Monodisperse Micron-sized Polystyrene Particles by Seeded Polymerization Using Reactive Macrosurfactants

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Abstract−Monodisperse micron-sized polystyrene particles could be prepared through a two-staged seeded swelling and polymerization method using reactive surfactants. The seed was obtained by emulsifier-free emulsion polymerization. To prepare conventional surfactant-free monomer emulsion droplet in swelling process, a tri-block diol diacrylate (t-BDDA), which is poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) tri-block copolymer containing two chain ends capped with acryloyl chloride, was employed as a reactive surfactant instead of conventional surfactants. Thermodynamic consideration of the effect of monomer droplet size and interfacial tension on the swelling process ensured that two-staged monomer swelling could be effectively performed by using t-BDDA as a surface-active macromonomer. From the surface tension measurement and optical microscope observation, it was found that the t-BDDA had a favorable surface activity when the monomer emulsion was prepared under its cloud point. From the X-ray photoelectron spectroscopy, it was found that most of the t-BDDA resided on the final particle surfaces.

Key words: Monodisperse Micron-Sized Polystyrene Particles, Seeded Polymerization, tri-Block Diol Diacrylate (t-BDDA), Swelling Process, Surface-Active Macromonomer

INTRODUCTION

Polymeric microspheres in the size range of about 0.5 μm to 100 μm or larger are useful as solid supports for a wide range of biotechnology applications including biochromatography, solid phase synthesis, solid phase extraction, cell separation and other related applications [Ugelstad et al., 1992; Asua, 1997; El-Aasser and Fitch, 1987]. Especially, the particles with well-defined surfaces can be used directly in protein immobilization, medical diagnostics, and many biomedical processes. Considering the material efficiency, high monodispersity of the particles is emphasized and quite necessary for such applications.

In general, dispersion polymerization technique has been widely used to produce monodisperse micron-sized polymer particles directly in the size range of 0.5-20 μm. However, though direct dispersion polymerization has a great advantage to produce highly monodisperse micron-sized polymer particles, it has a restricted application area due to the limitation of monomer types applicable to this technique. Therefore, step-wise seeded polymerization containing monomer-swelling process has been widely studied for the production of various polymer composite particles to overcome this disadvantage, and several methods have been proposed. Vanderhoff et al. developed a successive seeded polymerization method in a gravity-free condition [Vanderhoff et al., 1984, 1986]. Similarly, Ugelstad et al. invented a useful two-staged swelling method for

the production of various monodisperse micron-sized polymer particles [Ugelstad et al., 1979, 1980, 1992]. This method is characterized by utilizing an oligomer having extremely low solubility in water as an effective monomer-swelling agent. In the methods mentioned above, however, stabilizers or surfactants are used in preparing the monomer emulsions, which has the shortcoming that the surfactant may affect the surface properties of the final particles [Okubo et al., 1991; Okubo and Nakagawa, 1992]. When a high purity of particles is required, e.g., protein immobilization and biomedical applications, it may become an important issue.

In this study, we investigate the role of tri-block diol diacrylate (t-BDDA) as a novel surface-active macromonomer in the seeded polymerization. The t-BDDA is the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) [PEO-PPO-PEO] copolymer of which the diol end groups are capped with acryloyl chloride. Since the t-BDDA has surface activity as well as polymerizable vinyl end groups, we expect that the particles prepared by using t-BDDA reactive surfactant can be directly utilized in biomedical applications. Not only thermodynamic equilibrium of the swollen particle with monomer but the effect of t-BDDA on the swelling process was investigated.

THERMODYNAMIC CONSIDERATIONS

Partial molar free energy, $\Delta\overline{G}$ of monomer in the linear polymer seeds during the swelling is composed of the following two contributions:

$$\Delta\overline{G} = \Delta\overline{G}_m + \Delta\overline{G}_t \tag{1}$$

Partial molar free energy change by the absorption of the mono-

mer droplets is generally given as follows:

$$\Delta\overline{G} = RT\left[\ln\phi_m + \left(1 - \frac{1}{j_p}\right)\phi_p + \phi_p^2\chi_{mp} + \frac{2\overline{V}_m\gamma}{rRT}\right] \quad (2)$$

From Eq. (2), Ugelstad et al. proposed a thermodynamic equation for the swelling of the particles consisting of polymer, swelling agent and monomer thereof [Ugelstad et al., 1979, 1980, 1992]. The partial molar free energy was given as follows:

$$\Delta\overline{G} = RT\left[\ln\phi_m + \left(1 - \frac{1}{j_s}\right)\phi_s + \left(1 - \frac{1}{j_p}\right)\phi_p + \phi_s^2\chi_{ms} + \phi_p^2\chi_{mp}\right.$$
$$\left. + \phi_s\phi_p\left(\chi_{ms} + \chi_{mp} - \frac{\chi_{sp}}{j_s}\right) + \frac{2\overline{V}_m\gamma}{rRT}\right] \quad (3)$$

When the seed polymer particles have a very large molecular weight, $1/j_p$ can be set equal to zero in Eq. (3). If the monomer droplets are smaller than the seed particles, r can be represented as follows:

$$\frac{1}{r} = \frac{1}{r_s} - \frac{1}{r_m}; \quad r_s = r_0\left[\frac{V_m + V_s + V_p}{V_p}\right]^{1/3} \quad (4)$$

