Soapless Emulsion Polymerization of Butyl Methacrylate Through Microwave Heating

WEI-DONG HE, CAI-YUAN PAN, TAO LU

Department of Polymer Science and Engineering and The Open Laboratory of Bond-selective Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

ABSTRACT: Soapless emulsion polymerization of *n*-butyl methacrylate (BMA) was carried out through microwave heating with potassium persulfate (KPS) as an initiator at $73 \pm 2°C$. The influence of the monomer amount, the initiator amount, and the addition of ethanol on the monomer conversion, the particle size, and its distribution were studied. The results indicate that microwave polymerization had a much higher rate and produced smaller particles with a slightly broader size distribution compared with normal polymerization. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2455–2459, 2001

Key words: soapless emulsion polymerization; microwave heating; *n*-butyl methacrylate; particle-size distribution

INTRODUCTION

Latex particles prepared through soapless emulsion polymerization have many virtues such as a narrow size distribution and a "clean" surface. Thus, they can be used in a variety of areas and have attained much research interest.[1–5] However, normal soapless emulsion polymerization proceeds very slowly because fewer particles are produced.[6] Compared with normal heating, microwave heating is homogeneous and powerful. Some interesting phenomena should be observed when it is used in soapless emulsion polymerization. However, only one article presented the preparation of polystyrene latex particles with a nano-scale narrow size distribution by microwave emulsion polymerization in the presence of no or little surfactant.[7]

This article reports the microwave soapless emulsion polymerization of BMA, and the particle size and its distribution obtained were deter-mined by dynamic light scattering (DLS). The factors affecting the monomer conversion, the particle size, and the size distribution were studied.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA) and ethanol were analytical reagents. BMA was washed with a 10% sodium hydroxide (NaOH) aqueous solution and distilled water three times, dried with anhydrous magnesium sulfate, and stored in a refrigerator. It was distilled under a vacuum just before use. Potassium persulfate (KPS) was recrystallized from its saturated aqueous solution at 40°C.

Decomposition Rate Constant of KPS

Distilled water (200.0 mL) was added into a 500-mL flat-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, and a special condenser and then heated to 80°C in a modified

microwave oven. After being purged with nitrogen for 10 min, a certain amount of KPS dissolved in distilled water (50.0 mL) was added. While the reaction mixture was kept at 73 ± 2°C, a 10.00 mL solution was taken out at an interval of time. The residual KPS was titrated according to the method described in the literature.[8] The decomposition rate constant (k_{dw}) was calculated based on the following equation:

$$\ln \frac{[I]_0}{[I]_t} = k_{dw}t \qquad (1)$$

where $[I]_t$ and $[I]_0$ are the KPS concentration at time t and the initial concentration, respectively.

## Microwave Soapless Emulsion Polymerization

A 500-mL flat flask equipped with a mechanical stirrer, a nitrogen inlet, and a special condenser was placed in a modified microwave oven and then distilled water (200.0 mL) was added. The water was heated to 80°C while being purged with nitrogen. KPS dissolved in distilled water (50.0 mL) and BMA were added one by one, and the temperature of the reaction mixture was kept at 73 ± 2°C. A stable white latex was obtained after the reaction stood for 1.5 h in a nitrogen atmosphere.

Normal Soapless Emulsion Polymerization

Distillated water (200.0 mL) was added into the same flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser, but was heated to 80°C in an oil bath while being purged with nitrogen. KPS dissolved in distilled water (50.0 mL) and BMA were added one by one, and the temperature of the reaction mixture was kept at 73 ± 2°C. A stable white latex was obtained after the reaction stood for 12 h under a nitrogen atmosphere.

