene 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, $M_w = 1.0 \times 10^3$ gmol^{-1}, Hyosung BASF), poly(vinylpyrrolidone) (PVP K-30, $M_w = 4.0 \times 10^4$ gmol^{-1}, Aldrich Chemical Co.), 1-chlorododecane (CD, TCI), and 2-methoxyethanol (Kanto Chemical Co.) were used as received. Poly(vinylalcohol) (PVA, $M_w = 8.8 \times 10^4$–9.2×10^4 gmol^{-1}, 87–89% hydrolyzed) was kindly supplied by Kuraray Co. The inhibitors in 2-hydroxyethyl methacrylate (HEMA, Aldrich), St (Junsei Chemical Co.), *n*-butylmethacrylate (BMA, Junsei), GMA (Junsei), and ethylene glycol dimethacrylate (EGDMA, Junsei) were removed through a removing column (Aldrich). 2,2-Azobis(isobutyronitrile) (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-meyhoxyethanol, 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 sonification 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, EGDMA) 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 stabilized 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 N_2, 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 RuO_4 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)

Ingredient	Weight (g)
Styrene	1.00
Urethane acrylate	0 or 0.03
Poly(vinylpyrrolidone) K-30	0.18
Aerosol Ot[a]	0.04
2,2-Azobis(isobutyronitrile)	0.01
2-Methoxyethanol	4.39
Ethanol	4.39

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

and the contact angle was measured. The copolymer film was prepared as follows. BMA and GMA were copolymerized in xylene with AIBN initiator. The copolymerization was carried out in a four-necked glass reactor equipped with a mechanical stirrer, a reflux condenser, and a nitrogen inlet system. The mixture of BMA, GMA, 1 wt% of AIBN, and xylene was mixed in N_2 for 1 h. Then, the temperature was raised to 55 °C, after which the polymerization was carried out for another 12 h. The solid content was fixed at 10 wt% of the total amount of reactants with varying GMA content. The conversion was reached at 93%, which was measured from gas chromatography. The xylene solution, which contained poly(BMA-*co*-GMA), was poured into well-polished glass plates and dried at 70°C for 48 h in vacuo, and the contact angles of films against water and methylene iodide were measured using a goniometer (Erma contact angle meter, Model G-1) at room temperature. Ten individuals were measured and the average was taken. The surface tension of each copolymer film was calculated from the harmonic mean equation [25].

The presence of the glycidyl ether group was confirmed from Fourier transform (FT) IR spectra (Nicolet, Mahgna IR-550). From the relative intensity of the peaks obtained from both copolymer film and composite particles, the concentration of the functional group was calculated. These values were compared with the values obtained from the HCl–dioxane back titration method. The purified particles were redispersed into dry dioxane, after which 0.1 mol/l HCl solution in absolute dioxane was added and the particles were left to react at room temperature for 3 h. The unreacted fraction of acid was then determined with a 0.1 mol/l methanolic solution of KOH.

Results and discussion

PS seed particles and two-staged swelling

The production of micron-sized polymer particles has usually been achieved by employing two-staged swelling and consecutive polymerization [14–19]. One of the important characteristics of this process is that once the seed particles were monodisperse, their monodispersity was maintained throughout the process. In our recent studies [26, 27], we also succeeded in producing monodisperse large PS particles by two-stage monomer swelling and polymerization. It was found that the seed cross-linking was one of the decisive factors to govern the morphology of the final particles in the seeded polymerization. On the basis of this result, here in this study, we try to elucidate the particle morphology and functionality in the seeded polymerization that utilizes linear/cross-linked PS seed particles and functional monomer.

The PS seed particles were produced by conventional dispersion polymerization. In cross-linking the PS seed particles, UA was incorporated to treat the surface characteristics of the primary particles during the stage of particle growth [18–20]. A SEM photograph of the PS seed particles is shown in Fig. 1a. As shown, all the particles produced were highly monodisperse. The characteristics of the particles are summarized in Table 2. The degree of cross-linking for the UA-cross-linked PS seed particles was determined by fitting the transport rate of monomers from the medium to the seed phase during the two-stage monomer swelling procedure [26].

