Nanosize Polymer Latices Made by Microemulsion Copolymerization: Preparation and Characterization

Yuying Zhang, Tianying Guo, Guangjie Hao, Maodao Song, Banghua Zhang

Nankai University and Tianjin University Joint Academy, State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

ABSTRACT: Polymer nanoparticles were prepared by a methyl methacrylate/butyl methacrylate/2-hydroxyethyl methacrylate/acrylate or methyl acrylate microemulsion copolymerization process. A microemulsion copolymerization method was used. With this process high polymer : surfactant weight ratios ($\geq 15:1$), relatively concentrated (~ 30 wt %) lattices, and small (~ 60 nm) particle diameters were obtained. Properties of the latices were characterized in detail by TEM, DSC, dynamic light scattering, spectrophotometry, and tensile strength testing. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3625–3630, 2003

Key words: emulsion polymerization; copolymerization; nanotechnology; surfactants; latices

INTRODUCTION

During the last decade, a great deal of research has been devoted to nanostructured materials. Many publications have appeared dealing with metal, ceramic, semiconductor nanoparticles,[1] and polymer-related nanostuctured materials, for example, polymer/metal (or semiconductor) nanocomposites.[2]

Recently, the study on the preparation of polymer nanoparticles has been the focus of increasing attention. Microemulsion polymerization is the most common method of preparing polymer nanoparticles. It has been widely studied since the seminal studies by Stoffer,[3,4] Atik,[5] and others in the early1980s. A microemulsion may be defined as a thermodynamically stable and optically transparent dispersion composed of water, oil, and surfactant; in many cases a cosurfactant is required. The microemulsion polymerization process can yield stable polymer latices with particle size of about 10 to 100 nm. Since 1980 a number of studies have described microemulsion polymerization.[6–18] There are two major drawbacks, however, that have limited the applications of microemulsion polymerization: (1) high surfactant concentration (up to 20 wt % of the total reactor charge) is required to obtain small particles; thus, monomer/surfactant weight ratios are usually smaller than 1; and (2) the microlatices can be made only at low concentrations: the polymer content is usually less than 10 wt %. High surfactant levels and low polymer contents limit the application of microemulsion latices in industry.

In this study methyl acrylate (MAA) [or acrylate (AA)] and 2-hydroxyethyl methacrylate (HEMA) were used as reactive cosurfactants, and a microemulsion copolymerization method demonstrated the preparation of polymer nanolatices composed of polymer nanoparticles with average diameters ≤ 60 nm, polymer content about 30 wt %, and monomer/surfactant weight ratios of 15 : 1. The resulting polymer latices had high polymer contents as well as nanosize particles with narrow size polydispersity.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA; ICI Acrylics, UK), butyl acrylate (BA; ICI Acrylics), acrylate (AA, analytical grade), methyl acrylate (MAA, analytical grade), and 2-hydroxyethyl methacrylate (HEMA, analytical grade) were distilled under reduced pressure before polymerization. AA, MAA, and HEMA were purchased from the Institute of Chemical Reagents, Tianjin, China. Ammonium persulfate [$(NH_4)_2S_2O_8$, APS], purchased from the Institute of Chemical Reagents (Tianjin, China), was recrystallized before use.

Aerosol A-501 surfactant (mixture, main component: disodium isodecyl sulfosuccinate, 35% aqueous solution) was purchased from Professional Chemical Product Co. (Shanghai, China). Aerosol A-102 surfactant [mixture, main component: polyethyleneglycol alkyl (C10–C12) ethersulfosuccinate, disodium salt, 35% aqueous solution] was also purchased from Professional Chemical Product Co.

