

Modified Emulsifier-Free Emulsion Polymerization of Butyl Methacrylate with Ionic or/and Nonionic Comonomers

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ABSTRACT: A modified emulsifier-free emulsion polymerization of butyl methacrylate (BMA) with ionic or/and nonionic comonomers was successfully used to prepare nanosized poly(butyl methacrylate) (PBMA) latices with high polymer contents. After seeding particles were generated in an initial emulsion system, consisting of a portion of BMA, water, ionic comonomer [sodium styrenesulfonate (NaSS)] or nonionic comonomer [2-hydroxyethyl methacrylate (HEMA)] and potassium persulfate, most of the BMA monomer or the mixture of BMA and HEMA was added dropwise to the polymerizing emulsion over a period of 6–12 h. Stable latices with high PBMA contents up to 27% were obtained. It was found that the latex particle sizes ($2R_{ii}$)

were largely reduced (34 nm) by the continuous addition of monomer(s) compared to those (107 nm) obtained by the batch polymerization method. The effect of comonomer concentration on the particle size, the number of PBMA particles/mL of latex (N_{ii}), and the molar mass (M_w) of copolymer during the polymerization were discussed. The surface compositions of latex particles were analyzed by X-ray photoelectron spectroscopy, indicating that the surface of latex particles was significantly enriched in NaSS or/and HEMA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3080–3087, 2004

Key words: emulsion polymerization; ionic or/and nonionic comonomers; latices; high polymer contents; surfactants

INTRODUCTION

Polymer latices are usually prepared by emulsion polymerization and microemulsion polymerization using surfactants as emulsifiers.^{1–5} The latices prepared from such a process are often stabilized by adsorbed nonpolymerizable surfactants, which may desorb and migrate in the polymer films for film-forming polymers. Desorption of surfactants from the polymer particles can lead to latex destabilization and coagulation,⁶ whereas surfactant migration in the polymer films can confer water sensitivity to the films, which is a drawback for protective coatings. However, reactive surfactants or hydrophilic monomers can copolymerize with the main monomer and become covalently bound to form an integral polymeric material. Desorption of surfactant from the polymer particles or surfactant migration in the polymer film is thus impeded. As a result, stability of the latices can be improved and water sensitivity of the polymer films can be lowered.

Since Matsumoto et al.⁷ showed that monodisperse polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) latices could be prepared in the absence of

emulsifier, the emulsifier-free emulsion polymerization of hydrophobic monomers has received much attention^{8–12} because of its practical and academic interests.^{13,14} This technique enables us to obtain rather monodisperse and “clean” polymer particles, which are used not only for the calibration of various measuring instruments and techniques such as electron microscopes, light-scattering instruments, and medical diagnostic tests, but also as model systems for studying coagulation, flocculation, and rheology of colloids.^{15,16} Juang and Krieger⁸ reduced the particle size from about 0.5–1.0 μm , obtained by emulsifier formulations, to about 0.15–0.40 μm by incorporating about 0.5% ionic comonomer [sodium styrenesulfonate (NaSS)] in the emulsifier-free polymerization of styrene. Goodall et al.⁹ found that potassium persulfate (KPS) plays a key role in the stabilization of the latex particles in the emulsifier-free polymerization of styrene. Chen and Chang¹⁰ investigated the emulsifier-free emulsion polymerization of styrene in the presence of the water-soluble comonomer, 2-hydroxyethyl methacrylate (HEMA). They concluded that the nucleation ability of HEMA was weak, resulting in the formation of larger particles of 150 to 600 nm. Kim et al.¹¹ reported that the rate of the emulsifier-free polymerization of styrene was increased significantly by adding a small amount of NaSS. Xu et al.¹² studied the formation of highly monodisperse cationic poly(meth-

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ylstyrene) latex particles in the presence of an appropriate initiator concentration of 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50).

We recently prepared nanosized emulsifier-free latices with high polystyrene contents up to 25% using water-soluble NaSS or/and HEMA comonomers.¹⁷ This article reports a similar method for the preparation of nanosized emulsifier-free poly(butyl methacrylate) latices with high polymer contents.

