

Concentrated Emulsion Copolymerization of Butyl Acrylate and Vinyl Acetate Initiated by a Redox Initiator at Lower Temperature

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ABSTRACT: The concentrated emulsion copolymerization of butyl acrylate and vinyl acetate with an ammonium persulfate/sodium hydrogen sulfate mixture as a redox initiator, with a sodium dodecyl sulfate/cetyl alcohol mixture as a compound surfactant, and with poly(vinyl alcohol) as a liquid film reinforcer was carried out at lower temperature. In less than 3 h, the polymerization conversion was greater than 95%. The effects of the surfactant, the initiator, the volume fraction of the monomer, and the temperature on the stability of the concentrated emulsion, the kinetic process, and the average size of the latices were examined. The morphology of the polymer particles was observed by transmission electron microscopy, and the average size and distribution of the particle diameter were measured by photon

correlation spectroscopy. The kinetic equation was $R_p = k[M]^{0.38}[I]^{0.89}[E]^{-0.80}$ at 30°C (where R_p is the polymerization rate, $[I]$ is the initiator concentration, $[M]$ is the monomer concentration, and $[E]$ is the concentration of the compound surfactant), and the apparent activation energy was 22.69 kJ/mol. The thin-layer polymerization of the concentrated emulsions, which enabled the removal of the heat of polymerization, was performed first. In comparison with test-tube polymerization, thin-layer polymerization provided a more regular morphology of the polymer particles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 570–576, 2004

Key words: emulsion copolymerization; initiators; kinetics (polym.)

INTRODUCTION

Concentrated emulsions are gel-like emulsions in which the volume fraction of the dispersed phase (ϕ) is greater than 0.74. The dispersed phase is in the form of spherical or polyhedral cells separated by a continuous-phase network of thin films. Concentrated emulsions have three important characteristics:^{1–3} (1) the reduced monomer mobility between cells, because of the presence of a reinforced surfactant layer, can generate an earlier gel effect, which leads to a delay in the bimolecular termination reaction and, therefore, a higher molecular weight; (2) the particle size can be controlled easily by the selection of a suitable surfactant type and concentration; and (3) a polymer containing little water, from which powdery resins are easily formed, can be obtained through concentrated emulsion polymerization.

In comparison with the four methods of free-radical polymerization (bulk, solvent, suspension, and emulsion), concentrated emulsions have not only a paste-like appearance and a high solid content but also a

nucleation mechanism for the latex particle; the morphology of latex products is different from that of conventional emulsion polymerization. For these reasons, concentrated emulsion polymerization deserves to be studied deeply and widely. Earlier, in studies on concentrated emulsion polymerization, thermolysis initiators were examined.^{4,5} For example, concentrated emulsions initiated by 2,2'-azobisisobutyronitrile have been investigated in our laboratory.^{6–8} In these systems, a reaction temperature greater than 50°C is indispensable, but this leads to the instability of a concentrated emulsion. As a solution to this problem, concentrated emulsion polymerizations initiated at lower temperature by redox initiators^{9–11} have been studied in recent years, but all the redox initiators that have been used are oil-soluble. A concentrated emulsion polymerization of butyl acrylate (BA) and vinyl acetate (VAc), initiated by a water-soluble redox initiator made of ammonium persulfate (APS) and sodium hydrogen sulfate (SHS), has not previously been reported. Because the latices of BA/VAc are widely used as coatings and pressure-sensitive adhesives, we have researched the concentrated emulsion polymerization of BA/VAc with a distinct reaction vessel in detail.

Latices of BA/VAc were prepared via concentrated emulsion polymerization with a water-soluble APS/SHS redox system as an initiator in the presence of sodium dodecyl sulfate (SDS)/cetyl alcohol (CA) as a

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compound surfactant and poly(vinyl alcohol) (PVA) as a liquid film reinforcer at lower temperature. The dependence of the kinetics and the average particle size on various parameters, such as the concentrations of the compound surfactant and initiator, the monomer volume fraction, and the polymerization time and temperature, were examined in detail. The morphology of the latex particles was observed by transmission electron microscopy (TEM), and the particle size and particle diameter distribution were determined by photon correlation spectroscopy (PCS). Because of the gel-like appearance of the concentrated emulsions, the thin-layer polymerization of the concentrated emulsions was first used to solve the thermal conduction problem. The kinetics of the thin-layer polymerization of the concentrated emulsions was also studied, and this provided some fundamental parameters of thin-layer polymerization at lower temperature.