TABLE I
Recipes Used in the Modified Microemulsion Copolymerization

No.	Cosurfactant (wt %)			Surfactant (wt %)		Monomer (wt %)		Temperature (°C)	Particle size (nm)
	AA	MAA	HEMA	A-501	A-102	BA	MMA		
A1	4.7	—	2.0	5.0	—	50.0	43.3	75	129.7
A2	6.0	—	2.0	5.0	—	46.7	43.3	75	183.0
A4	6.0	—	2.0	5.0	—	46.7	43.3	70	142.6
A5	6.0	—	2.0	5.0	—	46.7	43.3	65	134.1
A3	11.3	—	2.0	5.0	—	43.3	43.3	75	213.0
G0-1	—	—	—	6.7	—	53.3	46.7	70	84.6
G0-2	—	—	—	5.0	—	53.3	46.7	70	99.1
G1	—	2.0	3.3	5.0	—	50.0	44.7	70	73.9
G2	—	2.0	3.3	6.7	—	50.0	44.7	70	72.3
G3	—	2.0	3.3	—	6.7	50.0	44.7	70	58.1
G4	2.0	—	3.3	—	6.7	50.0	44.7	70	60.1

Microemulsion copolymerization process

A typical microemulsion copolymerization procedure is as follows: a 250-mL four-neck flask, equipped with a reflux condenser, two addition funnels, Teflon stirrer, nitrogen inlet, and feed inlet, was loaded with 2.0 g of emulsifier, 30.0 g of water, and 10.0 g of component A (40.0 g of water, 0.2 g of APS, 0.15 g of NaHCO$_3$). The flask was heated to 75°C and maintained at that temperature for 15 min. Then components A and B (13.4 g of MMA, 15 g of BA, 0.6 g of AA, 1.0 g of HEMA) in the feeding funnels were continuously and slowly added into the flask over a period of 5–6 h with mild stirring (~ 200 rpm). After the addition was complete, the flask was maintained at 70°C for 1 h. After the polymerization, the pH of the microemulsion was adjusted to 8.5.

Characterization

Transmission electron microscopy (TEM; Hitachi-600, Ibaraki, Japan). The high solid content latex was diluted to 1%, one droplet of which was dropped onto a copper sieve coated with polyvinyl butyrate, dyed by phosphato-tungstic acid, and dried at room temperature for 3 min.

TABLE II
Influence of Surfactant and Initiator of the Microemulsion

	A-501 (wt %)	A-102 (wt %)	APS (wt %)	Solids content (%)	Particle size (nm)
G0-1	6.7	—	0.67	30	84.6
G0-2	5.0	—	0.67	30	99.1
G1	5.0	—	0.67	30	73.9
G2	6.7	—	0.67	30	72.3
G3	—	6.7	0.67	30	58.1
G6	—	6.7	0.33	30	98.1

Dynamic light scattering (DLS). The particle size and size distribution were determined using a photon-correlation spectroscope (Brookhaven Instruments Corp.), equipped with an argon ionic laser (λ = 515.5 nm), a BT-9000 AT correlator, and a BI 200 SM photometer (Coherent Corp.). The measurements were performed at appropriate dilutions at angle θ = 90°C, λ = 515.5 nm, and T = 25°C.

Differential scanning calorimetry (DSC; Netzsch DSC 204, Germany). Nitrogen was used as the sweeping gas. Samples (~ 15 mg) were heated at a scan rate of 5°C/min from −100 to 150°C.

Spectrophotometry (UV-9100). The high solid content latex was diluted to 0.6%. Transmittance was measured at λ = 600 nm.

Tensile strength testing machine (Testometric M500-25kN, UK). Tensile properties were recorded with a Testometric at a crosshead speed of 20 mm/min and a tensile load of 250 N at 23°C. The dimension of the sample was 20 × 4 × 0.8 mm^3. The tensile properties of each sample were determined from an average of at least five tests.

