Preparation of Narrowly Distributed Nanoparticles of Poly(*n*-butyl methacrylate-*co*-vinyl pyrrolidone) through Microemulsion Polymerization

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ABSTRACT: Narrowly distributed nanoparticles of poly (*n*-butyl methacrylate-*co*-vinyl pyrrolidone) were prepared through microemulsion polymerization with a nonionic surfactant of Tween-80 as emulsifier (6 wt % of the latex) and *n*-butanol as coemulsifier. The polymerizations were initiated with benzoylperoxide (BPO), potassium persulfate (KPS), KPS/ferric sulfate ($FeSO_4$), and BPO/$FeSO_4$, respectively, where the initiation in the case of BPO/$FeSO_4$ took place mainly at the interphase between the oil phase and the reaction media. Namely, this interfacial-initiated microemulsion polymerization resulted in larger particles with relatively narrower particle size distribution as well as higher limiting monomer conversion but lower polymerization rate compared with the polymerization initiated with KPS/$FeSO_4$. In this article, the influences of initiation method, monomer ratio, and addition of water-soluble components on microemulsion polymerization and latex particle size were studied to discuss the mechanism of interfacial-initiated microemulsion polymerization. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2334–2340, 2004

Key words: interface; microemulsion copolymerization; nanoparticle

INTRODUCTION

Classic (macro)emulsion is an opaque mixture with a dispersion size in the range of several hundreds to thousands nanometers and a kinetically stable system. On the other hand, microemulsion is a transparent/translucent and thermodynamically stable system with a dispersion size below 100 nanometers.[1] Due to the large interfacial area, the low interfacial tension, the high solubilization capacity, and the low viscosity, it has many applications in a variety of fields, such as oil recovery, microreactors, controlled release of drugs, etc.[2–5]

Microemulsion polymerization offers convenient access to the preparation of narrowly distributed polymeric nanoparticles with polymer molecular weights over 1×10^6. Compared with classic emulsion polymerization, only two intervals without a constant rate region are observed in microemulsion polymerizations. The maximum polymerization rate appears at about 39% conversion for the monomer having low water solubility and low polymer glass transition temperature[6,7] and significantly below this value for others.[8,9] Generally, only a small fraction of micelles is used for the nucleation and the stabilization of latex particles. The initiation locus of microemulsion polymerization initiated by an oil- or water-soluble initiator is considered to be the monomer-swollen micelles. The initiation involves two events: the formation of initiating radicals by the decomposition of initiator in the reaction media and the entry of oligomeric radicals into the micelles. As for oil-soluble initiators, the initiating radicals result from the desorption of primary radicals in the micelles or the decomposition of the initiators dissolved in water.[10] The latex particles hardly compete with the monomer-swollen micelles in capturing radicals. Each entry of radicals into the monomer-swollen micelles leads to a nucleation event. The unstable primary particles obtained agglomerate each other or with other monomer-swollen micelles to form stable colloid latex particles.[11]

Both oil- and water-soluble initiators are used in oil-in-water microemulsion polymerizations. The initiator used affects the polymerization rate and limits monomer conversion. Capek et al.[12] carried out microemulsion polymerization of butyl acrylate with sodium dodecylsulfate as emulsifier and ammonium persulfate (APS) or benzoylperoxide (BPO) as initiator, respectively. Higher polymerization rates and limiting monomer conversion for potassium persulfate (KPS)-initiated polymerization than those for BPO were observed. Redox initiators have been used in microemulsion polymerization. Microemulsion polymerization of styrene was kinetically studied using