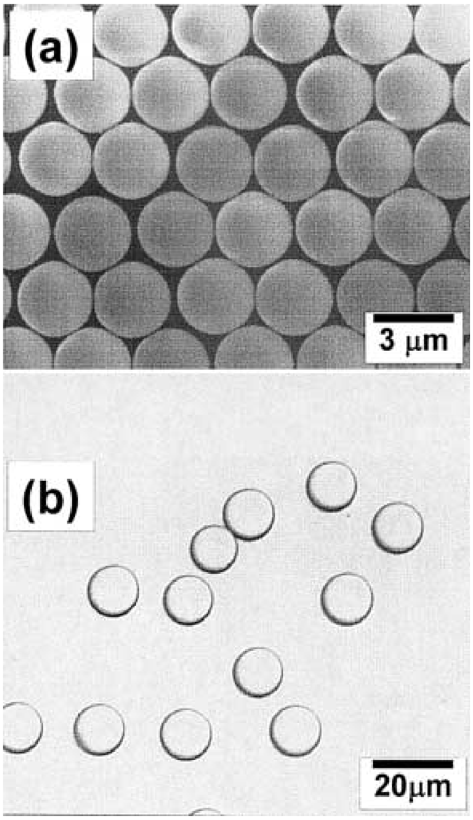

Fig. 1 **a** Scanning electron micrographs of polystyrene (*PS*) seed particle and **b** optical microscopic image of monomer swollen PS0 seed particles

Table 2 The characteristics of linear and cross-linked polystyrene (*PS*) particle

Symbol[a]	D_n (μm)	Particle size distribution, D_w/D_n	M_w (gmol^{-1})	Molecular weight distribution, M_w/M_n	N (molm^{-3})[b]
PS0	3.04	1.01	5.3×10^4	2.69	–
PS3	2.85	1.01	–	–	87.1

[a] PSα; α corresponds to the concentration of urethane acrylate (wt%, based on total styrene monomer weight)

[b] Effective number of chains in the cross-linked network [26]

OM photographs of the PS0 particles swollen with the monomer mixture are shown in Fig. 1b. At a given swelling condition, all the PS seed particles maintained their spherical shape and uniformity in size. In the monomer swelling of the cross-linked PS seed particles more than 100 times against the seed weight, a number of small droplets of the monomer emulsions existed in the medium even after 24 h swelling time. This was because the PS seed particles cross-linked with 3 wt% of UA reached its equilibrium swelling state before the full diffusion of the second monomer emulsions into the seed particle [26]. Therefore, in this study, the swelling ratio of the second monomers to the seed particles was fixed at 100-fold by weight.

Particle morphology after seeded polymerization

OM and SEM images of composite particles are shown in Figs. 2 and 3, respectively. All the particles displayed uniformity in size. The characteristics of each particle under the experimental conditions given are listed in Table 3.

From the OM images of the particles, some interesting morphological features were found. In the case of low GMA content, there existed several high contrast domains inside the particle (Fig. 2a, b); however, when the GMA content increased, the domains disappeared (Fig. 2c, d). A similar trend can be observed in the SEM images in Fig. 3. The particles of low GMA content displayed rough and bumpy surfaces (Fig. 3a, b), whereas particles with high contents of GMA did not (Fig. 3c, d). TEM photographs of ultrathin cross-sections of PS0–10 and PS0–50 particles are shown in Fig. 4. The particles with low GMA content (Fig. 4a) displayed some dark and white regions. This was believed to be the phase separation between the PS seed polymer and the second polymeric phase; however, this phase separation vanished at high GMA content (Fig. 4b).