EXPERIMENTAL

Butyl methacrylate (BMA) from Aldrich (Milwaukee, WI) and 2-hydroxyethyl methacrylate (HEMA) from Tokyo Chemical Industry (TCI, Tokyo, Japan) were distilled under reduced pressure to remove inhibitor and stored at 4°C. Sodium styrenesulfonate (NaSS) and potassium persulfate (KPS) from Aldrich were used as received.

A four-neck round-bottom flask equipped with a reflux condenser, a thermometer, a pressure equilibrating addition funnel (nitrogen inlet), and a magnetic stirring bar was charged with 0.6 g of BMA and 79.4 g of water. The system was immersed in an oil bath at 70°C and stirred at 350 rpm with a continuous flush of nitrogen. The initiator KPS (162 mg, 6 mM) and functional comonomer NaSS (400 mg) in 10 g of water were then introduced into the system. After about 30 min of prepolymerization, an additional 9.4 g of BMA with or without HEMA (0.3 or 0.6 g) in the addition funnel was added dropwise into the prepolymerizing system over a period of about 6 h. During the period of monomer addition, about 2 mL of sample was drawn at different polymerization intervals with a syringe through a rubber septum. The latex sample was diluted and used for the particle size determination by light-scattering technique. After thorough washing with water and drying, the purified sample was then used for the measurements of X-ray photoelectron spectroscopy (XPS) and size-exclusion chromatography (SEC). The conversions of BMA for final latices were determined by a gravimetric method.

Quasi-elastic light-scattering (QLS) measurements were performed with a Brookhaven model BI-200SM goniometer, Brookhaven model BI-9000AT correlator, and a Lexel 300-mW Ar laser. All experiments were performed at 90° angle and 25°C. The intensity-intensity correlation function was obtained. For systems with only one population of particles, the data were analyzed using the method of cumulants to provide the average decay rate $\langle\Gamma\rangle$ and the variance ν . The latter is a measure of the width of the distribution of the decay rate and is given by

$$\nu = (\langle\Gamma\rangle^2 - \langle\Gamma^2\rangle)/\langle\Gamma\rangle^2$$

The diffusion coefficient D was determined from $\langle\Gamma\rangle$ according to

$$\langle\Gamma\rangle = 2q^2D$$

where $q = 4\pi n \sin(\theta/2)/\lambda$ is the scattering vector, where n is the medium refractive index, θ is the scattering angle, and λ is the wavelength of the incident light in the medium, respectively.

The diffusion coefficient D is related to the hydrodynamic radius R_h of the particle in the high-dilution limit as follows:

$$R_h = \lim_{\phi \rightarrow 0} \frac{kT}{5\pi\eta_0 D} \quad (1)$$

For systems having more than one population of particles, CONTIN was used to analyze the data.

The purified polymer sample was further dried in a vacuum oven for 2 days before it was analyzed by XPS. The surface analysis of each copolymer was carried out in a VG ESCALAB Mk II spectrometer (VG Scientific) with a Mg-K $_{\alpha}$ X-ray source (1253.6 eV) and with an energy analyzer set at a constant retarded ratio of 40. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The powder sample was mounted on the standard sample studs by means of double-sided adhesive tape. The pressure in the analysis chamber during the measurements was maintained at or lower than 10⁻⁸ mbar. To compensate for surface-charging effects, all binding energies were referred to the C(1s) neutral carbon peak at 284.6 eV. The peak areas for the calculation of oxygen, sulfur, and carbon compositions were corrected by experimentally determined instrumental sensitivity factors. Based on a similar derivation described in the appendix of our previous work,¹⁷ the fractions of NaSS and HEMA on the particle surface can be calculated from the following equations:

$$F_{\text{NaSS}} = 12A_s f_s / (A_c f_c + 2A_o f_o - 2A_s f_s + 4A'_s f'_s) \quad (2)$$

$$F_{\text{HEMA}} = (-2A_c f_c + 8A_o f_o - 8A_s f_s - 32A'_s f'_s) / (A_c f_c + 2A_o f_o - 2A_s f_s + 4A'_s f'_s) \quad (3)$$

where F_{NaSS} and F_{HEMA} refer to the fractions of NaSS and HEMA on the particle surface of poly(butyl methacrylate); A_c , A_o , A_s , and A'_s are the peak areas of carbon, oxygen, and sulfur in NaSS, and sulfur in KPS in the certain XPS spectrum, respectively; and f_c , f_o , and f_s refer to the instrumental sensitivity factors of carbon, oxygen, and sulfur, which are 1, 0.5978, and 0.3157, respectively.