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KPS/*p*-methyl benzaldehyde sodium bisulfite adduct as the redox initiation system and the influences of initiator concentration and temperature were discussed.[13] Xu et al.[14] prepared nanosized polymeric latex with high polymer/emulsifier ratio by microemulsion polymerization via hollow-fiber feeding of monomers using APS-tetramethylethylenediamine as a redox initiation system. Until now, the investigation of microemulsion polymerization initiated with a water-soluble chemical and an oil-soluble chemical as the redox initiation system has not been reported to our knowledge. Microemulsion copolymerizations have also been studied in several research groups but few reports are concerned with the microemulsion copolymerization of a water-soluble monomer and an oil-soluble monomer. Puig et al.[15] reported the copolymerization of styrene and acrylic acid in cationic microemulsion; only 60% overall conversion was reached. Pokhriyal et al.[16] prepared transparent or translucent latices of poly(2-ethylhexyl acrylate-*co*-acrylonitrile) with a high weight ratio of polymer to surfactant, but the particles size distribution is wide to some extent. The effects of initiator type and concentration, polymerization temperature, monomer feed ration, and cosurfactant concentration on kinetics were also investigated.[17] In another paper, reactivity ratios and the sequence distribution of copolymer were discussed in detail.[18]

Clearly, it is very difficult for a highly water-soluble monomer and a highly oil-soluble monomer to undergo emulsion copolymerization completely because of their different loci. In this paper, a microemulsion polymerization, interfacial-initiated microemulsion polymerization (IMEP), was used to prepare a nanolatex of *n*-butyl methacrylate (BMA) and *N*-vinyl pyrrolidone (NVP) in a nonionic microemulsion polymerization in the presence of 6 wt % emulsifier Tween 80. The effects of the initiation method, the addition of the water-soluble components, and the amount of NVP on emulsion polymerization were discussed.

EXPERIMENTAL

Materials

BMA and NVP were distilled under vacuum before use. Sorbitate (Tween 80), *n*-butanol, and ferric sulfate hydrate ($FeSO_4{\cdot}7H_2O$) are analytical reagents and were used as received. BPO and KPS were recrystallized and stored in a refrigerator.

IMEP BMA with NVP

For IMEP, the oil-soluble chemical BPO and the water-soluble chemical $FeSO_4$ were used as the redox initiator system. BPO (30.0 mg) was dissolved in BMA (5.0 g). Tween 80 (3.0 g) and butanol (0.40 g) were dissolved in distilled water (the amount was changed to make the total weight of the reaction mixture 50 g). Those solutions were mixed and emulsified by the aid of a supersonic cleaner for 20 min, resulting in a translucent microemulsion. The microemulsion was heated to 40°C while being purged with nitrogen. The aqueous solution, containing a certain amount of NVP and $FeSO_4{\cdot}7H_2O$ (40 mg) in distilled water (5.0 mL), was added into the microemulsion in a batch or continuously with a Sp1001 Syringe Pump for 8 h. The reaction continued for 12 h to ascertain the limiting monomer conversion.

Regular redox-initiated microemulsion polymerization of BMA with NVP

KPS and $FeSO_4$, both water soluble, were used as the redox initiator system for regular redox-initiated microemulsion copolymerization of BMA with NVP. KPS (30.0 mg) was dissolved in the microemulsion before polymerization. The solution containing NVP and $FeSO_4{\cdot}7H_2O$ (40 mg) in distilled water (5.0 mL) was added into the microemulsion. The copolymerizations were carried out in the same way as described as above.

Monocomponent-initiated microemulsion copolymerization of BMA with NVP

Only KPS (30.0 mg) or BPO (30.0 mg) was used as the initiator in this case. BPO was dissolved in BMA and KPS was dissolved in aqueous solution before polymerization. The other copolymerization parameters were the same as described above except that the temperature was kept at 65°C and the polymerization lasted for 24 h.

Determination of monomer conversion and kinetics study

After the polymerization, water, butanol, and unreacted monomer were removed from the latex in the presence of 1,4-diphenol under vacuum at 35°C until the weight of remaining substances no longer changed. The solid contents of latex (*SC*) were obtained and the final values of overall conversion of monomers (*Con*) were calculated as below.

$$Con = \frac{SC \times 50 - A - B}{W_1 + W_2} \times 100\% \qquad (1)$$

where A, B, W_1, and W_2 were the amounts of the emulsifier, initiator(s), BMA, and NVP, respectively.