EXPERIMENTAL

Materials

BA (chemical grade) and VAc (chemical grade) were distilled under reduced pressure for the removal of the inhibitor and then were stored in a refrigerator until they were used. SDS, CA, and PVA were purchased from Japan. APS and SHS were analytical grade and were used directly. Water was deionized.

Preparation and polymerization of the concentrated emulsions

Certain amounts and ratios of SDS/CA, PVA, APS, and H₂O were placed in a 250-mL, four-necked flask equipped with a mechanical stirrer, a funnel, and a nitrogen inlet. Monomer mixtures of BA and VAc were dropped into the flask under stirring at a suitable dropping rate so that phase separation would be avoided. The whole dropping process lasted about 15 min, and then a water solution of the reducer SHS was injected into the system and dispersed completely. Stirring was stopped after 5 min. The entire experi-

TABLE I
Typical Recipes Used in the Preparation of Concentrated Emulsions

Components	Amount (g)
Dispersed phase: mass of BA/mass of VAc = 9/1	50.00
Continuous phase: H ₂ O	10.00
Surfactant: SDS	1.00
Cosurfactant: CA	0.50
Liquid film reinforcer: PVA-1788	0.1
Oxidant: APS	0.16
Reducer: SHS	0.06

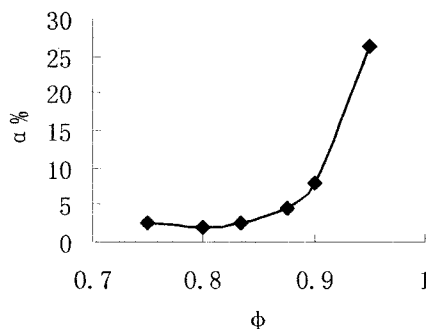


Figure 1 Effect of ϕ on the stability of the concentrated emulsions ([E] = 0.15 g/mL of H₂O, mass of SDS/mass of CA = 2/1, PVA = 1% H₂O).

ment was conducted at room temperature. The polymerization was carried in two ways.

Test-tube polymerization

Each prepared gel-like emulsion was transferred into a preweighed 10-mL centrifugal test tube that was sealed with a rubber septum. A mild centrifugation rate (1300 rpm, <1 min) was used to pack the concentrated emulsion. Then, the test tube was placed in a temperature-controlled water bath, and the polymerization was carried out for a certain time.

Thin-layer polymerization

Each prepared concentrated emulsion was transferred to a mold to form a thin layer, and then the mold was placed in a temperature-controlled oven. The basic recipe for the concentrated emulsion polymerization is presented in Table I.

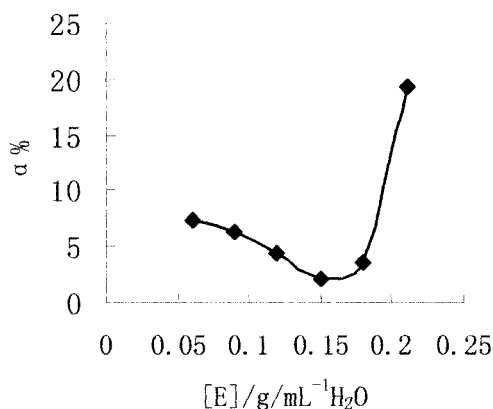


Figure 2 Effect of the compound surfactant concentration on the stability of the concentrated emulsions ($\phi = 0.833$, mass of SDS/mass of CA = 2/1, PVA = 1% H₂O).

TABLE II
Effect of the Temperature on the Concentrated Emulsion Stability

	Temperature (°C)						
	0	10	20	30	40	50	60
α (%)	None	1.337	2.943	3.579	6.273	16.992	None

[E] = 0.15 g/mL of H₂O; mass of SDS/mass of CA = 2/1; PVA = 1% H₂O; temperature = 30°C; ϕ = 0.833.