Consequently, the partial molar free energy, $\Delta\overline{G}$, of the monomer in the polymer particles during the swelling gives

$$\Delta\overline{G} = RT\left[\ln\phi_m + \left(1 - \frac{1}{j_s}\right)\phi_s + \phi_p + \phi_s^2\chi_{ms} + \phi_p^2\chi_{mp}\right.$$
$$\left. + \phi_s\phi_p\left(\chi_{ms} + \chi_{mp} - \frac{\chi_{sp}}{j_s}\right) + \frac{2\overline{V}_m\gamma}{RT}\left(\frac{1}{r_s} - \frac{1}{r_m}\right)\right] \quad (5)$$

At equilibrium states, therefore, the following thermodynamic equation can be obtained:

$$\ln\phi_m + \left(1 - \frac{1}{j_s}\right)\phi_s + \phi_p + \phi_s^2\chi_{ms} + \phi_p^2\chi_{mp}$$
$$+ \phi_s\phi_p\left(\chi_{ms} + \chi_{mp} - \frac{\chi_{sp}}{j_s}\right) + \frac{2\overline{V}_m\gamma}{RT}\left(\frac{1}{r_s} - \frac{1}{r_m}\right) = 0 \quad (6)$$

Equilibrium monomer swelling is achieved from the calculation of Eq. (5) and (6).

EXPERIMENTAL

1. Materials

Styrene (Kanto Chemical Co.), ammonium persulfate (APS, Yakuri Pure Chemical Co.), 1-chlorododecane (CD, TCI Co.), triethylamine (TEA, Aldrich Chemical Co.) and acryloyl chloride (AC, Acros Organics Co.) were all reagent grade. PEO-PPO-PEO triblock copolymers (M_w=1,100, 2,000, 2,950 g·mol⁻¹, Aldrich) were vacuum distilled for 48 h before use. Poly(vinyl alcohol) (PVA, M_w= 8.8×10^4~9.2×10^4 g·mol⁻¹, 87-89% hydrolyzed) was kindly supplied by Kuraray Co. Benzoyl peroxide (BPO, Junsei Chemicals) was recrystallized from methanol before use. The inhibitor in styrene was removed through a removing column (Aldrich).

2. Synthesis of tri-Block Diol Diacrylate (t-BDDA) [Kim et al., 2001]

The t-BDDA was synthesized by the reaction of PEO-PPO-PEO tri-block copolymer with AC stoichiometrically. All the block copolymers have the same PEO/PPO composition ratio. At first, 1 mole of PEO-PPO-PEO tri-block copolymers with different molecular weights, M_w=1,000, 2,000, 2,950, dissolved in tetrahydrofuran was
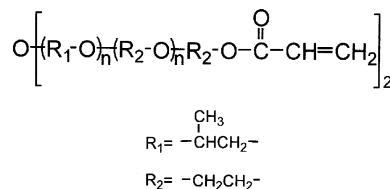
Scheme 1. The molecular structure of tri-block diol diacrylate, t-BDDA.

poured into a 500 ml round-bottomed flask and cooled to 0 °C. Then, TEA (2 mole) and AC (2 mole) were added step-wise into the reactor and reacted at 50 °C for 5 h under vigorous stirring. The reaction mixture was filtered to remove the salt, triethanolamine hydrochloride, and the solvent was evaporated completely. Continuously, residual salts and unreactants were washed fully with methylene chloride/water mixture for several times. After the moisture was trapped, the solution was evaporated until a viscous liquid was recovered. The molecular structure of t-BDDA is represented in the Scheme.

3. Preparation of Polystyrene (PS) Seed Particles

PS seed particles were produced by surfactant-free emulsion polymerization in water with APS initiator. APS (0.2 g), $MgCl_2$ (0.03 g) and water (170 g) were weighted and poured into a four-necked glass reactor. Under a nitrogen atmosphere, the reactor was submerged in a thermostatted water bath and stirred with a rotation speed of 400 rpm at 80±0.1 °C. After 10 min, styrene (30 g) was added to the reactor and polymerized for 10 h. Number average diameter (Dn) and particle size distribution (PSD; Dw/Dn) of the seed particles were 1.0 μm and 1.01, respectively.

4. Two-Staged Swelling and Polymerization

Two-staged swelling and polymerization was carried out in the four-necked glass reactor equipped with a mechanical stirrer, a reflux condenser, and a nitrogen gas inlet system. First, the seed particles redispersed in 1.0% t-BDDA ethanol/water 1/5 (v/v) solution by 10 min sonication were swollen with CD emulsified by ultrasonic homogenizing in the same solution at 30 °C for 10 h. The stirring speed was fixed at 200 rpm throughout the process. After the complete disappearance of CD droplets, ethanol was removed by evaporation. Then, the mixture of styrene, t-BDDA and BPO (1 wt% against the monomer weight) was emulsified in ethanol/water 1/5 (v/v) mixture by using ultrasonic homogenization and poured into the reactor. The content of t-BDDA was varied from 1 wt% to 5 wt% against the total content of second monomers. The swelling was continued at ambient temperature for another 6 h. The swollen particles were stabilized with 5 wt% PVA aqueous solution and the PVA concentration was fixed at 1 wt% to the total content. Polymerization in the aqueous phase was inhibited by adding sodium nitrite [Okubo et al., 1996]. After deaerating with nitrogen gas, the polymerization was carried out at 80 °C for 10 h. The particles produced were washed repeatedly by decantation in water and ethanol and then dried at room temperature for 48 h *in vacuo*.