To follow monomer conversion, a portion of the latex was taken out from the reaction mixture and added to 1,4-diphenol solution with known content. The mixture then was dried under vacuum until no

TABLE I
Comparison of Microemulsion Polymerizations with Different Initiation Methods[a]

Latex	Addition of the water-soluble component	Initiators (mg)			NVP (g)	Temp (°C)	Time (h)	Limiting monomer conversion (%)	Particle size[b]	
		BPO	KPS	$FeSO_4 \cdot 7H_2O$					R_h (nm)	PDI
Y-220	Batch	—	30	—	—	65	24	83	26	0.110
Y-213	Batch	—	30	—	0.5	65	24	90	32	0.048
Y-210	Batch	30	—	—	0.5	65	24	81	41	0.054
Y-209	Batch	30	—	40	0.5	65	12	88	24	0.134
Y-301	Batch	30	—	40	0.5	40	12	97	20	0.064
Y-221	Batch	—	30	40	0.5	40	12	90	18	0.106
Y-307	Continuous	30	—	40	0.5	40	12	91	24	0.034
Y-207	Continuous	30	—	—	0.5	40	24	68	25	0.054

[a] The polymerizations of BMA (5.0 g) and NVP were carried out in the presence of Tween 80 (3.0 g) and *n*-butanol (0.40 g).
[b] R_h, hydrodynamic radius of particle; PDI, the standard deviation of R_h.

change in the weight of the remaining substances was observed. *Con* was calculated in the same way as above, with the addition of 1,4-diphenol.

Determination of the size of latex particles

Dynamic laser light scattering (LLS) was performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and a He-Ne laser (output power = 10 mw at 632 nm) to obtain the latex particle size at 25°C. Before DLS measurement, the latex was diluted with distilled water to a given concentration and a filter was used to eliminate any dust (0.45 μm). The intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured. The Laplace inversion of $G^{(2)}(t,q)$ resulted in a line-width distribution $G(\Gamma)$.[19] For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $\Gamma/q^2 = D$ at $q \rightarrow 0$ and $C \rightarrow 0$, so that $G(\Gamma)$ can be directly converted to the translational diffusion coefficient distribution $G(D)$ or the hydrodynamic radius distribution $f(R_h)$ by using the Stocks–Einstein equation: $R_h = k_BT/(6\pi\eta D)$ with k_B, T, and η being the Boltzman constant, the absolute temperature, and the solvent viscosity, respectively. The polydispersity index (PDI) of R_h was defined shown in eq. (2).[19]

$$\mathrm{PDI} = \mu_2/\bar{\Gamma}^2 \text{ and } \mu_2 = \int (\Gamma - \bar{\Gamma})^2\, G(\Gamma) d\Gamma \qquad (2)$$

RESULTS AND DISCUSSION

Influence of initiation on microemulsion polymerization rate

Various microemulsion polymerizations were carried out in the presence of a sterically stabilized emulsifier of Tween 80 initiated by BPO, KPS, BPO-$FeSO_4$, or KPS-$FeSO_4$ to compare interfacial-initiated microemulsion polymerization with others. The obtained latices were translucent and stable. The recipe and other polymerization parameters are listed in Table I. Typical variation of overall monomer conversion with time is summarized in Figure 1.

At higher temperatures, the shape of the conversion-time profiles exhibits the S-shape of typical emulsion polymerization to some extent, especially for BPO-initiated polymerization. On the other hand, the shape in polymerizations initiated by redox initiation systems at lower temperatures exhibits the characteristics of microemulsion polymerization. Only two polymerization intervals without rate-constant period deviated from the curves. The limiting conversion and rate of BPO-initiated polymerization were the lowest and those of BPO-$FeSO_4$-initiated polymerization were the highest, indicating the influence of initiation type on microemulsion polymerization.