Determination of Monomer Conversion

The solid content (SC) was determined by a modified method similar to that described in the literature.[8] The water and unreacted monomer of the weighed latex were evaporated under a vacuum at 30°C until the weight of the remainder became constant. The monomer conversion (Con) was calculated according to the following equation:
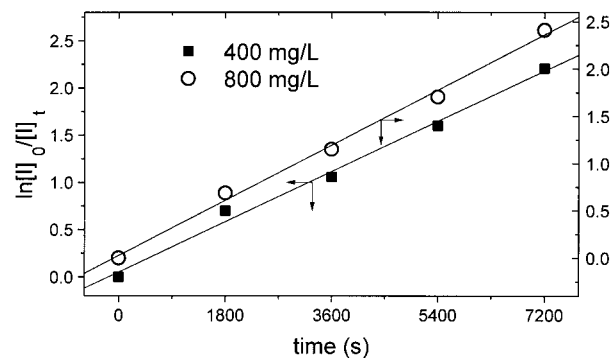
Figure 1 Decomposition rate of KPS under microwave heating at 73 ± 2°C. KPS concentration: (○) 800 mg/L; (●) 400 mg/L.

$$\text{Con} = \frac{A(V_{water}\rho_{water} + V_{BMAr}\rho_{BMAr} + V_{ethanol}\rho_{ethanol})}{V_{BMA}\rho_{BMA}} \qquad (2)$$

where V_i and ρ_i are the volume and the density of the different components, respectively.

Determination of Particle Size and Size Distribution

The latex was thinned with deionized water to a desirable concentration and passed through a 0.8-μm filter to discharge any dust. After the sample stood at 25°C in the cell chamber for 20 min, the hydrodynamic radius (R_h) and the size distribution was determined on a modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and a solid-state laser (ADLAS DPY425II, outpower = ~400 mV at λ = 532 nm).

RESULTS AND DISCUSSION

Decomposition of KPS

To investigate fully the influence of microwave heating on soapless emulsion polymerization, the decomposition of KPS under microwave heating was first studied and the results are shown in Figure 1. For different concentrations of KPS, its decomposition under microwave heating also followed a first-order reaction. Compared with k_d under normal heating (2.33×10^{-5} s^{-1} at 70°C), k_{dw} under microwave heating (3.10×10^{-4} s^{-1}) was about 10 times larger, indicating that microwave heating improved KPS decomposition.

Table I   Influence of Monomer Addition on Polymerization Under Microwave Heating

Latex	BMA (g)	Solid Content (%)	Conversion (%)	Polymerized Monomer (g)	R_h (nm)	PDI	Surface Area of Total Particles[a] ($10^4 \times$ m^2)
ST-5	4.47	1.33	76	3.38	88.0	<0.02	1.10
ST-6	5.36	1.89	90	4.83	88.5	<0.02	1.56
ST-7	6.26	2.36	97	6.05	96.0	<0.02	1.80
ST-7*[b]	6.26	2.07	85	5.31	107.7	<0.02	1.41
ST-8	7.15	2.75	99	7.07	114.2	<0.02	1.77
ST-9	8.04	2.89	93	7.46	108.2	0.06	1.97
ST-10	8.94	2.86	83	7.41	106.3	0.04	1.99

The soapless emulsion polymerization was carried out in the presence of 100 mg KPS at 73 ± 2°C under microwave heating at a stirring speed of 300 rpm in 250 mL distilled water for 1.5 h.
    [a] The surface area of the total particles was calculated based on the polymerized monomer considering R_h as the average radius of the particles.
   [b] The polymerization was carried out in oil bath at 73 ± 2°C for 12 h.

Effect of Monomer Amount

Monomer drops were clearly seen in the reaction mixture at the beginning, and then the mixture gradually became white. The recipe and results of the soapless emulsion polymerization with different monomer concentrations are listed in Table I. It is seen the that monomer conversion increased to the maximum when less than 7.15 g of the monomer was added and then decreased when more than 7.15 g of BMA was added. No change in the surface area of the total particles might suggest that the amount of KPS initiating polymerization did not increase in the cases of ST-9 and ST-10 because the particles were stabilized by the KPS ionic residues in the soapless emulsion polymerization. Therefore, the increase of the KPS decomposition rate and the number of formed nuclei with the addition of the monomer[9] would lead to a higher monomer conversion at a lower monomer concentration. On the contrary, not sufficient KPS would give rise to a decrease of the monomer conversion at a higher monomer concentration.