5. Particle Characterizations

The swelling procedure of the seed particles was monitored by an optical microscope (OM; Nikon Microphot Fax). The morphology of the particles produced was observed with a scanning electron microscope (SEM; JSM-6300, JEOL). In order to determine the particle diameter, at least 100 individual particles were counted

from SEM photographs and the average was taken. To investigate the phase transition temperature of t-BDDA aqueous solutions, a thermo optical analyzer (TOA; Mettler FP90) was used. The surface tension of t-BDDA aqueous solution was measured with tensiometer with varying temperature. For analyzing the composition of the particle surfaces, X-ray photoelectron spectroscopy (XPS; Kratos XSAM-800) was used. The spectra were recorded by using magnesium radiation (1253.6 eV) at a potential of 10 kV and an X-ray current of 15 mA. The pressure in the measurement chamber was ca. 8×10^{-10} Torr. Samples for XPS measurement were obtained as follows. The PVA adsorbed on the particle surface was removed by centrifugal washing several times with water/ethanol 50/50 (w/w) solution and once with distilled water. The complete removal of PVA on particle surface was confirmed from FT-IR spectroscopy. Because the carbonyl peak of PVA was very weak, the influence of the residual PVA on the XPS analysis could be neglected. Then, the particles were powdered by freeze-drying and stored *in vacuo*. The dried particles were pelletized with a hydraulic compressor (Carver, model 4040) into disk-type specimen.

RESULTS AND DISCUSSION

1. Thermodynamics of Monomer Swelling Procedure

For the production of micron-sized polymer particles, many researchers have employed the two-staged seeded polymerization method. In the monomer swelling procedure, the effect of the size of monomer droplets can be negligible if the size of monomer droplet is much larger than that of seed particles. On the other hand, when very fine monomer droplets are prepared by ultrasonic homogenization, the swelling capacity of the seed particle is greatly affected by the size of monomer droplet [Ugelstad et al., 1980]. Because t-BDDA is used in the preparation of monomer emulsions in this study,

it is also expected that the amount and characteristics of t-BDDA will play an important role in determining the size of monomer droplets. We tried to understand the effect of the size of monomer droplets containing the t-BDDA on the monomer swelling procedure in the two-staged swelling method from the thermodynamic viewpoint.

Fig. 1 shows plots of the equilibrium monomer swelling as a function of seed diameters at various diameters of the monomer droplet. From the result, it is obvious that the swelling capacity is significantly dependent on the diameter of monomer droplets. As the diameter of monomer droplets increases, the expected swelling ratio decreases drastically. In other words, relatively a large amount of monomer can be absorbed into seed polymer particles by making monomer droplets much smaller than seed particles, which maybe results from the increase in chemical potential contribution from the interfacial energy of monomer droplets [Okubo et al., 1998].

It is known that the equilibrium monomer swelling also depends on the interfacial tension between the monomer droplets and the dispersing medium. The effect of the interfacial tension on the swelling capacity of seed particles is depicted in Fig. 2. As one can see, when the interfacial tension decreases, the swelling capacity of the seed particles increases. Because the rate of Ostwald ripening is directly proportional to the solubility of the dispersed phase in the dispersion medium [Taylor, 1998], the diffusion of monomer molecules in the emulsion droplet will increase as the interfacial tension decreases. That is, the swelling capacity of seed particles is inversely proportional to the interfacial tension. In addition, because the interfacial tension and the monomer diffusion will be affected by the amount and the characteristics of t-BDDA in the monomer emulsion, the effect of t-BDDA on the swelling capacity should also be considered.

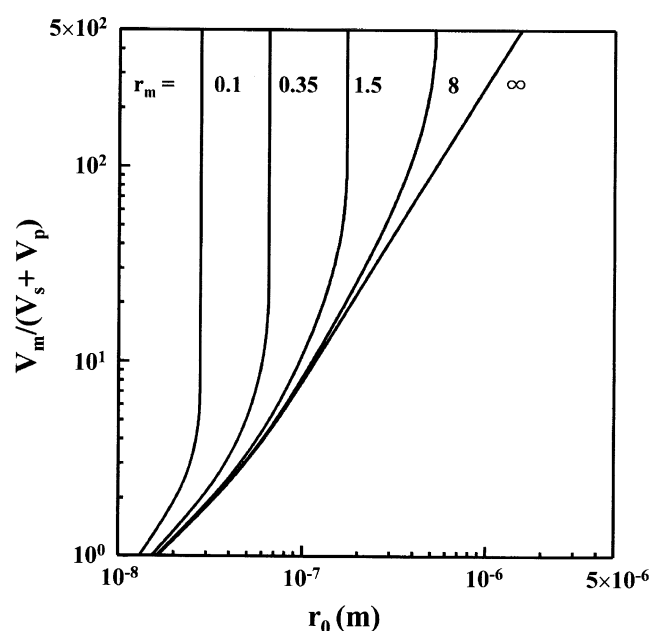Plots of partial molar free energy change versus monomer swell-

Fig. 1. Simulated monomer swelling ratio ($V_m/(V_s+V_p)$) with the seed radius (r_0) at the different radius of monomer droplet (r_m) under the conditions of $\chi_{mp}=0.5$, $\chi_{sp}=0$, $j_s=5$, $V_s=V_p=0.5$, $\overline{V}_m=10^{-4}$ m^{3}mol^{-1}, T=283 K, and $\gamma=36.37$ mNm^{-1}.