Stability of the concentrated emulsions

Each concentrated emulsion (free of initiators) was transferred into a 10-mL centrifugal tube with a spatula. After mild centrifugation, the tube containing the concentrated emulsion was placed in a 30°C temperature-controlled water bath for 24 h. The stability was measured in terms of the weight fraction (α) of the bulk phases separated from the concentrated emulsion. The larger α was, the lower the stability was of the concentrated emulsion.

Kinetics of the polymerization

During the polymerization process, 0.5-g samples were taken from the reaction vessel at regular intervals and placed in a preweighed culture dish containing hydroquinone. The samples were dried in a vacuum oven until the weight was constant. The polymerization conversion was calculated by a gravimetric method. The slope (dc/dt) of the conversion–time curves [the conversion was 20–70% when the polymerization rate (R_p) was relatively constant] and the linear correlation coefficient (r), and R_p were calculated with the following equation: $R_p = dc/dt \times [M]_0$

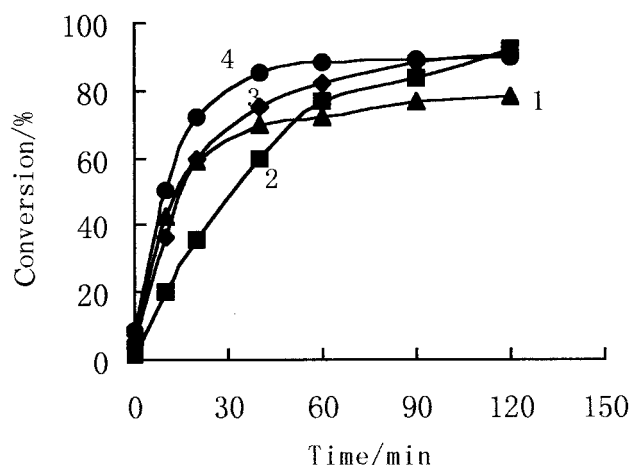


Figure 3 Conversion versus time at various values of β : (1) 1.2, (2) 1.75, (3) 2.67, and (4) 0.83 ([E] = 0.55 mol/L of H₂O, mass of SDS/mass of CA = 2/1, temperature = 30, PVA = 1% H₂O, ϕ = 0.83).

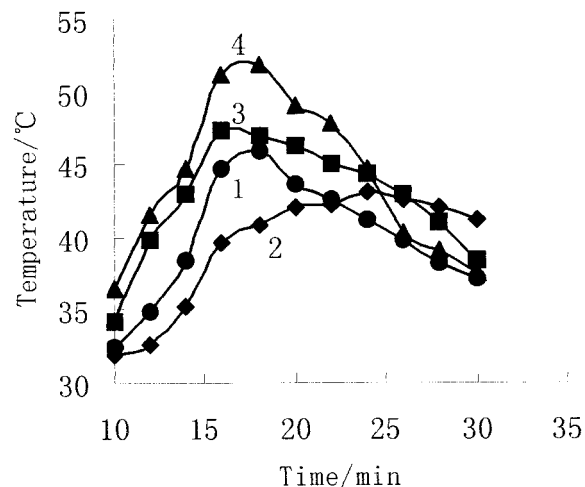


Figure 4 Change in the reaction temperature with time according to various values of β : (1) 1.2, (2) 1.75, (3) 2.67, and (4) 0.83 ([E] = 0.55 mol/L of H₂O, mass of SDS/mass of CA = 2/1, temperature = 30°C, PVA = 1% H₂O, ϕ = 0.83).

(where $[M]_0$ represents the initial monomer molar concentration).¹²

TEM

The morphology of the latex particles was examined with TEM (JEM-100XS, JEOL Ltd., Tokyo, Japan).

PCS

The average particle diameter (nm) and particle diameter distribution (which varied between 0 and 1) were determined by PCS (Loc-Fc963 autosizer, Malvern, England).

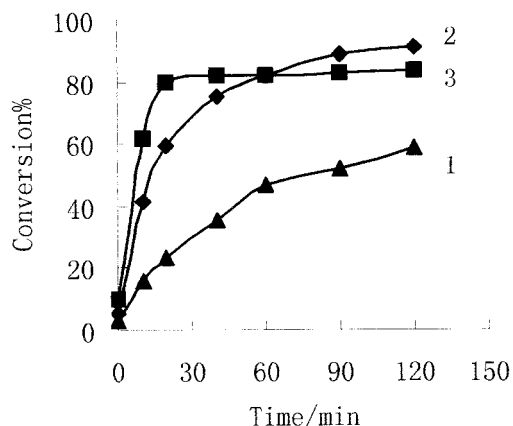


Figure 5 Conversion versus time at various initiator concentrations: (1) 0.06395, (2) 0.1279, and (3) 0.2558 mol L⁻¹ ([E] = 0.55 mol/L of H₂O, mass of SDS/mass of CA = 2/1, mass of APS/mass of SHS = 2.67, temperature = 30°C).