In the seeded polymerization, the interfacial tension between polymeric constituents has been reported to be one of the decisive factors to determine the final particle morphology [28, 29]. Thus, if the interfacial tension between the polymeric phase is determined exactly, we can predict the morphological change more precisely. However, the change in interfacial tension between two polymerizing bulk states during seeded dispersion polymerization could not easily be measured directly because the interfacial tension was largely dependent upon the conversion of second polymer phase. Moreover, the interfacial tension between two polymer phases is also changed by their molecular weight. On the other hand, Chen et al. [30, 31] predicted the particle morphology by measuring the change in surface tension of PS and poly(methyl methacrylate) bulk phase in seeded emul-

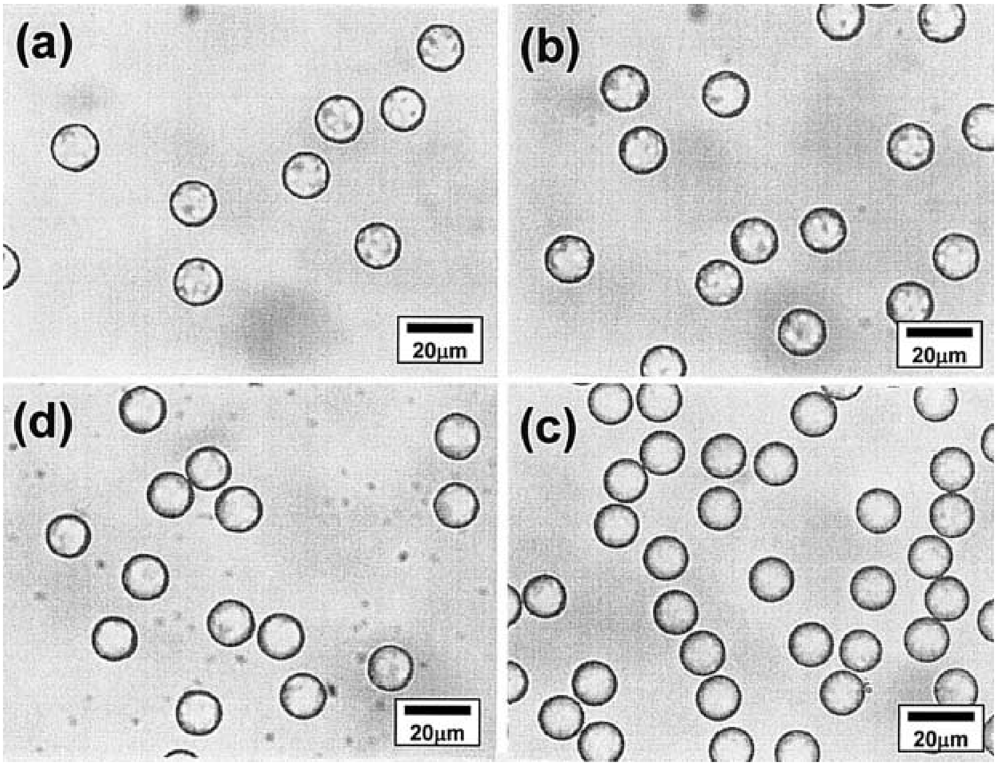

Fig. 2 Optical microscopic images of composite particles with different contents of glycidyl methacrylate (*GMA*): **a** PS0-0, **b** PS0-10, **c** PS0-30, **d** PS0-50