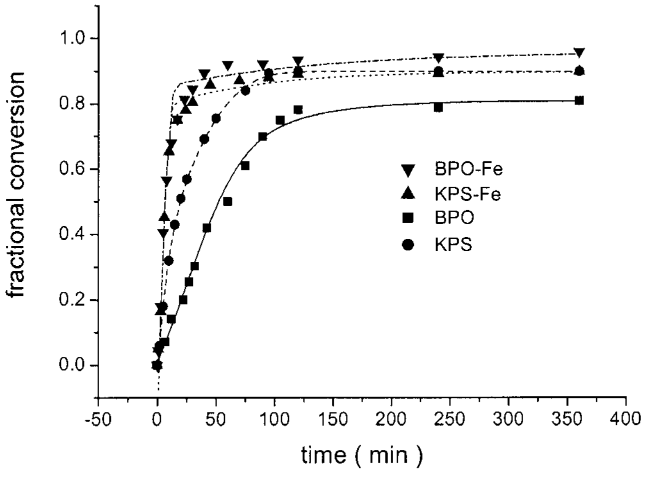

Figure 1 *Con*–time curves of different microemulsion polymerizations (■ and ——: initiated with BPO at 65°C; ● and – – –: initiated with KPS at 65°C, ▲ and ·······: initiated with KPS-$FeSO_4$ at 40°C; ▼ and —·—: initiated with BPO-$FeSO_4$ at 40°C).

TABLE II
***Q*, *e* and Reactivity Ratio (*r*) of BMA and NVP**

Monomer	*Q*	*e*	*r*
BMA	0.67	0.43	2.44
NVP	0.14	−1.14	0.034

Recently, considering a combination of nonlinear monomer partitioning, nonnegligible bimolecular termination, and, in some cases, diffusion limitations to propagation, Renko et al.[20] developed an elaborate model for microemulsion homopolymerization kinetics of *n*-butyl methacrylate (*n*-BMA), *t*-butyl methacrylate (*t*-BMA), *n*-hexyl methacrylate (*n*-HMA), and styrene with dodecyltrimethyl-ammonium bromide as the emulsifier. In the present study, microemulsion copolymerization of water-insoluble BMA with highly water-soluble NVP is quite complicate due to their different loci. Despite the great difference in their solubility in water, there is also large diversity in their reactivity ratios. Those values were calculated based on the Q-e Equation and are listed in Table II. Thus it is not easy for them to copolymerize in microemulsion polymerization. Therefore, the above model was modified to describe the copolymerization behavior as expressed in eq. (3), certainly, not considering the copolymerization might cause a discrepancy from the actual situation.

$$Con = Con_{\lim} - a_1 \exp(-A_1 t^2) - a_2 \exp(-A_2 t) \quad (3)$$

where α_1 and α_2 are the initial molar fractions of BMA and NVP in the microemulsion, respectively. $Con_{\lim}$ is the limiting conversion of monomer.

The experimental data obtained were nonlinearly fitted using Origin 6.1 software and the fit results are demonstrated as the lines in Figure 1. Thus the R_p dependences on time and conversion (*Con*) were obtained and the profiles are shown in Figure 2.

As shown in Figure 1, the results are a good fit with the experimental data for the microemulsion polymerizations with single component initiators. On the other hand, the results fit well with the experiment data in the early and late stages, but there is some discrimination in the range of medium conversion for the microemulsion polymerizations initiated by redox initiation pairs, which might be caused by the neglect of copolymerization of BMA with NVP.

Microemulsion polymerizations initiated by redox initiation pairs have a much higher R_p than those by single component initiators, although the former were carried out at lower temperatures; this is further confirmed by the comparisons of Y-307 with Y-207 and Y-209 with Y-210. The maximum R_p is located at about 31 and 27% conversion for BPO/$FeSO_4$- and KPS/$FeSO_4$-initiated polymerization, respectively. $R_{p,\max}$ for BPO-initiated polymerization appears at about 25%, while, strangely, the polymerization initiated by KPS does not show the rate-increase interval.