Fig. 2. Simulated monomer swelling ratio ($V_m/(V_s+V_p)$) with the seed radius (r_0) at the different interfacial tension (γ) under the conditions of $\chi_{mp}=0.5$, $\chi_{sp}=0$, $j_s=5$, $V_s=V_p=0.5$, $\overline{V}_m=10^{-4}$ m^{3}mol^{-1}, T=283 K, and $r_m=3.5 \times 10^{-7}$ m.

Fig. 3. Simulated partial molar free energy ($\Delta \overline{G}/RT$) change with the monomer swelling ratio ($V_m/(V_s+V_p)$) under the conditions of $\chi_{mp}=0.5$, $\chi_{sp}=0$, $j_s=5$, $V_s=V_p=0.5$, $\overl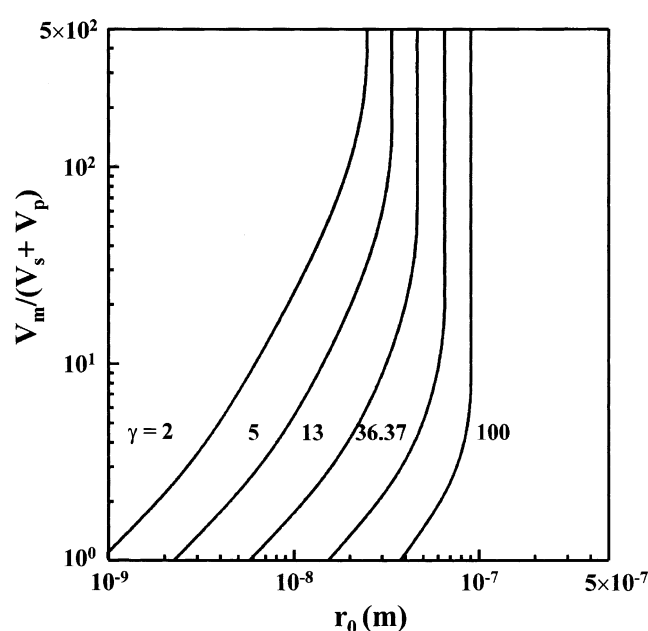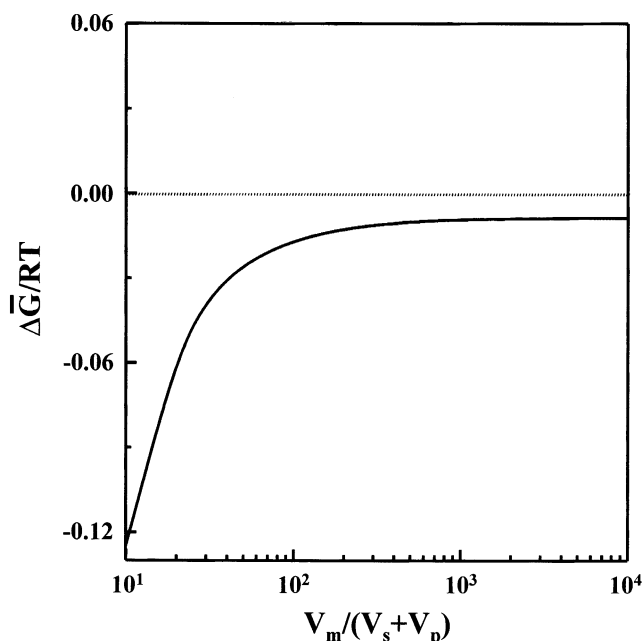ine{V}_m=10^{-4}$ m³mol⁻¹, T=283 K, and $\gamma=36.37$ mNm⁻¹, $r_m=3.5\times10^{-7}$ m, and $r_0=1.0\times 10^{-6}$ m.

ing ratio at $\gamma=36.37$ mN/m of 3 wt% t-BDDA concentration are shown in Fig. 3. As can be seen, the total partial molar free energy, $\Delta\overline{G}$, remained negatively within the volume range investigated, which means that the monomer swelling procedure can take place spontaneously. From these results, it appears that relatively accept-
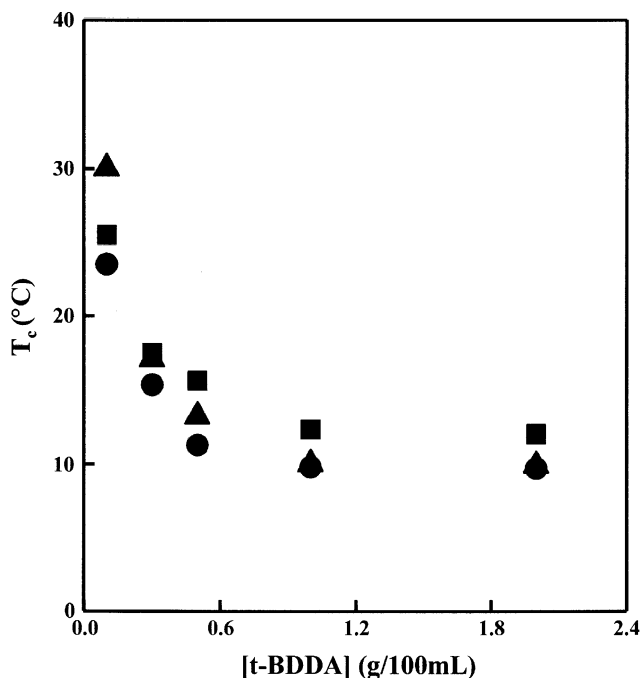
able monomer swelling could be achieved when the t-BDDA was used to prepare monomer emulsions during the two-staged swelling process in the absence of any other surfactant addition.