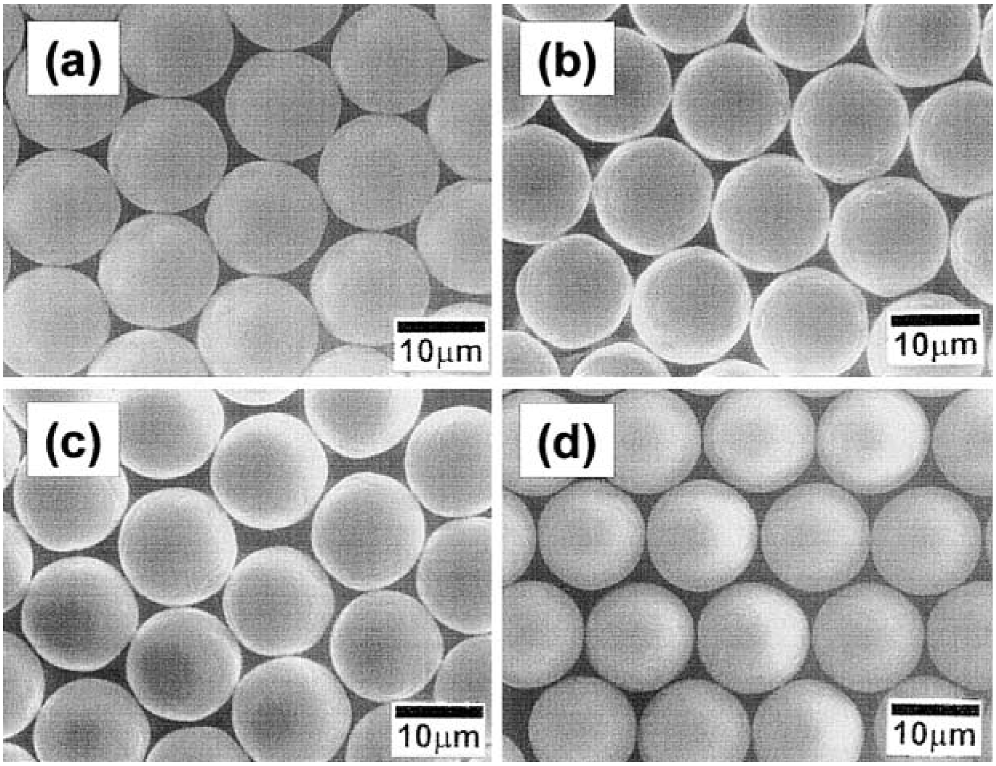

Fig. 3 Scanning electron micrograph of composite particles with different scontent of GMA: **a** PS0-0, **b** PS0-10, **c** PS0-30, **d** PS0-50

Table 3 Characteristics of the composite particles produced by seeded polymerization. 70 °C; 10 h; 4% solid content, The concentration of ethylene glycol dimethacrylate in the second monomer mixture was fixed at 10 wt% of the total monomer weight

Symbol[a]	$D_n(\mu m)$	Particle size distribution, D_w/D_n	Remarks
PS0-0	13.4	1.01	Heterophase
PS0-10	13.5	1.01	Heterophase
PS0-30	13.4	1.01	Heterophase
PS0-50	13.4	1.01	Homophase
PS3-30	13.2	1.01	Engulfing

[a] PSα-β: α corresponds to the concentration of urethane acrylate in the seed particles and β corresponds to the concentration of glycidyl methacrylate in the seeded polymerization (wt%, based on total monomer weight)

sion polymerization. They found that the surface polarity of the polymer particle plays a key role in deciding the particle morphology in the seeded emulsion polymerization. Most of all, they pointed out that the kind of initiator and surfactant had a significant effect on the final particle morphology because these two factors influenced the surface polarity of each polymeric surface, resulting in the change in surface tension. It goes without saying that the same explanation cannot be applied in our seeded polymerization because the effects of initiator and surfactant on the surface polarity of the second polymeric phase were negligible. However, from the fact that the GMA content was the only variable in