TABLE III
Effect of the Initiator Concentration on R_p

[I] (mol L ⁻¹)	dc/dt (min ⁻¹)	R	R_p (mol L ⁻¹ min ⁻¹)	$\ln R_p$	$\ln [I]$
0.0639	1.0250	0.9919	0.6999	-0.3568	-2.7497
0.1279	2.700	0.9825	1.8437	0.6117	-2.0479
0.2558	3.5035	0.9614	2.3923	0.8723	-1.3634

RESULTS AND DISCUSSION

Stability of the concentrated emulsions

The stability of the concentrated emulsions refers to the resistance to the formation of two separate phases. Concentrated emulsions should remain stable not only at room temperature but also at the reaction temperature. The stability of the concentrated emulsions is closely related to the subsequent polymerization reaction. Here we discuss the effects of ϕ , the concentration of the compound surfactant ([E]), and the temperature on the stability.

Effect of ϕ

Figure 1 presents the relationship between ϕ and the stability of the concentrated emulsions. The stability of the concentrated emulsions decreased with increasing ϕ because the thin films separating the cells ruptured more easily. When ϕ was greater than 0.9, stable concentrated emulsions of this system could hardly be prepared.

Effect of the compound surfactant concentration

Figure 2 shows the proper range of the compound surfactant concentration for the preparation of stable concentrated emulsions in this system. Mechanically

strong interfacial films could ensure the stability of the cells of the concentrated emulsions. The interfacial films that adsorbed surfactant molecules were condensed to form strong lateral intermolecular interactions. When the concentration of the compound surfactant was less than 0.06 g/mL of H₂O, an insufficient number of compound surfactant molecules were adsorbed into the interfacial films to form strong enough interfacial films. With an concentration of the compound surfactant, more surfactant molecules were adsorbed, preventing the coalescence of the cells. However, when the concentration of the compound surfactant reached 0.21 g/mL of H₂O, the viscosity of the system was too high, and this hindered the cooperation of the continuous phase with the dispersed phase. The most suitable concentration of the compound surfactant was 0.15 g/mL of H₂O.

Effect of the temperature

Table II shows the relationship between the temperature and stability of the concentrated emulsions. The stability decreased with increasing temperature, and this was due to the increasing coalescence of the cells. However, when the temperature was less than 0°C or greater than 60°C, no concentrated emulsion was formed.

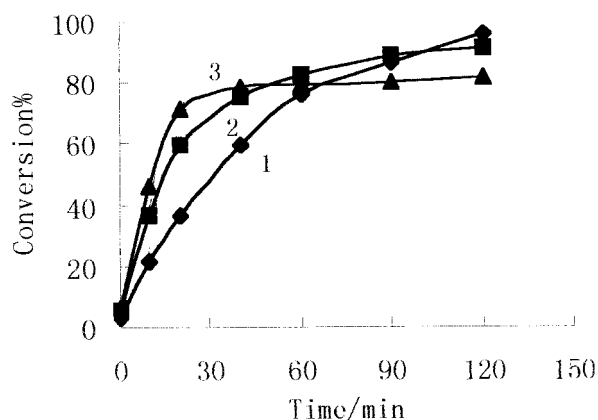


Figure 6 Conversion versus time at various concentrations of the compound surfactant: (1) 0.21, (2) 0.15, and (3) 0.09 g/mL of H₂O (mass of SDS/mass of CA = 2/1, PVA = 1% H₂O, temperature = 30°C, mass of APS/mass of SHS = 2.67, [I] = 0.1279 mol L⁻¹).