TABLE I
Effect of NaSS Concentration on BMA Polymerization

Emulsifier-free system ^a	Sample			
	1	2	3	4
Initial composition				
BMA (wt %)	0.6	0.6	0.6	0.6
Water (wt %)	89.8	89.7	89.6	89.4
NaSS (wt %)	0.2	0.3	0.4	0.6
Additional component				
BMA (wt %)	9.4	9.4	9.4	9.4
Microlatex characteristics				
$2R_h$ (nm)	68.9	50.5	41.9	30.6
Poly	1.10	1.12	1.17	1.28
M_w (10^4 , g/mol)	14.5	13.0	10.6	8.2
N_d (10^{15} particles/mL)	0.57	1.5	2.6	6.6
NaSS on surface (%)	8.6	18.7	33.8	60.4

^a The concentration of KPS was fixed at 6 mM based on the total weight of each system. All polymerizations were carried out at 70°C.

Molar masses (M_w) of copolymers were determined by size-exclusion chromatography (SEC) using a Waters 410 differential spectrometer detector (Waters Chromatography Division/Millipore, Milford, MA). The Phenomenex SEC column (300×7.8 mm) with phenogel packing material as stationary phase was used. The eluent was HPLC-grade tetrahydrofuran (THF), which contained 0.0025% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer. The flow rate was maintained at 0.8 mL/min. PS standards were used for the calibration. The SEC samples were prepared by dissolving each purified polymer sample into THF and filtering the obtained solution by a Teflon membrane filter (pore size 0.45 μ m).

The number of PBMA particles/mL of microlatex (N_d) was calculated as an approximation from an

equation that appears in a previous paper reported by Ming et al.¹⁸

RESULTS AND DISCUSSION

In the present study, as polymerization proceeded, the emulsifier-free systems changed from bluish-transparent to bluish-opaque as the copolymer contents were increased in the systems. The conversions of BMA for all polymerizations exceeded 95%. All latices prepared remained stable up to 8 months.

Emulsifier-free latices

Table I shows the concentration effect of NaSS on the BMA polymerization. When the initial NaSS was increased from 0.2 to 0.6 wt %, the particle size ($2R_h$) sharply decreased from about 69 to 31 nm, whereas the particle size polydispersity (hereafter designated Poly) increased significantly from 1.10 to 1.28. In addition, the M_w decreased by about half, from 14.5×10^4 to 8.2×10^4 g/mol. However, the number of PBMA particles/mL of microlatex (N_d) sharply increased from 0.57×10^{15} to 6.6×10^{15} , which clearly indicates that the possibility of continuous homogeneous nucleation increased significantly with the increase of NaSS concentration in the early stage of polymerization. This leads to a higher N_d , resulting in formation of particles of smaller size.

The concentration effect of HEMA (Samples 1–3) on the BMA polymerization using 0.4 wt % NaSS is shown in Table II. The particle size decreased from about 42 to 37 to 34 nm and M_w from 10.6×10^4 to 8.4×10^4 to 6.9×10^4 g/mol as the amount of HEMA was increased from 0 to 0.3 to 0.6 wt %, respectively. On

TABLE II
Effect of HEMA Concentration on BMA Polymerization

Emulsifier-free system ^a	Sample					
	1	2	3	4	5	6
Initial composition						
BMA (wt %)	0.6	0.6	0.6	0.6	0.6	0.6
Water (wt %)	89.6	89.3	89.0	89.4	88.8	88.2
NaSS (wt %)	0.4	0.4	0.4	0	0	0
HEMA (wt %)	0	0	0	0.6	0.6	0.6
Additional components						
BMA (wt %)	9.4	9.4	9.4	9.4	9.4	9.4
HEMA (wt %)	0	0.3	0.6	0	0.6	1.2
Microlatex characteristics						
$2R_h$ (nm)	41.9	37.4	33.8	202.6	197.5	194.7
Poly	1.17	1.20	1.30	1.06	1.09	1.11
M_w (10^4 , g/mol)	10.6	8.4	6.9	13.4	11.8	9.3
N_d (10^{15} particles/mL)	2.6	3.7	5.2	0.023	0.026	0.029
NaSS on surface (%)	33.8	30.5	28.2	0	0	0
HEMA on surface (%)	0	7.8	31.7	59.2	58.4	60.5

^a The concentration of KPS was fixed at 6 mM based on the total weight of each system. All polymerizations were carried out at 70°C.