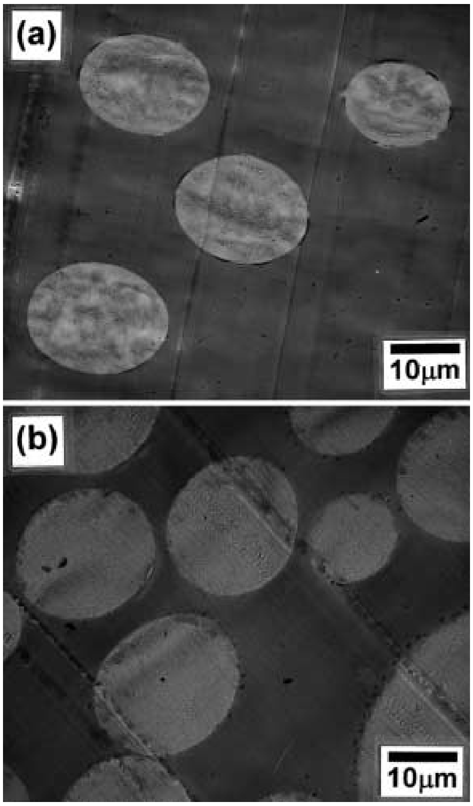

Fig. 4 Transmission electron micrographs of the composite particles: **a** PS0-10, **b** PS0-50

our seeded polymerization, it is obvious that the surface tension of the second polymeric phase, poly(BMA-*co*-GMA), changed with the GMA content, resulting in morphological change. To confirm this, the surface tension of poly(BMA-*co*-GMA) was investigated by varying the concentration of GMA. The surface tensions of PS, PBMA, and each copolymer are shown in Fig. 5 as a function of the GMA content. In the absence of GMA (PBMA homopolymer), there is a large difference in the surface tension between PBMA and PS. This indicates that PS is more bulk-hydrophobic than PBMA. When GMA was copolymerized, the surface tension of the copolymer increased with the content of GMA and approached to that of PS. This implies that the bulk hydrophobicity of poly(BMA-*co*-GMA) was enhanced at high GMA content. Therefore, the tendency of phase separation of the polymer phases in the composite particles during the seeded polymerization was expected to decrease.

Effect of seed cross-linking on particle morphology

When the seed was cross-linked, the final particles showed some peculiar morphology. The OM and SEM images of the resultant particles are shown in Fig. 6. The characteristics of the particles produced are also summarized in Table 3. The particles polymerized exhibited high monodispersity and were in a similar size range to the case where the linear PS seed was used (Fig. 6a), while the SEM image showed some different aspects (Fig. 6b). Unlike other composite particles produced by using a linear PS seed, a clearly separated phase emerged upon the particle surface, exhibiting the engulfing morphology. Since the volume fraction of the second polymeric phase is much higher than that of the PS domain, the domains projected on the particle surfaces are believed to be the cross-linked seed domain separated from the second polymeric phase. These projections of the cross-linked seed on the particle surfaces have been considered theoretically in another study [27]. The elastic force of the cross-linked PS seed network generated at the polymerization temperature made the PS network phase-separate with a single domain in the second polymer phase. From these results, it could be found that the content of GMA and the cross-linking of the seed particle are two main factors that determine the morphology of the final particles in the seeded polymerization.

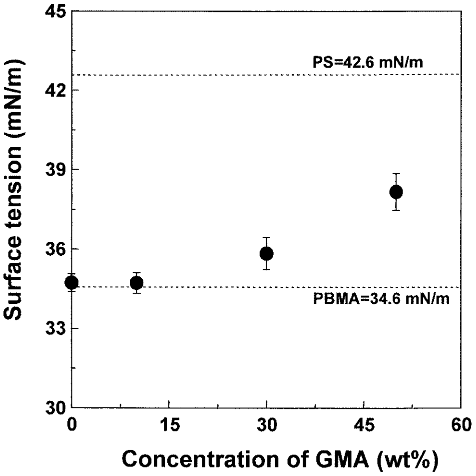

Fig. 5 Surface tension of the copolymer of *n*-butylmethacrylate (*BMA*) and GMA [poly(BMA-*co*-GMA)] with different contents of GMA. The surface tensions of PS and PBMA were from Ref. [25]