2. Temperature Effect on the t-BDDA-Containing Emulsions

Numerous papers reported that the PEO-PPO-PEO copolymers of molecular weight 1,000-3,000 in aqueous solutions displayed a thermally induced phase transition around 40-60 °C [Alexandridis and Hatton, 1995]. This phase transition has been reported to originate from the enhanced chain mobility, especially, of PEO blocks in water phase. As the temperature increases, more 'nonpolar' conformations of PEO block will also increase, resulting in the decrease in the water-PEO block interactions [Lindman et al., 1990; Hurter et al., 1993; Linse, 1993]. Fig. 4 presents the cloud point, T_c, versus the concentration of t-BDDA in the aqueous solution. It can be seen that T_c of t-BDDA aqueous solution locates mainly around 10-15 °C. Interestingly, the t-BDDA displayed somewhat lower phase transition range than the conventional PEO-PPO-PEO tri-block copolymers. It is because the triblock copolymers were end-capped with the hydrophobic acrylate groups; more nonpolar conformation of the chain-end would be favorable, resulting in the shrinkage of the t-BDDA molecules at a relatively low temperature. More-
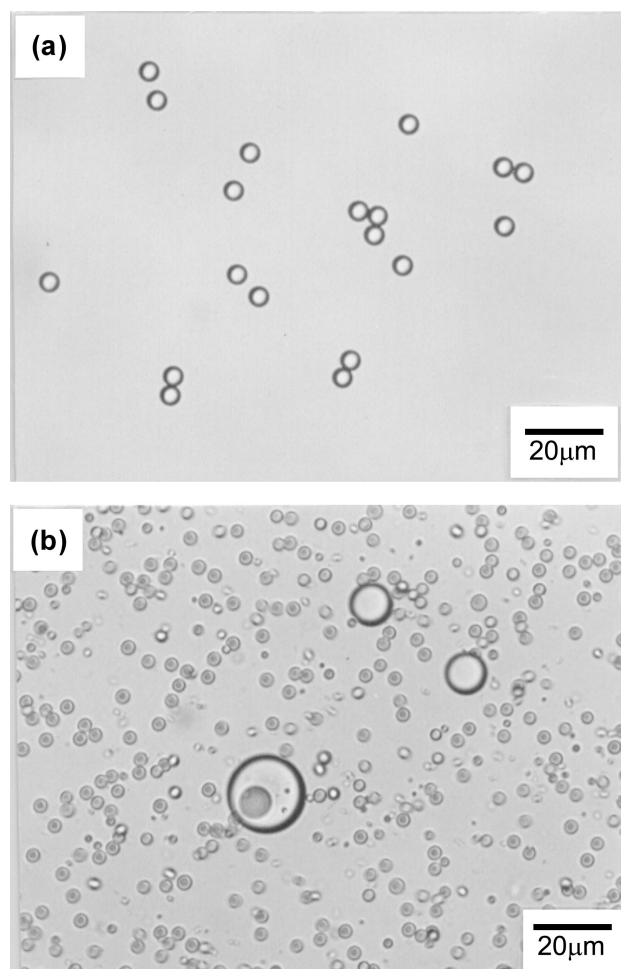

Fig. 5. OM photographs of monomer-swollen particles with different temperature during the preparation of monomer emulsion and monomer swelling process: (a) 9 °C and (b) 30 °C.

Fig. 4. Critical temperature with polymer weight percents at different molecular weight of t-BDDA: 1100 (-■-), 2000 (-●-), and 2950 (-▲-).