TABLE III
Effect of BMA Concentration on Polymerization

Emulsifier-free system ^a	Sample				
	1	2	3	4	5
Initial composition					
BMA (wt %)	0.6	0.6	0.6	0.6	0.6
Water (wt %)	89.0	86.0	83.4	77.8	71.8
NaSS (wt %)	0.4	0.4	0.4	0.6	0.6
Additional components					
BMA (wt %)	9.4	12.4	15.0	20.4	26.4
HEMA (wt %)	0.6	0.6	0.6	0.6	0.6
Microlatex characteristics					
Copolymer content (%)	10.8	13.6	16.2	21.3	27.0
$2R_h$ (nm)	33.8	58.9	81.4	44.7	55.2
Poly	1.30	1.22	1.17	1.15	1.10
M_w (10^4 , g/mol)	6.9	9.7	12.1	11.9	17.5
N_d (10^{15} particles/mL)	5.2	1.2	0.56	4.5	3.1

^a The concentration of KPS was fixed at 6 mM based on the total weight of each system. All polymerizations were carried out at 70°C.

the other hand, N_d increased sharply from 2.6×10^{15} for the system containing only 0.4 wt % NaSS to 3.7×10^{15} for the system using 0.4 wt % NaSS and 0.3 wt % HEMA or 5.2×10^{15} for the system containing 0.4 wt % NaSS together with 0.6 wt % HEMA. This indicates that there existed a combining effect of NaSS and HEMA on the particle nucleation. When HEMA was used alone without NaSS, the number of latex particles formed was relatively low ($N_d \approx 2.6 \times 10^{13}$; Samples 4–6 in Table II) and their particles were relatively large ($2R_h \approx 200$ nm), which implies that HEMA plays only a weaker role in the particle nucleation compared to that of NaSS.

Table III shows the effect of BMA concentration on polymerization. For the system containing 0.4 wt % NaSS, the particle size sharply increased from about 34 to 81 nm as additional BMA was increased from 9.4 to 15.0 wt %. Their respective Poly values decreased slightly from 1.30 to 1.17. However, M_w increased by about twofold, from 6.9×10^4 to 12.1×10^4 g/mol, and N_d sharply decreased from 5.2×10^{15} to 5.6×10^{14} , which indicates that the interparticle aggregation occurred at higher polymer content that was insufficiently protected by the limited amount of NaSS. When the amount of NaSS was increased from 0.4 to 0.6 wt %, the total polymer content could be further increased to about 27%. With sufficient protection from particle agglomeration by NaSS, the particle size remained small (~ 55 nm) at high value of N_d at 3.1×10^{15} .

It was found that for the system containing 0.6 wt % initial BMA, 0.4 wt % initial NaSS, 0.6 wt % additional HEMA, and 9.4 wt % additional BMA using KPS as an initiator at 70°C (Sample 3 in Table II), the particle size ($2R_h$) and polydispersity (Poly) of the final latices remained almost unchanged at about 34 nm and 1.3, respectively, as the KPS concentration was increased

from 2 to 8 mM. This may indicate that KPS plays a minor role in the particle nucleation process; however, their M_w did decrease significantly from about 1.6×10^5 to 1.0×10^5 to 7.0×10^4 to 4.0×10^4 g/mol because of the increase of radical termination rate.