Limiting monomer conversion is often observed in microemulsion polymerization and can be attributed to the partial consumption of both initiator and monomer and the radical capture by the polymer particles especially at high conversion. In the present research, the limiting conversion depends on the initiator used. From Table I, it can be seen that the polymerization with BPO as initiator has a fairly low limiting conversion, which might be caused by the slow formation of

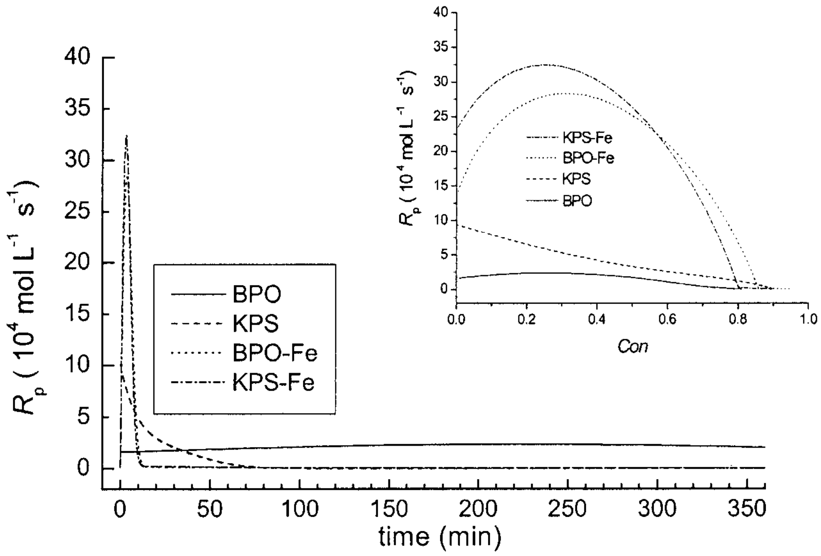

Figure 2 Theoretical variation of R_p of different polymerizations (———: initiated with BPO at 65°C; – – –: initiated with KPS at 65°C, ·······: initiated with KPS-$FeSO_4$ at 40°C; —·—: initiated with BPO-$FeSO_4$ at 40°C).

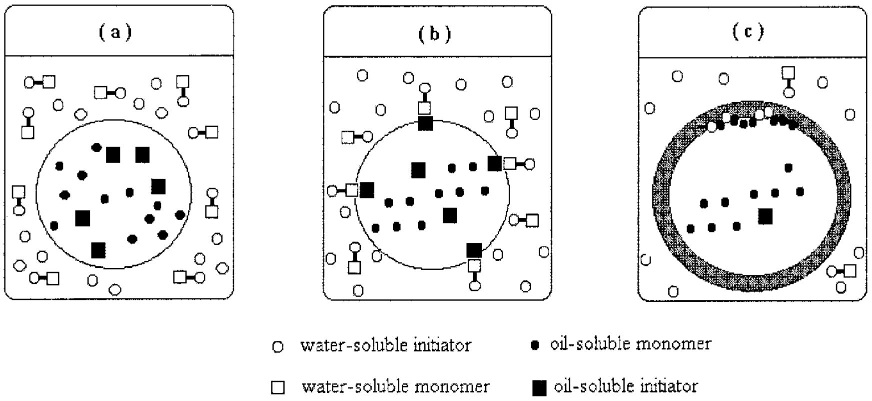

Figure 3 Demonstration of interfacial-initiated microemulsion polymerization.

primary radicals and latex nuclei. Moreover the decomposition of BPO molecules in the micelles and particles increased the noninitiation by-reaction possibility of primary radicals. After the reductive component of Fe^{2+} was used, both polymerization rate and limiting conversion increased. When the polymerization was carried out with the redox system at 40°C, one reaction event of BPO or KPS with Fe^{2+} only formed a radical. Therefore, primary termination, chain transfer, and other by-reactions were decreased to some extent. Furthermore, in the case of polymerization initiated by BPO/Fe^{2+}, two components of the initiation system are located in different phases and the formation of primary radicals is also dominated by the diffusion of two components to the interface of latex particles and monomer-swollen micelles, leading to low polymerization rate and by-reaction possibility of primary radicals.