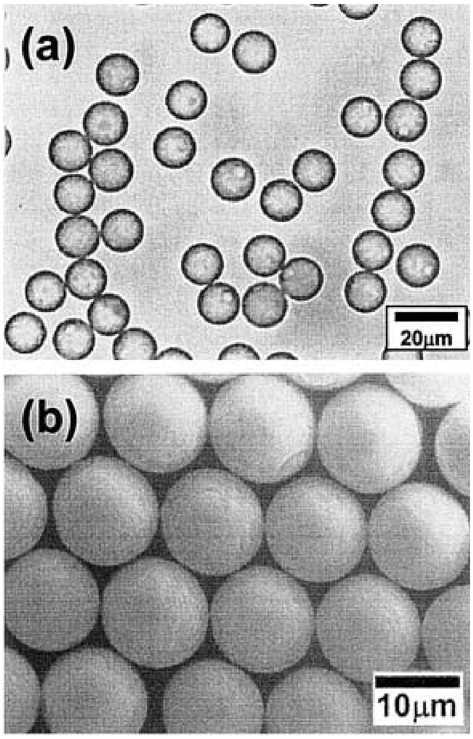

Fig. 6 a Optical microscopic image and **b** scanning electron micrograph of PS3-30

Characterization of the glycidyl ether group

During the polymerization process, the glycidyl ether group in GMA may be opened by the cross-linking side reaction or through the hydrolysis. Thus, quantification of the residual glycidyl ether groups is critical to the assessment of our synthesis procedure. From the characteristic peaks at 991 and 904 cm^{-1} of the FT-IR spectra, we could confirm the presence of glycidyl ether groups in the particles. Moreover, as the amount of GMA increased, the intensity of the peak increased.

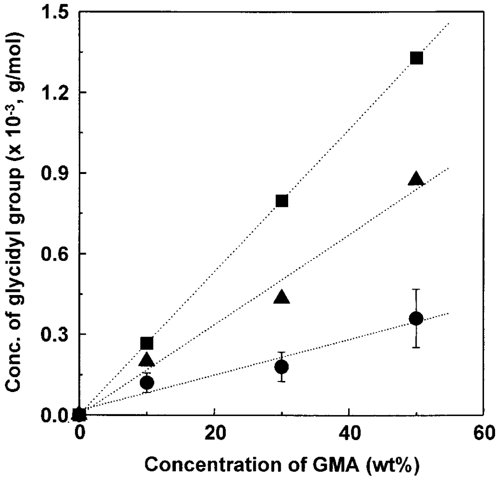

Fig. 7 Amount of glycidyl ether in the composite particles with the content of GMA: calculated (-■-), measured from Fourier transform IR spectroscopy (-▲-), and from titration (-●-)

The content of the residual glycidyl ether groups was estimated through both FT-IR spectra and the HCl–dioxane back titration method. The values obtained are compared in Fig. 7. As can be seen, the concentration of the glycidyl ether groups in the composite particles measured from FT-IR spectroscopy was lower than that in the the copolymer film. As far as the values obtained from the FT-IR spectra were concerned, about 55–60% of glycidyl ether groups remained in the final particles. This indicates that the ring-opening side reaction of the glycidyl ether groups occurred during the seeded polymerization in aqueous media. Interestingly, the values obtained from the HCl–dioxane back titration was much lower than those obtained from FT-IR spectroscopy of the copolymer films and composite particles. In this experiment, all the composite particles were cross-linked with EGDMA for dimensional stability. Thus, it can be expected that the reaction of the glycidyl ether groups with HCl would occur near the particle surfaces because the degree of swelling of the composite particle was largely confined in the dioxane medium. Even concerning the possible side reactions, i.e. hydrolysis or cross-linking of glycidyl ether groups, it is worth noting that 20–30% of the glycidyl ether groups was detected, which is expected to be sufficient for further chemical modification.