A comparison between the present modified emulsifier-free emulsion polymerization (continuous monomer addition) and the conventional one-pot emulsifier-free emulsion polymerization method is shown in Table IV. It was found that the size of latex particles from the present method was much smaller (~ 34 nm) than that of particles (~ 107 nm) from the conventional method. However, N_d for the former is 5.2×10^{15} , which is much larger than that (1.6×10^{14}) of the latter. However, M_w of the copolymer from the

TABLE IV
Comparison Between the Present and the Conventional Emulsifier-Free Emulsion Polymerization

Emulsifier-free system ^a	1 (Present)	2 (Conventional)
Initial composition		
BMA (wt %)	0.6	10
Water (wt %)	89.0	89.0
NaSS (wt %)	0.4	0.4
HEMA (wt %)	0	0.6
Additional components		
BMA (wt %)	9.4	0
HEMA (wt %)	0.6	0
Microlatex characteristics		
$2R_h$ (nm)	33.8	107.3
Poly	1.30	1.28
M_w (10^4 , g/mol)	6.9	20.3
N_d (10^{15} particles/mL)	5.2	0.16
NaSS on surface (%)	28.2	10.7
HEMA on surface (%)	31.7	36.6

^a The concentration of KPS was fixed at 6 mM based on the total weight of each system. Both polymerizations were carried out at 70°C.

conventional method is 2.0×10^5 g/mol, which is about 3 times higher than that (6.9×10^4 g/mol) obtained by the present method. Although a higher concentration of comonomers can reduce the particle size by the conventional emulsifier-free emulsion polymerization, using one of the ionic type or nonionic type comonomers, the broader particle distribution and the production of homopolymers are inevitable.

The present study of the emulsifier-free emulsion polymerization of butyl methacrylate (by continuous addition) in the presence of both ionic NaSS and nonionic HEMA enables one to prepare nanosized latices containing high polymer contents. The initial emulsion system is composed of BMA droplets, water, and the dissolved BMA in water. Once the KPS initiator decomposed at 70°C, the formed primary radicals directly reacted with BMA monomer and NaSS or HEMA dissolved in the aqueous phase to form oligomeric radicals. Because of the high solubility of NaSS or HEMA in water, these oligomeric radicals form particles stabilized by NaSS or HEMA according to the homogeneous nucleation mechanism.

After about 30 min of prepolymerization, BMA droplets were exhausted after forming primary polymer particles. This is the polymerization state where monomer-starved growing polymer particles prevailed. Under this circumstance, the continuous controlled addition of BMA, with or without HEMA, to the polymerization system favors the newly added monomer(s) to diffuse into the primary PBMA particles for further growth. Some copolymerization of HEMA could also occur on the surface of PBMA particles. It is viewed that the added BMA monomer is rapidly transported into the growing polymer particles to maintain the dynamic equilibrium of BMA in the system. Because the $-\text{SO}_3^-$ groups of NaSS and the $-\text{OH}$ groups of HEMA are hydrophilic, they tend to distribute on the surface of the growing polymer particles. XPS analysis showed that the average surface compositions of latex particles consisted of 8.6–60.4% NaSS and 7.8–60.5% HEMA in the form of copolymers. For the system containing only NaSS, the growing particles were well stabilized by $-\text{SO}_3^-$ groups from NaSS. With a higher amount of NaSS, the number of the primary polymer particles formed in the homogeneous nucleation process increased. Thus, the latex particle size decreased significantly from about 69 to 31 nm as NaSS was increased from 0.2 to 0.6 wt %, as listed in Table I.

It has been long desired to obtain nanosized latices containing higher polymer contents at lower surfactant concentrations, ideally, without using any emulsifiers. In our previous study,¹⁹ we produced nearly monodisperse polystyrene (PS) microlatices with PS contents up to 14 wt % using only 1 wt % cetyltrimethylammonium bromide (CTAB) as a surfactant. Their particle sizes were less than 50 nm. We also

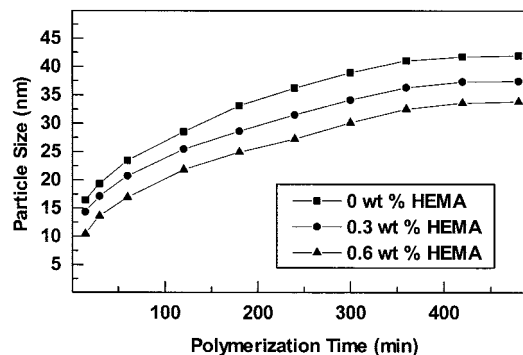


Figure 1 Growth of PBMA latex particle size ($2R_h$) during the emulsifier-free emulsion polymerization at 70°C for Samples 1, 2, and 3, as listed in Table II.