Influence of initiation on particle size and its distribution

As shown in Tables I and III, different microemulsion polymerizations result in the formation of nanoparticles, but the size depends on the initiation methods.

As for microemulsion polymerizations carried out at 65°C, homo-PBMA latex (Y-220) had the lowest particle size, with rather broad distribution, compared with copolymer lattice. It was thought that copolymer latex particles with smaller sizes should be obtained due to copolymerization of BMA with NVP. Although copolymerization would increase the particle hydrophilicity by "grafting" water-soluble PNVP units and strengthen the tendency of polymerization in water to some extent, the number of monomer-swollen micelles is too large, so that the homogeneous nucleation should be neglected. In other words, the presence of NVP may not increase the number of particles through the homogeneous nucleation. In microemulsion polymerization, continuous nucleation occurs throughout the whole polymerization and the latex size slightly changes with the conversion. It is very difficulty for the latex particles to interfuse and to form larger particles due to the hindrance of the surfactant "wall" after the nucleation. Thus, the monomer migration from free monomer-swollen micelles to the polymerizing latex particles should be responsible for the size increase in the microemulsion copolymerization and its tendency depends on the nature and the formation of primary radicals. In copolymerization, graft PNVP units might prohibit the movement of radicals through the latex interface, leading to longer radical life. Therefore, the BMA monomer would migrate from free monomer-swollen micelles to polymerizing particles to supplement the decrease in monomer concentration. This explanation is demonstrated by the fact that the latex particles using BPO as the initiator are larger than those using KPS as the initiator. Monomer migration from free monomer-swollen micelles to polymerizing particles also decreases the probability of continuous nucleation and results in a narrower distribution of particle size.

Latex Y-209 prepared with BPO/$FeSO_4$-initiated microemulsion polymerization has a smaller particle size and a wider size distribution compared with latex 210 without $FeSO_4$. In the former case, the radical formation at the interface of monomer-swollen micelles creates an easy way for the primary radicals to initiate the polymerization in the micelles. Therefore, more nucleation leads to the results above.

Comparing emulsion polymerization at different temperatures, the larger size of the latex particles prepared at 65°C was caused by the increase in surfactant solubility and the collision possibility of latex particles, which also might cause the broader size distribution. Moreover, the size of latex particles prepared by BPO/$FeSO_4$-initiated polymerization was larger than that by KPS/$FeSO_4$-initiated polymerization.

Thus, IMEP was suggested as demonstrated in Figure 3. The water-insoluble components of BPO and BMA in the micelle and particle and the water-soluble

TABLE III
Interfacial Initiated Microemulsion Polymerization of St with NVP in the Presence of Tween 80 (3.0 g) and *n*-Butanol (0.40 g) at 40°C

		Monomer conversion (%)			Particle size[a]	
Latex	NVP (g)	Overall	NVP	Polymerized NVP (g)	R_h (nm)	PDI
Y-307[b]	0.5	95.5	50.4	0.25	24	0.034
Y-308[b]	0.8	93.2	50.9	0.41	24	0.048
Y-309[b]	1.1	91.5	52.7	0.58	22	0.053
Y-410[b]	1.4	91.6	61.4	0.86	24	0.078
Y-411[b]	1.7	89.7	59.4	1.01	24	0.044
Y-412[b]	2.0	88.7	60.6	1.21	22	0.064
Y-431[b]	2.5	85.8	57.5	1.43	24	0.033
Y-301[c]	0.5	93.6	30.2	0.15	20	0.064
Y-302[c]	0.8	90.7	32.8	0.26	20	0.048
Y-303[c]	1.1	87.5	30.8	0.34	22	0.053
Y-304[c]	1.4	88.5	47.6	0.67	20	0.062
Y-306[c]	1.7	87.6	51.0	0.87	18	0.060
Y-413[c]	2.0	85.4	48.8	0.98	18	0.050
Y-432[c]	2.5	81.8	45.5	1.14	19	0.33

[a] R_h, hydrodynamic radius of particle; PDI, the standard deviation of R_h.

[b] The water-soluble components of NVP and $FeSO_4$ were added continuously over 8 h.