Water resistance of the polymers was characterized by soaking in distilled water (23°C) and weighing the amount of water absorbed at a preset time. The dimension of the sample was 20 × 10 × 0.8 mm^3. Water absorption is defined as wt % = $(W - W_0)/W_0$, where W_0 is the presoaking weight and W is the weight that soaked for the preset time.
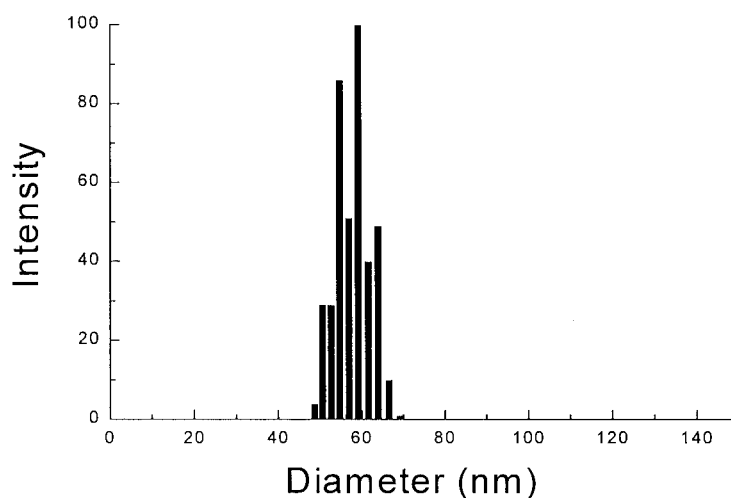
RESULTS AND DISCUSSION

Preparation

The microemulsion copolymerization procedure in our laboratory includes three steps: (1) all the emulsifier, 1/4 the amount of initiator aqueous solution, and part of the water were added in the initiation of the polymerization; (2) the remaining initiator aqueous solution and all the monomer were continuously and
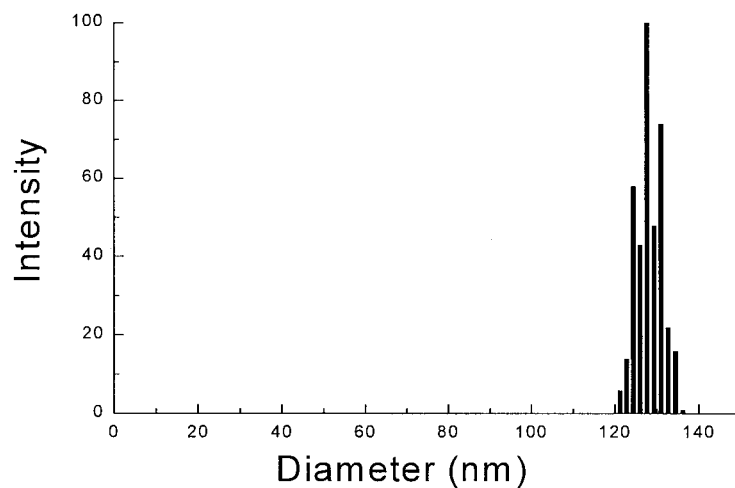
a

b

Figure 1 Particle size distribution of the latex from recipes A1 and G3.

slowly added into the polymerizing microemulsion; and (3) postammoniated procedure.

The microlatex, especially the O/W microlatex, requires high surfactant concentration to form stable polymer latices with polymer content of less than 10 wt %. High surfactant levels and low polymer content limit the application of microemulsion latices in industry. It is thus desirable to minimize the surfactant amount and maximize the polymer content. In this study hydrophilic monomers [MAA (AA) and HEMA] were used as reactive cosurfactants. When the reactive cosurfactant is added to the latex, it can copolymerize with the polymer monomer. The hydrophilic monomer is apt to aggregate on the surface of the latex particles, which form a hydrophilic layer bound to the latex particles; thus the stabilization of the particles is improved. Therefore the cosurfactant can partly replace the surfactant. The surfactant amount is minimized, the properties of the latex can be significantly improved, and the solids content can be increased.
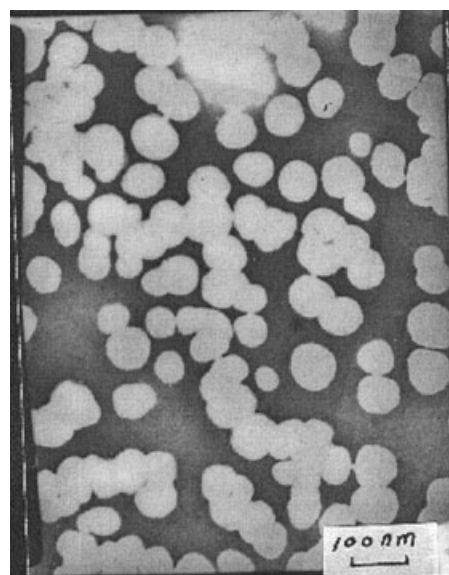

Figure 2 Transmission electron micrographs of G3.