produced PS microlatices²⁰ with high polymer/surfactant weight ratios (up to 15 : 1) using a polymerizable surfactant ω -methoxy poly(ethylene oxide)₄₀ undecyl- α -methacrylate (PEO-R-MA-40) and CTAB. These latex particles ranged from 50 to 80 nm in diameter. With the present method, we can now produce stable PBMA latices of high polymer contents up to 27% having small particle sizes less than 60 nm, as shown in Table III. The stability of these latices could be attributed to the synergic effect of the electrostatic repulsion and steric effect from comonomers NaSS and HEMA in which the particle surface was chemically enriched, although the effect of NaSS on the nucleation and stability of particles is predominant.

It is well known that the micelle (loci) polymerization (emulsion or microemulsion) proceeds at a faster rate in forming higher M_w ($\sim 10^6$ g/mol), attributed to the lower termination rates than those from solution (no loci) polymerization. Similarly, the molar masses of copolymers obtained from copolymerization of BMA with a small amount of NaSS were quite low ($M_w \sim 10^4$ – 10^5 g/mol). Because the sulfonate ion $-\text{SO}_3^-$ is a strong electron-withdrawing group, it will not only reduce the electron density of the vinyl group $-\text{CH}=\text{CH}_2$ at the *para*-position of the benzene ring of NaSS, but also significantly reduce the electron density of growing radical $\sim\text{CH}-\text{CH}_2$, which in turn reduces the reactivities of monomer NaSS and the growing radical $\sim\text{CH}-\text{CH}_2$ for continuous polymerization. As a result, M_w was quite low ($M_w \sim 1.5 \times 10^5$ g/mol) by the effect of only 0.2 wt % NaSS. As the content of NaSS was increased to 0.6 wt % (Table I), M_w further decreased to about 8×10^4 g/mol.

Characteristics of latices during the polymerization

The effects of additional HEMA concentration on the growth of the particle size ($2R_h$) and the change of copolymer particles/mL of latex (N_d) during the polymerization are shown in Figures 1 and 2, respec-

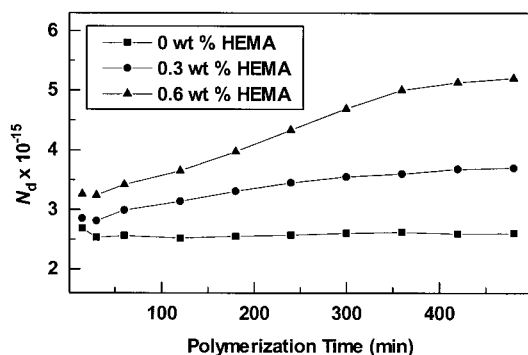


Figure 2 Change of number of PBMA particles/mL of latex (N_d) during the emulsifier-free emulsion polymerization at 70°C for the same samples as in Figure 1.

tively. The particle size seemed to continuously increase up to about 6 h of polymerization. However, it is noted that N_d remained rather constant at about 2.6×10^{15} for the system containing no HEMA throughout the polymerization. N_d did increase slightly, from about 2.8×10^{15} to 3.7×10^{15} , for the system containing 0.3 wt % HEMA. However, the significant increase of N_d , from about 3.2×10^{15} to 5.2×10^{15} , was observed for the system containing 0.6 wt % HEMA. For the systems with the additional HEMA and BMA, the surface of the polymer particles was enriched in more -OH groups of HEMA. Thus the latex particles became more stable, given the additional steric stabilization exerted by hydrophilic -OH groups. However, the formation of new secondary particles (by homogeneous nucleation) might be inevitable because of the good solubility of HEMA in water. At a lower HEMA content of 0.3 wt %, the effect of homogeneous nucleation was insignificant. As the HEMA content was increased to 0.6 wt %, the homogeneous nucleation became significant, as reflected from the increasing trend of N_d shown in Figure 2.