Conclusion

Functional composite particles containing the glycidyl ether groups were produced through a two-stage swelling method and consecutive polymerization. The particles produced were highly monodisperse and in the size range of 13–14μm. It was found that both the composition of the monomer mixture and the cross-linking of seed particles largely influenced the final particle morphology. As the content of GMA increased, the surface tension of poly(BMA-*co*-GMA) approached that of PS, which led to reduced phase separation in the final composite particles. When the seed was cross-linked, the final particle displayed engulfing morphology, which means the complete phase separation between the seed particle and the second polymeric phase. From the HCl–dioxane back titration, it was found that about 20–30% of the initial glycidyl ether group remained on the final particles. By utilizing these glycidyl ether groups, we expect that various chemical modifications, such as hydrolysis and ammonolysis, will be possible in further studies.

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Reference

1. Robbins JL, Hill GA, Carle BN, Carlquist JH, Marcus S (1962) Proc Soc Exp Biol Med 109:321
2. Singer JM (1961) Am J Med 31:766
3. Margel S, Offarim M (1982) Anal Biochem 128:342
4. Grag GR (1980) Anal Chem 52:9R
5. Pittner F, Miron T, Pitter G, Wilchek M (1980) J Solid Phase Biochem 5:147
6. Pittner F, Miron T, Pitter G, Wilchek M (1980) J Solid Phase Biochem 5:167
7. Tokes ZA, Rogers KE, Rembaum A (1982) Proc Natl Acad Sci USA 79:2026
8. Margel S, Nov E, Fisher I (1991) J Polym Sci Part A Polym Chem 29:347
9. Yang W, Hu J, Tao Z, Li L, Wang C, Fu S (1999) Colloid Polym Sci 277:446
10. Lee W, Chen C (1999) J Polym Sci Part A Polym Chem 37:1457
11. Sáenz JM, Asua JM (1996) J Polym Sci Part A Polym Chem 34:1977
12. Sáenz JM, Asua JM (1998) Macromolecules 31:5215
13. Sáenz JM, Asua JM (1999) Colloids Surf 153:61
14. Ugelstad J, Berge A, Ellingsen T, Schmid R, Nilsen TN, Mork PC, Stenstad P, Hornes E, Olsvik O (1992) Prog Polym Sci 17:87
15. Ugelstad J (1978) Makromol Chem 179:815
16. Ugelstad J, Kaggerud KH, Hansen FK, Berge A (1979) Makromol Chem 180:737
17. Ugelstad J, Mork PC, Kaggerud KH, Ellingsen T, Berge A (1980) Adv Colloid Interface Sci 13:101
18. Vanderhoff JW, El-Aasser MS, Micale FJ, Sudol ED, Tseng CM, Silwanowicz A, Kornfeld DM (1984) J Dispersion Sci Technol 5:231
19. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
20. Kim JW, Suh KD (1998) Colloid Polym Sci 276:870

21. Kim JW, Suh KD (1999) Colloid Polym Sci 277:210
22. Ryu JH, Kim JW, Suh KD (1999) Colloid Polym Sci 277:1205
23. David DJ, Staley HB (1969) (eds) Analytical chemistry polyurethane high polymer series, XVI, part III. Wiley-Interscience, New York
24. Okubo M, Yamashita T, Shimizu T (1997) Colloid Polym Sci 275:288
25. Wu S (1982) Polymer interface and adhesion. Dekker, New York
26. Kim JW, Suh KD (2000) Polymer 41:6181
27. Lee DH, Kim JW, Suh KD Polymer (submitted)
28. Sundberg DC, Casassa AP, Pantazopoulos J, Muscato MR (1990) J Appl Polym Sci 41:1425
29. Chen YC, Dimonie V, El-Aasser MS (1991) Macromolecules 24:3779
30. Chen YC, Dimonie V, El-Aasser MS (1991) J Appl Polym Sci 42:1049
31. Chen YC, Dimonie V, El-Aasser MS (1992) J Appl Polym Sci 45:487