TABLE III
Properties of the Microlatexes

No.	η_{app} ($\times 10^3$ Pa · s)	γ (s^{-1})	D (nm)	Transmittance (%)	T_g (°C)	Degree of water adsorption (%)	Solids content (%)
A1	3.045	1310	129.7	4.5	18.6	32.34	30
A2	35.24	1310	183.0	6.9	17.2	132.45	30
A3	16.57	1310	213.0			166.02	30
A4	22.63	1310	142.6	29.5	14.3	96.33	30
G1	12.62	1310	73.9	50.3	18.4	61.56	30
G2	3.785	1310	72.3	49.0	13.8		30
G3	3.481	1310	58.1	68.6	13.4	25.84	30
G4	4.656	1310	60.1	68.0	14.1	16.56	30
G6	3.176	1310	98.1	21.0			30

The recipes used in the polymerization of methyl methacrylate (MMA) and butylacrylate (BA) are given in Table I. As shown, the particle size of the micro-emulsion obviously decreased when a reactive cosurfactant [MAA (AA) and HEMA] is added to the latex and the particle size increased with the increase of the molar ratio AA/HEMA. Only a slight difference of particle size was observed when the cosurfactant AA was changed to MAA. With the appropriate molar ratio of MAA (AA)/HEMA, the microlatices had high polymer contents as well as nanosize particles with narrow size polydispersity.

The reaction temperatures of A2, A4, and A5 were 75, 70, and 65°C, respectively; other experimental conditions were unchanged. The dependency of particle size on reaction temperature is illustrated in Table I. The particle size decreased as the temperature decreased from 75 to 65°C. With the increase of the reactive temperature, the rate of the reaction increased and stability of the initial latex particles decreased. Thus, the initial latex particles coalesced without difficulty and the particle size increased.

As may be observed in Table II, when surfactant A-501 content varied from 5 to 6.7%, the particle size of the latex decreased. When surfactant A-102 was used, the latices with smaller particle size were produced in the G series. The increase in the surfactant content resulted in the creation of large numbers of micelles at the initial stages of the polymerization. Thus the number of latex particles increased and the dimension decreased.

As shown in Table II, the particle size of microlatices obviously increased from 58.1 to 98.1 nm as the [APS] content was changed from 0.67 to 0.33%. With the increase of the [APS], the active center increased, the nucleation rate was expedited, and thus the particle size decreased.

Figure 1(a) and (b) show the particle size distribution of the latex from recipes A1 and G3, repectively. The distributions, obtained from DLS measurements, are very narrow. The mean diameter of latex A1 is 129.7 nm, with 5.2% of the particles less than 124 nm and 4.5% up to 134 nm. For latex G3, the mean diameter is 58 nm, with 8% of the particles less than 50 nm and none up to 70 nm.

TEM results

Illustrated in Figure 2 is the transmission electron micrograph of G3. The latex particles are small elastomer particles, whose boundary is rather blurry under TEM observation; thus the latex was dyed by phosphato-tungstic acid. As may also be observed in this figure, the particles were of uniform size and were evenly dispersed. From the micrographs, we obtained an average diameter of 50–80 nm. The value is comparable to the 58 nm measured by light scattering.