The dependency of N_d on the particle size for these three polymerization systems can be better shown in Figure 3. In the absence of HEMA, N_d was almost independent of the particle size for the system containing only 0.4 wt % NaSS. With the presence of 0.3 or 0.6 wt % HEMA, N_d increased with the growth of latex particles, and the effect was larger for the system containing a larger amount of HEMA.

In contrast to N_d , M_w of copolymer decreased with the increase of the particle size, especially for the system containing 0.6 wt % HEMA, as shown in Figure 4. The effect of HEMA on lowering M_w is attributed to the chain-transfer termination by HEMA, which has an active hydroxy group. In addition, it is also viewed²¹ that the preferential solvation or absorption of the sulfonated copolymers on the SEC column walls or stationary phase is inevitable, which results in increasing the elution time of the mobile phase in SEC

measurement, yielding lower M_w for the copolymers. The unexpected results for the present and the conventional emulsifier-free emulsion polymerization (Table IV) can now be explained. In the present method, 0.4 wt % NaSS was added initially together with only 0.6 wt % BMA. Under this monomer deficiency, NaSS copolymerized with BMA to a greater extent, with about 28% NaSS appearing on the particle surface. The latex particles were thus well stabilized to form smaller particles ($2R_h \approx 34$ nm). On the other hand, the poor reactivity of NaSS resulted in only about 11% NaSS appearing on the particle surface, which was mainly covered by 37% HEMA for the copolymer obtained by the conventional method. With less protection by NaSS, the latex particles may have agglomerated to produce much larger particles ($2R_h \approx 107$ nm) because those stabilized by HEMA only (Samples 4–6 in Table II). The much larger M_w value (2.0×10^5 g/mol) obtained by the conventional method could be attributable to fewer interactions with the SEC column because the particle surface consisted of only about 11% NaSS.

Characterization of particle surface

An X-ray photoelectron spectrometer was used to analyze the particle surfaces of the copolymer powders. The presence of abundant carbon, oxygen, and sulfur on the particle surface of each sample is revealed by three strong peaks, C(1s), O(1s), and S(2p), as shown in Figure 5. The surface compositions of latex particles were calculated using eqs. (2) and (3). As shown in Table I, the surface composition of these latex particles increased sharply from 8.6 to 60.4% NaSS as the NaSS content in the polymerization system was only increased from 0.2 to 0.6 wt %. This shows that the surface of latex particles was preferably enriched in NaSS. When HEMA was added to the NaSS-containing systems, as shown in Table II, the surface compo-

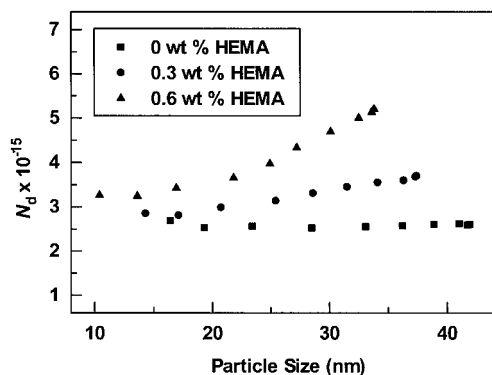


Figure 3 Relationship between $2R_h$ and N_d for the emulsifier-free emulsion polymerization at 70°C for the same samples as in Figure 1.

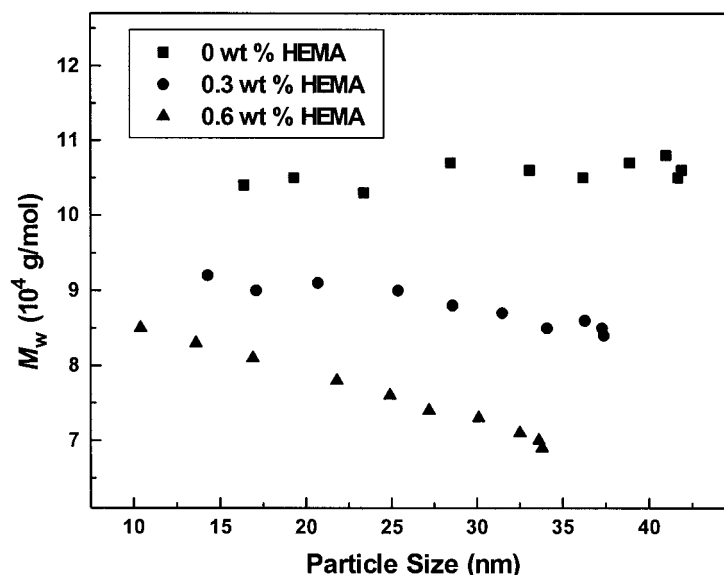


Figure 4 Effect of $2R_h$ on the molar masses (M_w) for the emulsifier-free emulsion polymerization at 70°C for the same samples as in Figure 1.