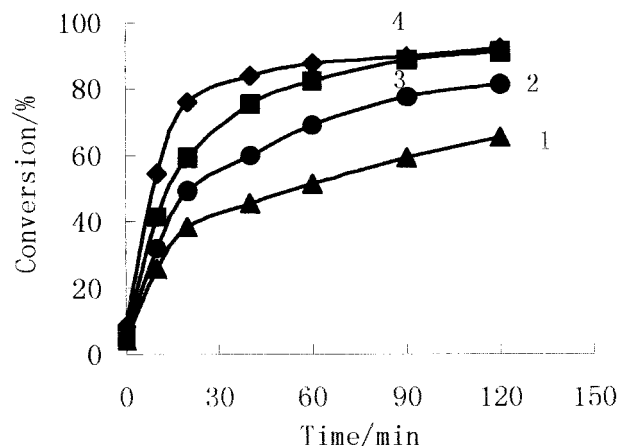


Figure 7 Conversion versus time at various values of ϕ : (1) 0.90, (2) 0.875, (3) 0.83, and (4) 0.80 ([E] = 0.55 mol/L of H₂O, mass of SDS/mass of CA = 2/1, temperature = 30°C, APS/SHS = 2.67 (g/g), [I] = 0.1279 mol L⁻¹, PVA = 1% H₂O).

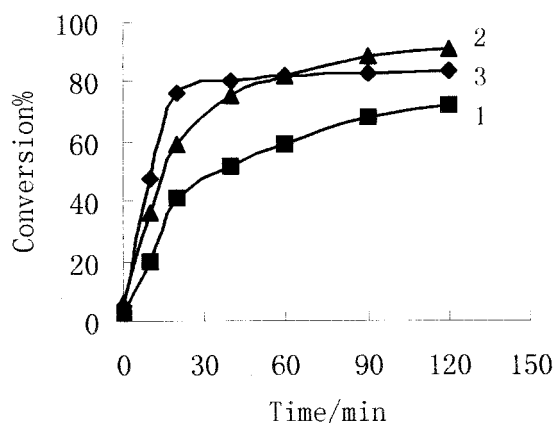


Figure 8 Conversion versus time at various temperatures: (1) 293, (2) 303, and (3) 313 K ([E] = 0.55 mol/L of H₂O, mass of SDS/mass of CA = 2/1, $\phi = 0.83$, APS/SHS = 2.67(g/g), [I] = 0.1279 mol L⁻¹, PVA = 1% H₂O).

Kinetics of the concentrated emulsion polymerizations

Effect of the APS/SHS mass ratio (β)

With the initiator/monomer mass ratio constant at 0.44 and with changes in β , time-conversion curves are given in Figure 3. During polymerization, the polymerization heat always made the internal temperature of the emulsion higher than the temperature controlled by the water bath. Figure 4 presents temperature-time curves at various β values. The experiments showed that too high a temperature inside the emulsions led to the rupture of the interfacial films and the coalescence of the cells; this resulted in larger α values of the bulk phases separated from the concentrated emulsions. A constant β value of 2.67 was suitable.

Effect of the initiator concentration ([I])

With β constant at 2.67, the conversion-time curves for different initiator concentrations are shown in Figure 5. The dc/dt values of the conversion-time curves and R (R is the correlation coefficient) were calculated by the linear regression method. R_p (mol L⁻¹ S⁻¹) was calculated from the equation as the Experiment section describes. The effect of the initiator concentration on R_p is shown in Table III. A conversion-time plot for various initiator concentrations showed that R_p increased with increasing initiator concentration because, as the concentration of the initiator increased, the number of primary free radicals increased and, consequently, R_p increased. Plotting $\ln R_p$ versus $\ln [I]$, we drew a straight line with a slope of 0.89; therefore, R_p proportional to $[I]^{0.89}$.

Effect of the surfactant concentration

Figure 6 shows the effect of the surfactant concentration on R_p . R_p increased as the concentration of the

compound surfactant decreased; which is one of the most important differences with respect to concentrated emulsions initiated by oil-soluble redox initiators. In this system, the initiators were dissolved in a continuous phase, and the higher concentration of the compound surfactant created stronger interfacial films, which made it difficult for primary free radicals decomposed by initiators to get into the cells to initiate the chain. The effect of the concentration of the compound surfactant on R_p was also studied by the plotting of $\ln R_p$ versus $\ln [E]$. A straight line with a slope of -0.80 represents $R_p \propto [E]^{-0.80}$.