over, the acrylate end groups of t-BDDA may enhance this nonpolar conformation, disturbing the hydrogen bonding between PEO and water. Thus, the aggregation of t-BDDA can occur at such low temperature.
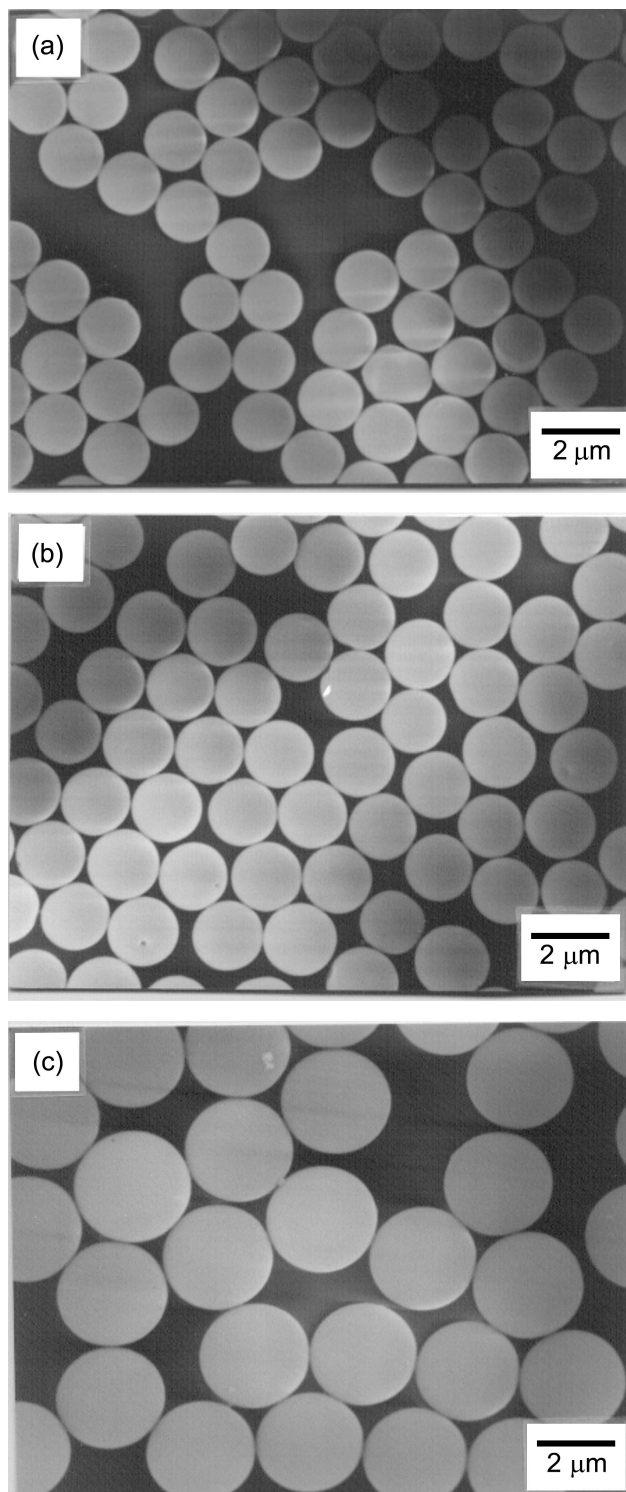
Fig. 6. SEM photographs of the polystyrene particles obtained after seeded polymerization with varying the swelling ratio: (a) P1, (b) P2, and (c) P3, respectively. All the monomer emulsions were prepared with 3 wt% of t-BDDA.

In this experiment, t-BDDA was used in preparing the monomer emulsion instead of conventional surfactants. Because the solubility of t-BDDA was largely influenced by the temperature change (Fig. 4), the size of monomer droplets, d_m, emulsified with t-BDDA was expected to be also dependent upon the temperature. To confirm this, the size of monomer droplets was measured with a size analyzer. At a temperature lower than T_c, d_m was about 200 nm. On the other hand, d_m increased to about 300 nm at temperatures higher than T_c of the t-BDDA. The effect of the size of monomer droplet on the swelling procedure is shown in Fig. 5. When the monomer emulsion was prepared under T_c and the temperature was maintained during the swelling procedure, monomer droplets almost disappeared in a few hours (Fig. 5a). The residual monomer droplets, however, remained throughout the whole swelling process when the temperature of the preparation of monomer emulsion and swelling procedure was kept over T_c (Fig. 5b). Even though the difference of d_m with temperature was about 100 nm or less, there existed a large difference in monomer swelling capacity.

3. Particle Morphologies After Seeded Polymerization

After the swelling process, the swollen particles were polymerized. The SEM photographs of the particles with the swelling ratio are shown in Fig. 6. All the particles produced displayed monodisperse size distribution, clear surface, and spherical shape. The characteristics of the particles are listed in Table 1. It can be seen in Fig. 6 that the size of the particles increased with the swelling ratio. The particle size could be controlled from 1.5 to 2.5 μm by varying the weight of second monomer. Fig. 7 shows the SEM photographs of the particles with the t-BDDA contents at the same monomer concentration. The characteristics of the particle are listed in Table 2. The resultant particles also displayed clear surface and spherical morphology. Actually, the size of the particle decreased as the amount of t-BDDA increased. Although the difference in particle size is not large (about 137 nm), the crosslinking density of P5-1000 would be higher than that of P1-1000.

The effect of t-BDDA molecular weight (M_w) on particle size distribution is shown in Fig. 8. The characteristics of the particles are also listed in Table 2. Unlike the low-M_w t-BDDA case (P3-2000), interestingly, particles with high-M_w t-BDDA (P3-2950) display bimodal size distribution. This phenomenon can be explained by the difference in occupied area per molecule of each series of t-BDDA. Alexandridis et al. disclosed that the adsorption area of PEO-PPO-PEO tri-block copolymers towards hydrophobic surface increased with the M_w of the copolymer [Alexandridis and Hatton, 1995]. Although the t-BDDA employed in our seeded polymerization has somewhat different characteristics with conventional PEO-PPO-PEO block copolymers, one possible explanation can be suggested

Table 1. Characteristics of the final particles prepared with the monomer swelling ratio[a]

Sample	PS seed (g)	Swelling ratio	Dn (μm)	PSD[b]
P1	0.75	2	1.503	1.002
P2	0.37	5	1.629	1.002
P3	0.11	10	2.562	1.023