It is known that the more KPS molecules that initiate the polymerization the more particles are produced and the smaller the particles are. At the same time, the diameter of the particles increases with the polymerized monomers when the particle number remains unchanged. Therefore, the influence of monomer addition on the hydrodynamic radius (R_h) and its distribution were similar to that on the monomer conversion as shown in Table I. At a lower monomer concentration, there was enough KPS to initiate the polymerization and stabilize the newly formed particles in respect to the surface increase. So, the particles

produced in those cases remained homodispersed. The increase of particle size with the monomer concentration would be caused mainly by the amount of the polymerized monomer although more nuclei would be formed at early stage of polymerization. At a higher monomer concentration, a higher rate of KPS decomposition led to more nuclei being produced. At the same time, the polymerized monomer was nearly equal. Therefore, the particle size decreased. Additionally, there was not enough SO_4^- to stabilize the newly formed surface and the particles became polydispersed, especially at the latices of ST-9 and ST-10. The size distributions of some latex particles determined by DLS are shown in Figure 2.

Supposing that the particle number in all latices was the same, the particle weight should be
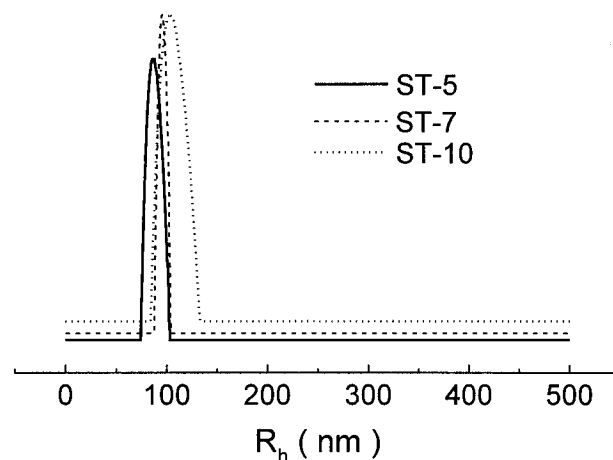
Figure 2 Effect of monomer addition on the size and its distribution of the latex particle: (——) ST-5 latex; (——) ST-7 latex; (······) ST-10 latex.

Table II   Influence of Initiator on the Polymerization Under Microwave Heating

Latex	KPS (mg)	Solid Content (%)	Conversion (%)	Polymerized Monomer (g)	R_h (nm)	PDI	Surface Area of Total Particles ($10^4 \times m^2$)[a]
K-1	125	1.70	72	4.51	101.9	0.01	1.26
K-2	150	2.10	86	5.38	107.3	0.02	1.43
K-2*[b]	150	2.37	97	6.08	116.4	0.01	1.49
K-3	175	2.19	90	5.62	114.9	0.02	1.40
K-4	200	2.30	94	5.90	150.4	0.10	1.12

The soapless emulsion polymerization of BMA (6.26 g) was carried out at 73 ± 2°C under microwave heating at a stirring speed of 200 rpm in 250 mL distilled water for 1.5 h.
[a] The surface area of the total particles was calculated based on the polymerized monomer considering R_h as the average radius of the particles.
[b] The polymerization were carried out in oil bath at 73 ± 2°C for 12 h.

3.38, 4.91, 7.85, 15.5, 13.9, and 13.0 g based on their radii with ST-5 as the standard. Compared with the data in Table I, it could be deduced that fewer particles were dispersed in other latices than in ST-5 and ST-6. While taking the monodispersity of particles of ST-7 and ST-8 into account, it was reasonable to consider that the initiation efficiency of KPS decreased with the monomer concentration and the mechanism of microwave soapless emulsion might be quite different from that of normal emulsion polymerization.

Effect of Initiator Amount

It is understandable that the solid content and monomer conversion increased with the initiator amount as listed in Table II. However, the increase of R_h with the initiator amount was very questionable considering the polymerized monomers, especially for the K-4 latex. Also, the particles of the K-4 latex became polydispersed. The probable reason might be the increase of the ion strength of the reaction mixture, which resulted in the instability of the latex particles. Thus, the particles could aggregate to form larger particles and the size distribution became broader. When the KPS concentration was high, the primary radicals and short-chain radicals would terminate each other at the early stage of polymerization. The decrease of KPS efficiency also led to larger particles with a broader size distribution.

All the polymerization conditions of ST-7 and K-1 except the stirring speed was the same, but monomer conversion and R_h are quite different. These results showed the importance of stirring.