Effect of the monomer concentration ([M])

Figure 7 shows the effect of the monomer concentration on R_p . Using the method mentioned previously, we could easily draw the conclusion that R_p was proportional to $[M]^{0.38}$.

Effect of the polymerization temperature

Figure 8 shows the relationship between the conversion and time at different polymerization temperatures. The same experiments at 20, 30, and 40°C were carried out, and then the plots of the conversion versus the time were also drawn. R_p increased with increasing temperature. Also, too high a temperature reduced the final conversion because a too high reaction temperature led to a serious rupture of the interfacial films and the coalescence of the cells; this resulted in a greater α value of the bulk phase separated from the emulsions. By plotting $\ln [R_p]$ versus T^{-1} , we calculated the slope to be 2729.4 and, therefore, the activation energy to be $2729.4 \times 8.314 = 22.69$ kJ/mol by an Arrhenius equation.

Analysis of the polymer particles

Latex particles of different sizes and size distributions were prepared by concentrated emulsion polymerization. The particle size was controlled by the diameter

TABLE IV
Effect of the Compound Surfactant on the Average Particle Size (D) and Dispersity

	[E] (g/mL of H ₂ O)	SDS/CA (g/g)	D (nm)	Dispersity
1	0.09	2/1	332.8	0.209
2	0.15	2/1	242.3	0.159
3	0.21	2/1	227.1	0.216
4	0.27	2/1	185.6	0.164
5	0.15	1/1	238.9	0.257
6	0.15	1/1.5	497.3	0.361

PVA = 1% H₂O; temperature = 30°C; APS/SHS = 2.67 (g/g); $\phi = 0.83$; [I] = 0.1279 mol L⁻¹.

TABLE V
Effect of ϕ on the Average Particle Size and Dispersity

ϕ	D (nm)	Dispersity
0.75	177.4	0.082
0.80	202.6	0.116
0.83	242.3	0.159
0.875	295.5	0.197

[E] = 0.55 mol/L; mass of SDS/mass of CA = 2/1; PVA = 1% H₂O; temperature = 30°C; [I] = 0.1279 mol L⁻¹; APS/SHS = 2.67 (g/g).

of the cells, so the particle size could be controlled by the adjustment of factors influencing the size of the cell, such as the type and concentration of the compound surfactant, the monomer volume fraction, the polymerization temperature, and the concentration of the initiator.

Effect of the compound surfactant

The effects of the surfactant concentration and the SDS/CA mass ratio on the particle size and particle size distribution are listed in Table IV. The average particle size decreased gradually with an increasing concentration of the compound surfactant because larger surface areas between the continuous and dispersed phases protected by the adsorbed surfactant became possible as the surfactant concentration increased. The presence of the long-chain alcohol CA increased the distance between the charged head group of the SDS molecule, and this reduced the electrostatic repulsion between them and increased the cohesion. The aforementioned experiments showed that when the SDS/CA mass ratio was 2/1 and the surfactant concentration was 0.15 g/mL of H₂O, the concentrated emulsions had optimum stability and dispersity. At relatively low surfactant concentrations, the coalescence of some cells could occur because there was not enough surfactant to cover the interfacial films. However, excessive surfactant produced a large ionic strength, which shielded against the static electricity repulsion of the cells; therefore, the coalescence of some cells occurred again.

TABLE VI
Effect of Temperature on the Average Particle Size (D) and Dispersity

Temperature (K)	D (nm)	Dispersity
293	231.6	0.0574
303	242.3	0.159
308	262.5	0.162
413	286.5	0.174

[E] = 0.55 mol/L; mass of SDS/mass of CA = 2/1; ϕ = 0.83; PVA = 1% H₂O; [I] = 0.1279 mol L⁻¹; APS/SHS = 2.67 (g/g).

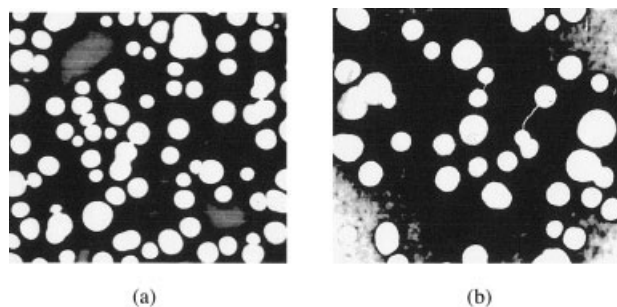


Figure 9 TEM images by (a) thin-layer polymerization and (b) test-tube polymerization (20,000 \times).