[a]The amount of second monomer was fixed at 5 g. All of the monomer emulsions were prepared with 3 wt% of t-BDDA 1000.
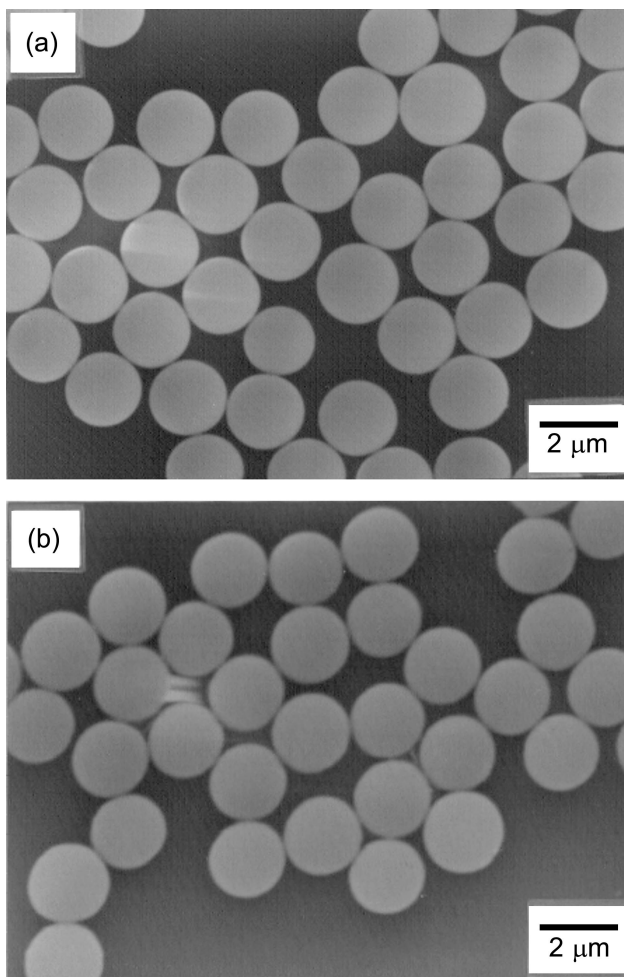[b]Particle size distribution, Dw/Dn.

Fig. 7. SEM photographs of the polystyrene particles obtained after seeded polymerization with t-BDDA contents: (a) P1.0-1000 and (b) P5.0-1000.

Table 2. Characteristics of the particles prepared by varying the content and the molecular weight of t-BDDA[a]

Sample[b]	Dn (μm)	PSD[c]	Remarks
P1-1000	1.903	1.007	Monodisperse
P5-1000	1.766	1.002	Monodisperse
P3-2000	1.645	1.001	Monodisperse
P3-2950	1.402	1.200	Bimodal

[a]The amount of PS seed and second monomer were fixed at 0.37 g and 5.0 g, respectively.
[b]Pα-β; α and β correspond to the wt% and molecular weight of t-BDDA, respectively.
[c]Particle size distribution, Dw/Dn.

to understand the resulting bimodal size distribution. When the swelling of monomer droplets stabilized with low-M_w t-BDDA (Fig. 8a) was completed before the polymerization, most of the t-BDDA was expected to locate at the interfaces between the continuous water phase and the swollen particles. This may be possible because the total surface area of swollen particle would be large enough for the t-BDDA with M_w of 2,000 to occupy. For the high-M_w t-BDDA, however, some of long-chain t-BDDA might still remain in contin-
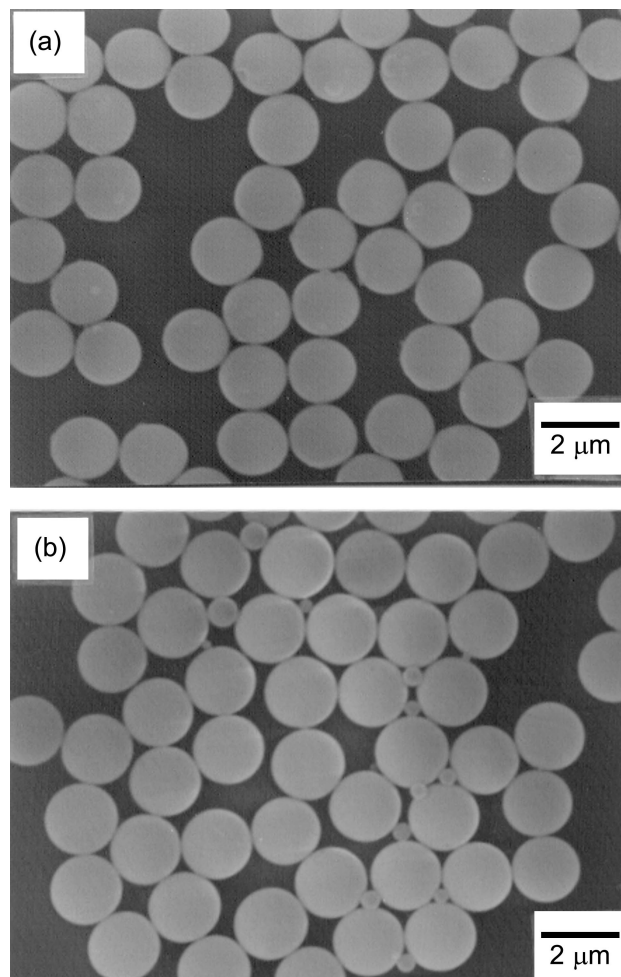
Fig. 8. SEM photographs of the polystyrene particles obtained after seeded polymerization with molecular weights of t-BDDA: (a) P3.0-2000 and (b) P3.0-2950.

uous aqueous phase as micellar form even after the equilibrium swelling, and it is reasonably thought that the surface of swollen particles was already saturated with surface-active long chain molecules of t-BDDA. Therefore, unswollen monomer droplets can produce new particles during the polymerization, resulting in bimodal size distribution.