TABLE IV
Mechanical Properties of the Copolymers

No.	Stress at peak (N/mm^2)	Stress at yield (N/mm^2)	Young modulus (N/mm^2)	Strain at break (%)
A1	15.11	4.30	2.47	480.8
A2	14.26	3.34	2.11	580.3
A3	13.12	3.51	2.10	506.3
A4	8.38	1.68	0.67	724.3
G1	15.79	5.60	2.62	430.2
G3	4.78	0.96	0.38	737.0
G4	5.28	1.06	0.34	852.3

Thermal analysis

The glass-transition temperature (T_g) of the copolymers can be designed according to Fox theory ($1/T_g = W_1/T_{g1} + W_2/T_{g2}$) by adjusting the monomer ratio. W_1 and W_2 are the mass fractions of 1 and 2 nonomeric units. From Hopfinger et al.[19] T_g values of PMMA and PBA were 105°C (378 K) and −54°C (219
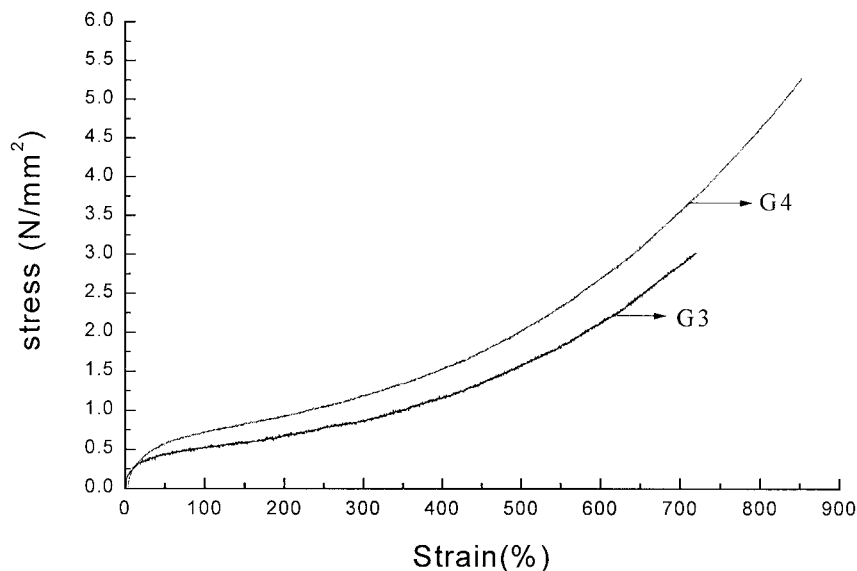
Figure 3 Typical tensile behavior of copolymer.

K), respectively, measured by DMA. The T_g of the copolymers was measured by DSC. As shown in Table III, only one T_g was observed, so the obtained polymer was illustrated to be an atactic copolymer.

Mechanical properties

Tensile strength and ultimate elongation were investigated by a tensile testing machine. The tensile stress is given relative to the original cross-sectional area A_0 of the sample, and the ultimate elongation is defined as $\epsilon = (L - L_0)/L_0$, where L_0 is the original length of the

sample and L is the ultimate length of the sample. Tensile testing data are listed in Table IV and stress–strain behavior of the copolymers is depicted in Figure 3.