Effect of ϕ

The average size of the particles and the dispersity increased when ϕ increased, as Table V shows. This may have occurred because increasing ϕ led to the interfacial area increasing and the surfactant, distributed in the films of every cell, decreasing, and so the coalescence of some cells occurred.

Effect of the temperature

The effects of the temperature on the average diameter and dispersity of the particles are listed in Table VI. The average particle size and dispersity increased with increasing temperature. This may have been due to the higher temperature, which resulted in the greater coalescence of the cells or particles.

Thin-layer polymerization of the concentrated emulsions

Because R_p initiated by a redox initiator is fast at low temperatures, thin-layer polymerization could be used to make the thermal conduction of this system easier. The differences in the particle morphology, average particle size, and polymerization kinetics between test-tube polymerization and thin-layer polymerization were determined.

Analysis of the polymer particles prepared by thin-layer polymerization

The latex particles prepared by thin-layer polymerization were smaller and more regular than those pre-

TABLE VII
Effect of the Polymerization Method on the Average Particle Size (D) and Dispersity

Polymerization method	D (nm)	Dispersity
Thin-layer polymerization	189.6	0.124
Test-tube polymerization	242.3	0.159

[E] = 0.55 mol/L of H₂O; mass of SDS/mass of CA = 2/1; PVA = 1% H₂O; temperature = 30°C, ϕ = 0.83; [I] = 0.1279 mol L⁻¹; APS/SHS = 2.67 (g/g).

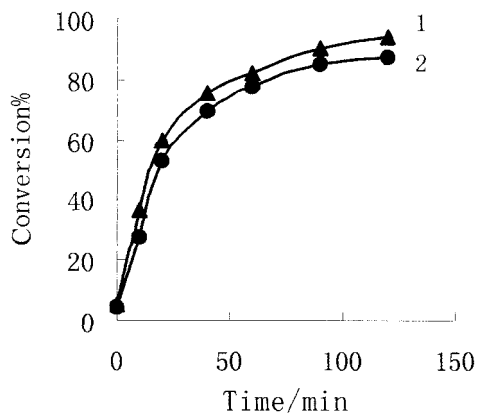


Figure 10 Conversion versus time: (1) test-tube polymerization and (2) thin-layer polymerization ($[E] = 0.55$ mol/L of H_2O , mass of SDS/mass of CA = 2/1, temperature = $30^\circ C$, APS/SHS = 2.67(g/g), $[I] = 0.1279$ mol L^{-1} , PVA = 1% H_2O , $\phi = 0.83$).

pared by test-tube polymerization, as Figure 9 and Table VII show. This was due to the excellent thermal conduction of thin-layer polymerization and reduced coagulation between the cells or particles.

Kinetics of thin-layer polymerization

The conversion–time curve of thin-layer polymerization is similar to that of test-tube polymerization (Fig. 10). This is due to easy thermal conduction and subsequent decreases in the internal temperature of the system, which led to the initial R_p decrease. Because the large surface area of the reaction system led to more monomer volatilizing, the final conversion of thin-layer polymerization also decreased.

CONCLUSIONS

BA/VAc concentrated emulsion polymerizations initiated by the water-soluble redox initiator APS/SHS were conducted at lower temperature:

1. Stable concentrated emulsions were obtained under the following conditions: $\phi < 0.9$, $[E] = 0.15$ g/mL of H_2O , and temperature = $20\text{--}40^\circ C$.
2. The kinetics of concentrated emulsion polymerization were studied, the kinetic equation being $R_p = k[M]^{0.38}[I]^{0.89}[E]^{-0.80}$ at $30^\circ C$ and the apparent activation energy being 22.69 kJ/mol.
3. Increasing the compound surfactant concentration, decreasing the temperature, and decreasing ϕ led to decreases in the average particle diameter and particle diameter distribution.
4. The latex particles prepared by thin-layer polymerization were smaller and more regular than those prepared by test-tube polymerization because of the excellent thermal conduction of thin-layer polymerization. However, the volatility of the monomer should be reduced in future studies.

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