4. X-ray Photoelectron Spectroscopy (XPS)

The composition on the particle surface was analyzed by X-ray photoelectron spectroscopy. Fig. 9a and 9b show XPS wide scan spectra of the PS particles without and with t-BDDA, respectively. While the PS particles without t-BDDA have only a strong carbon peak, the PS particles with t-BDDA exhibited a characteristic oxygen peak together with a strong carbon peak. This result indicates that there exist oxygen-containing PEO and/or PPO blocks at the particle surface of PS copolymerized with t-BDDA. In this way, clean and surfactant-free polymer particles can be produced by using t-BDDA.

CONCLUSIONS

Surfactant-free monomer swelling was carried out to prepare clean and monodisperse PS particles by two-stage seeded swelling and
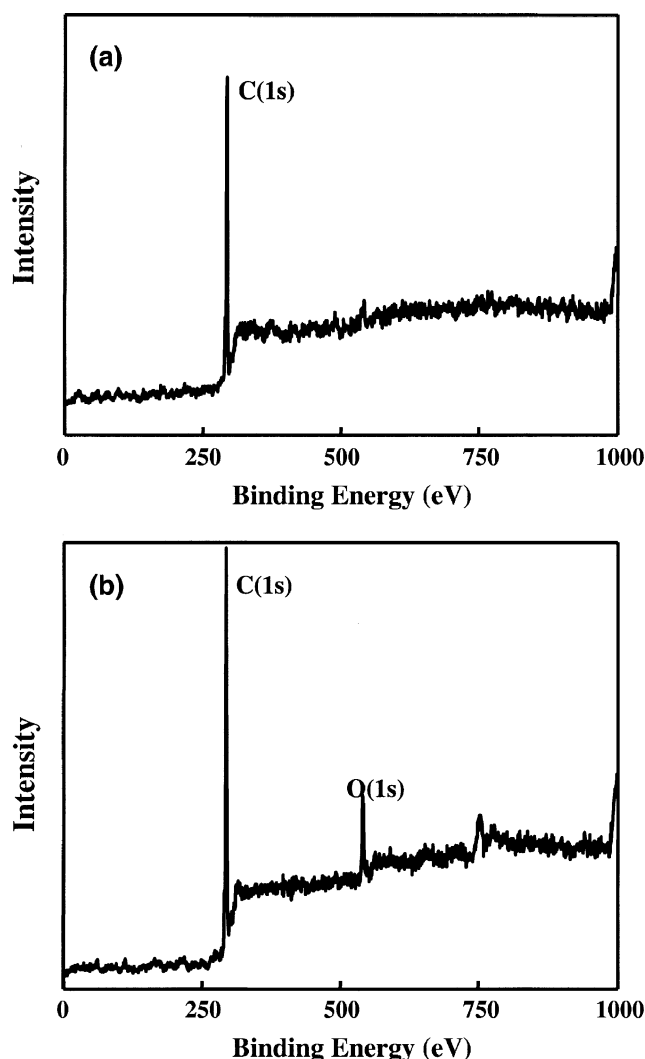
Fig. 9. XPS wide scan spectra of the PS particles (a) without t-DBBA and (b) with t-BDDA.

polymerization method. Actually, the t-BDDA could act as a surface-active agent as well as a macromonomer. It was confirmed in thermodynamic consideration that the swelling capacity was greatly affected by the size of monomer droplets and the interfacial tension, which are largely dependent on the t-BDDA concentration. From the thermo-optical analysis data, it was found that the phase transition temperature of t-BDDA was much lower than those of conventional PEO-PPO-PEO tri-block copolymers. The emulsion preparation and the swelling process conducted under the T_c of t-BDDA finally resulted in monodisperse and stable PS particles after the polymerization, revealing the t-BDDA played a crucial role in stabilizing the emulsions and swelling of monomer droplets. SEM and XPS results confirmed that the monodisperse micron-sized PS particles having surface PEO and/or PPO groups were successfully produced. We finally expect that these particles can be directly applicable to biomaterials without further purification.

ACKNOWLEDGMENT

NOMENCLATURE

$\Delta\overline{G}$: partial molar free energy of monomer in the polymer seed
$\Delta\overline{G}_m$: partial molar free energy of monomer-polymer mixing force
$\Delta\overline{G}_t$: partial molar free energy of particle-medium interfacial tension force
j_p : ratio of the molar volume of polymer to that of monomer
j_s : ratio of the molar volume of swelling agent to that of monomer
r : radius of the particles
r_0 : radius of the initial particles
r_m : radius of the monomer droplets
r_s : radius of the swollen particles
$\overline{V}_m$: partial molar volume of the monomer

Greek Letters
γ : interfacial energy
ϕ_m : volume fraction of the monomer
ϕ_p : volume fraction of the polymer
ϕ_s : volume fraction of the swelling agent
χ_{mp} : interaction parameter of monomer with polymer
χ_{ms} : interaction parameter of monomer with swelling agent
χ_{sp} : interaction parameter of swelling agent with polymer

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