[c] The water-soluble components of NVP and $FeSO_4$ were added in batch.

components of NVP and $FeSO_4$ in water diffused to the interfacial layer mainly composed of the surfactant and cosurfactant Figure 3(a). The redox reaction between BPO and $FeSO_4$ occurs and primary radicals are formed Figure 3(b). Therefore, copolymerization of BMA and NVP proceed in the interfacial layer. In this way, radicals are formed mostly at the interface between the oil and water phases and the possibility of copolymerization increases. On the contrary, radicals are formed in the oil phase or in water phase for other microemulsion polymerizations. Copolymerization behavior in terms of polymer composition and copolymer sequential distribution will be discussed in a later study.

Influence of the addition of water-soluble components on IMEP of BMA with NVP

IMEPs of BMA (5.0 g) and NVP were carried out by continuous or batch addition of the water-soluble components in the presence of Tween 80 (3.00 g) and *n*-butanol (0.40 g) at 40°C. The recipe and the results are listed in Table III. Because the IMEPs of BMA and NVP were almost complete in 12 min as shown in the inset profiles in Figure 2, BMA conversion was considered to be 100%. Thus the amount of polymerized NVP was calculated and the results are also listed in Table III.

Clearly, a higher initial concentration of NVP in the water phase for the polymerizations with batch addition than that for continuous addition would give rise to a higher overall conversion. However, the latter has higher overall monomer conversion than the former, which should result from more NVP participating in copolymerization as shown in Table III.

There are three possibilities of primary radicals produced at the interface in IMEP. First, they initiate copolymerization of BMA and NVP at the interface and the propagating chain end may stretch into or out of the latex particles. Second, they directly enter into the latex particles and couple with the propagating radicals, leading to the termination of polymerization in an individual latex particle or initiation of the monomer BMA in the latex particles. Third, they escape from the interphase and initiate homopolymerization of NVP. When the water-soluble components were added in batch, higher concentration of Fe^{2+} led to faster formation of primary radicals at the interface. Therefore, more nuclei were formed in the same duration compared with the case of continuous addition. At the same time, the second possibility happens to a greater extent and it increases the loss of BPO. After the nucleation, the increase of viscosity in the latex particles with polymerization made the diffusion of BPO more and more difficult. Fewer initiation events during the rate-decrease interval happened and less NVP was polymerized in this case. On the contrary, when the water-soluble components were added continuously, both initial concentrations of Fe^{2+} and NVP were very low. The nuclei number was much lower at the early stage of polymerization and increased with time. At the same time, noninitiation loss of BPO was reduced. While more and more nucleation took place, the decrease of BMA concentration in the polymerizing particles made it possible for the BMA monomer to migrate from free monomer-swollen micelles to polymerizing particles. Furthermore, more initiation events at the interphase of latex particles during the rate-decrease interval happened and more NVP monomers were graft-polymerized onto the particles. Therefore, larger particles were produced with higher overall monomer conversion.

With the increase of NVP amount, overall monomer conversion increases and it is caused by the increase of polymerized NVP. Unexpectedly, the particle size remains almost unchanged with the increase in NVP.

CONCLUSION

Latex particles of poly(*n*-butyl methacrylate-*co*-vinyl pyrrolidone) with radius below 25 nm and PDI below 0.08 were prepared through BPO-$FeSO_4$ IMEP with an nonionic surfactant of Tween-80 as emulsifier (6 wt % of the latex) and *n*-butanol as coemulsifier at 40°C. Its maximum polymerization rate appeared at about 31%

of monomer conversion. The polymerizations initiated by the KPS-$FeSO_4$ redox system resulted in larger latex particles and gave rise to a higher polymerization rate and lower limiting monomer conversion. Its maximum polymerization rate appeared to be about 27%. This phenomenon might be caused by the fast formation and greater noninitiation reaction of primary radicals. Comparing IMEPs with batch and continuous additions of water-soluble components, the latter had relative larger latex particles due to more NVP taking part in copolymerization.

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