Water absorption

Figure 4 shows the typical water absorption curves for copolymers G3 and G4. The water absorption of the copolymer decreased when the cosurfactant MAA was changed to AA. As shown in Table III, the water absorption of the modified microemulsion increased with the increase of the molar ratio AA/HEMA. The
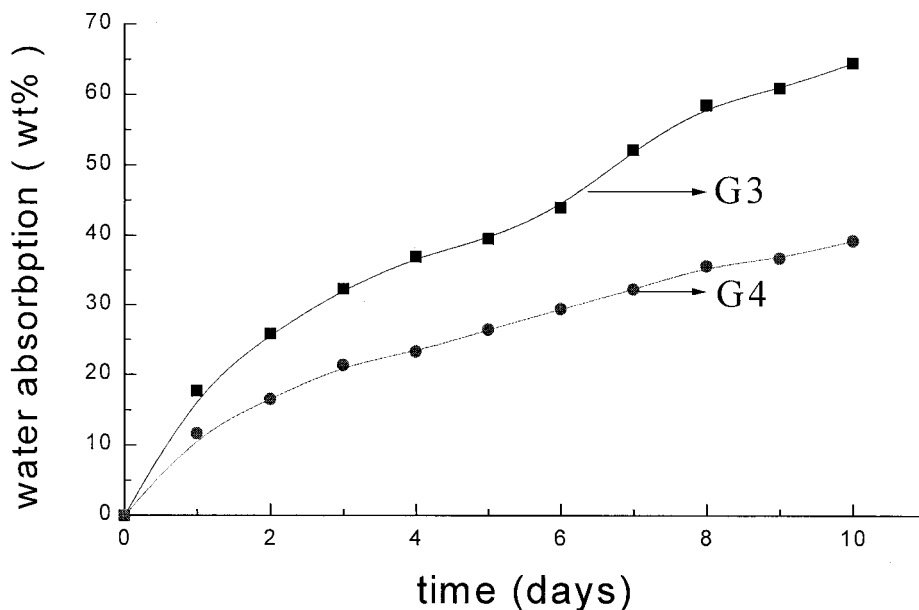

Figure 4 Typical water absorption curves for copolymer.

reaction temperatures of A2 and A4 are 75 and 65°C, respectively (while keeping other experimental conditions unchanged), as shown in Table I. The water absorption increased, whereas the particle size decreased as the temperature increased from 65 to 75°C.

CONCLUSIONS

MAA (AA) and HEMA were used as reactive cosurfactant. With the addition of the cosurfactant, the particle size of the latex obviously decreased. High monomer : surfactant weight ratios (15 : 1 or greater), relatively concentrated (~ 30 wt % latices, and small particle (~ 60 nm) diameters were obtained.

References

1. Chow, G. M.; Gonsalves, K. E., Eds. Nanotechnology: Molecularly Designed Materials; American Chemical Society: Washington, DC, 1996.
2. Siegel, R. W. Polym Mater Sci Eng 1995, 73, 26.
3. Stoffer, J. O.; Bone, T. J Polym Sci Part A: Polym Chem 1980, 18, 2641.
4. Stoffer, J. O.; Bone, T. J Dispersion Sci Technol 1980, 1, 37.
5. Atik, S. S.; Thomas, J. K. J Am Chem Soc 1981, 103, 4279.
6. Feng, L.; Ng, K. Macromolecules 1990, 23, 1048.
7. Candau, F.; Leong, Y. S.; Fitch, R. M. J Polym Sci Part A: Polym Chem 1985, 23, 193.
8. Carver, M. T.; Candau, F.; Fitch, R. M. J Polym Sci Part A: Polym Chem 1989, 27, 2179.
9. Candau, F.; Buchert, P.; Krieger, I. J Colloid Interface Sci 1990, 140, 466.
10. Holtzscherer, C.; Candau, F. Colloids Surf 1988, 29, 411.
11. Texter, J.; Oppenheimer, L. E.; Minter, J. R. Polym Bull 1992, 27, 487.
12. Gan, L. M.; Chew, C. H.; Lee, K. C.; Ng, S. C. Polymer 1994, 35, 2659.
13. Larpent, C.; Tadros, T. F. Colloid Polym Sci 1991, 269, 1171.
14. Ming, W.; Jones, F. N.; Fu, S. Macromol Chem Phys 1998, 199, 1075.
15. Santanu, R.; Surekha, D. Polymer 1997, 38, 3325.
16. Michael, D.; Bernd, T. Langmuir 1998, 14, 800.
17. Xu, X. J.; Siow, K. S.; Wong, M. K.; Gan, L. M. Colloid Polym Sci 2001, 279, 879.
18. Papp, S.; Dekany, I. Colloid Polym Sci 2001, 279, 449.
19. Hopfinger, J.; Koehler, M. G.; Pearistein, R. A.; et al. J Polym Sci Part B: Polym Phys 1988, 26, 2024.