sition of NaSS of latex particles remained about the same at around 30%, but the surface composition of HEMA sharply increased from about 8% at 0.3 wt % HEMA to about 32% at 0.6 wt % HEMA. Thus, more than half of the particle surface ($\sim 60\%$) of Sample 3 (Table II) was covered by both polymerized NaSS and HEMA functional groups. It is interesting to note that a similar particle surface coverage ($\sim 60\%$) was obtained for Sample 4 (Table II), which contained only 0.6 wt % HEMA and no NaSS. However, the increase of HEMA to 1.2 wt % as for Sample 5 or to 1.8 wt % as for Sample 6 did not further increase the particle surface coverage. The maximum surface coverage al-

lowed for HEMA or both HEMA and NaSS may be limited to about 60%.

CONCLUSIONS

Nanosized PBMA microlatices were successfully synthesized by the present modified emulsifier-free emulsion copolymerization of BMA with a small amount of NaSS or/and HEMA using KPS as initiator at 70°C. The maximum polymer content was up to 27% using only 0.6 wt % of both NaSS and HEMA. By varying the polymerization conditions, the latex particles, ranging from about 30 to 200 nm in diameter with

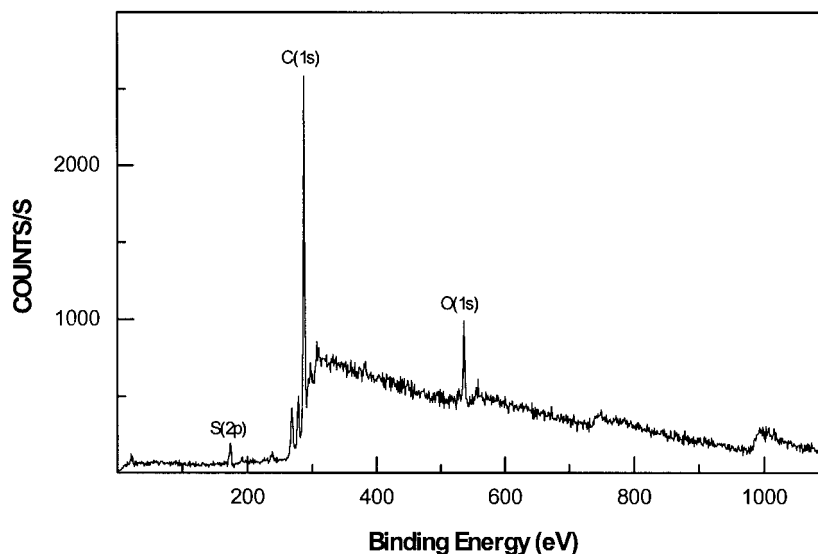


Figure 5 XPS spectrum (wide scan) of the copolymer particles for Sample 3, as listed in Table II.

molar masses (M_w) of copolymers ranging from 6.9×10^4 to 17.5×10^4 g/mol, can be obtained. It was found that the size of latex particles obtained from the present modified method was much smaller (~ 34 nm) than that of particles (~ 107 nm) obtained from the conventional emulsifier-free emulsion polymerization method. At lower concentrations of NaSS or/and HEMA, nearly monodisperse latex particles were obtained. The number of PBMA particles/mL of latex (N_d) during the polymerization remained almost constant for the system containing only 0.4 wt % NaSS. With the combination of 0.4 wt % NaSS and different amounts of HEMA, N_d increased with the increase of HEMA from 0.3 and 0.6 wt %. The electron affinity of sulfonate ion $-\text{SO}_3^-$ in NaSS and the chain-transfer termination by HEMA regulated the M_w of copolymers. The XPS results showed that the surface of latex particles was significantly enriched in NaSS and HEMA.

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