Effect of Ethanol Amount

Chonde et al. reported that the addition of an organic solvent such as ethanol increased the particle size and the size monodispersity in the soapless emulsion polymerization of styrene (ST) and sodium vinylbenzylsulfonate (Na-VBS).[10] Therefore, the influence of ethanol on the soapless emulsion of BMA under microwave heating was studied and the results are listed in Table III.

With increase of the ethanol volume, R_h increased but its distribution became worse. The addition of ethanol improved the compatibility of poly(BMA) (PBMA) with the media and the critical chain length for the chain radicals to precipitate became larger. Therefore, fewer nuclei were produced and larger particles were obtained. At the same time, the swelling of particles by ethanol would help the diffusion of the monomer into the particles and the polymerization rate increased. More monomers polymerized in the formed particles could cause a decrease of the charge density of the particle surface. Thus, latex particles aggregated, leading to larger particles and a broader size distribution. On the contrary, the addition of ethanol decreased the compatibility of chain radicals containing the ion side group in the polymerization of ST and Na-VBS.[10]

Comparison with Normal Soapless Emulsion Polymerization

Normal soapless emulsion polymerization of BMA under the same conditions as those under microwave heating are listed in the three tables and shown in Figure 3. Under microwave heating, polymerization proceeded more rapidly and

Table III   Infuence of Ethanol on the Polymerizaion Under Microwave Heating

Latex	EtOH (mL)	Solid Content (%)	Conversion (%)	Polymerized Monomer (g)	R_h (nm)	PDI	Surface Area of Total Particles ($10^4 \times m^2$)[a]
E-1	5	1.64	68	4.27	224.1	0.01	0.54
E-2	10	2.22	94	5.96	242.9	0.18	0.65
E-2* [b]	10	2.09	88	5.87	255.2	0.15	0.66
E-3	20	2.22	97	6.08	299.8	0.24	0.58

The soapless emulsion polymerization of BMA (6.26 g) was carried out in the presence of 100 mg KPS at $73 \pm 2°C$ under microwave heating at a stirring speed of 300 rpm in 250 mL distillated water for 1.5 h.

[a] The surface area of total particles was calculated based on the polymerized monomer considering R_h as the average radius of the particles.

[b] The polymerization was carried out in an oil bath at $73 \pm 2°C$ for 12 h.

smaller particles were obtained because of the higher rate of KPS decomposition. But the size distribution of the latex particle produced remained nearly unchanged.
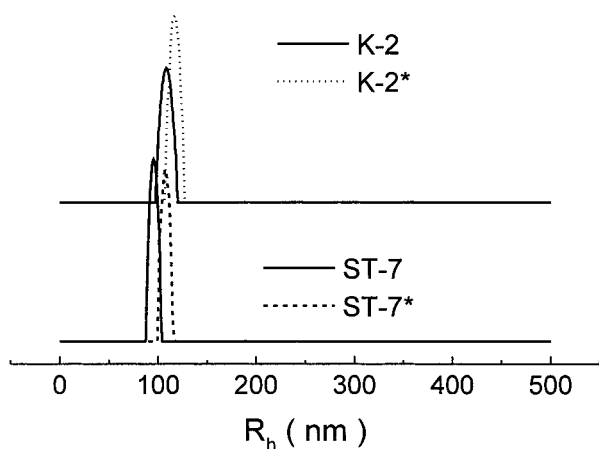
CONCLUSIONS

Soapless emulsion polymerization of BMA with KPS as the initiator were carried out under microwave heating at different initial concentrations of the monomer and the initiator. With increase of the monomer amount, the particle size increased to the maximum and then decreased due to the inadequacy of the initiator. Thus, the

particle-size distribution became broader at a high monomer concentration. The particle size increased with the increase of the initiator amount, while the particles became polydispersed due to an increase of the ion strength and a decrease of the initiator. The addition of ethanol gave rise to larger particles with a broad size distribution because of the improvement of compatibility of PBMA with the reaction media. In comparison with normal soapless emulsion polymerization, the microwave soapless emulsion polymerization rate was much higher and the particles produced were smaller with a similar size distribution.

Figure 3 Comparison of normal and microwave soapless emulsion polymerization: (—) ST-7 latex (lower) and K-2 latex (upper); (······) ST-7* latex (lower) and K-2* latex (upper).

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