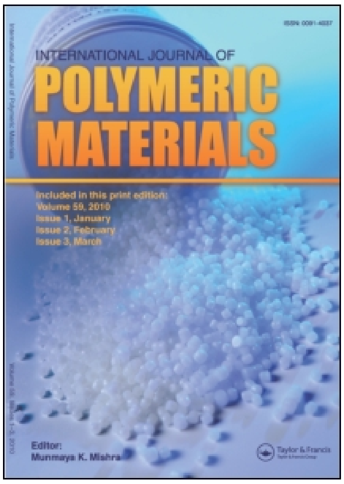

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Synthesis and properties of reactive polymer microspheres by emulsifier-free emulsion polymerization of styrene-butyl acrylate-2-hydroxyethyl acrylate

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SYNTHESIS AND PROPERTIES OF REACTIVE POLYMER MICROSPHERES BY EMULSIFIER-FREE EMULSION POLYMERIZATION OF STYRENE-BUTYL ACRYLATE-2-HYDROXYETHYL ACRYLATE

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Reactive polymer microspheres were prepared by emulsifier-free emulsion polymerization of styrene (St), butyl acrylate (BA), and 2-hydroxyethyl acrylate (HEA) by using Potassium persulfate (KPS) as initiator. The effects of different conditions, such as the amount of HEA and KPS, polymerization temperature and cosolvent-methanol, on the polymerization were studied. Increasing the temperature of polymerization and the concentration of HEA and KPS can improve conversion rate and decrease the particle size as well. Moreover, the particle size can be increased by adding methanol to the system. At the same time, the nucleation mechanism was investigated.

Keywords: emulsifier-free emulsion polymerization, particle size, nucleation mechanism

INTRODUCTION

Recently an increasing interest had been focused on the synthesis of functional latices suitable for fundamental research on colloid flocculation kinetics and rheology or for specific application, such as supports for biologic species, catalysts, special coating, separating materials, and so on. Usually these latices are prepared by emulsifier-free emulsion polymerization in order to obtain mono-dispersed and clean surface particles on which functional groups are bound chemically. Meanwhile, the disadvantages coming from emulsifier in emulsion polymerization can be overcome.

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In the emulsifier-free emulsion polymerization, the hydrophilic comonomers were often used to improve the stability of emulsions and make the particles functional. The system of styrene-comonomers has been reported. For instance, styrene-carboxylic monomers [1], styrene-anionic monomers [2–4], styrene-cationic monomers [5], styrene-acrylamide [6], styrene-2-hedroxyethylmethacrylate [7], styrene-butyl acrylate-carboxylic monomers [1, 8] and styrene-butyl acrylate-sulfopropylmethacrylate [8]. But latices prepared by conventional emulsifier-free emulsion polymerization recipes tend to have low solid content and small surface charge density. In order to speed up the conversion rate, the addition of a solvent for the monomers to the emulsifier-free system was suggested as a suitable method. Of the solvents for styrene, methanol was attractive for this purpose, because of its miscibility with both water and styrene, and its lack of solvency for the polymer [9].

In this work, reactive polymer microspheres were prepared by the emulsifier-free emulsion polymerization of styrene (St)-butyl acrylate (BA)-2-hydroxyethyl acrylate (HEA) by using potassium persulfate (KPS) as initiator. The effect of concentration of HEA and KPS, the temperature of polymerization and methanol on the conversion, particle size, and element constitution were discussed. The nucleation mechanism of polymerization was also investigated.

EXPERIMENTAL

Materials

St and BA was distilled under reduced pressure. KPS and methanol were of analytical grade. HEA was a gift from Beijing Dongfang Chemical Plant. Distilled water was used throughout.

Polymerization

The polymerization were carried out in a 4-inlet Pyrex flask equipped with stirrer, condenser, thermometer and nitrogen inlet. To exclude oxygen, purified nitrogen gas was passed through the reagents before polymerization and the materials were under nitrogen protection during the course of polymerization. The polymerization were initiated by KPS.

Analytical Methods

Small samples were taken from the reaction vessel to determine percent conversion. A JSM-35C electron microscopy was used for examination of the particles. Latex samples with uniform ratio $U < 1.05$ were considered mono-dispersed [6]:

$$U = D_w/D_n,$$

where

$$D_w = \sum_{i=1}^{n} D_i^4 \Big/ \sum_{i=1}^{n} D_i^3 \quad \text{and } D_n = \left(\sum_{i=1}^{n} D_i\right) \Big/ n$$

A MILLIPORE 150-C gelation permeation chromatometer was used for measuring molecular weight. A GmbH VarioE1 element analyser was used to analyze the element composition of particles. A PHI-510 X-rays photoelectron spectrometer was used for analyzing element content on particle surfaces.

RESULTS AND DISCUSSION

Conversion Rates

Conversion curves obtained in this work conformed to a typical shape (Figs. 1–4) which suggests a short initial period, then a rather linear conversion rate, followed by an accelerating conversion up to high level.

The effect of reaction temperature on conversion rate is shown in Figure 1. The conversion rate increased as the temperature progressively increased.

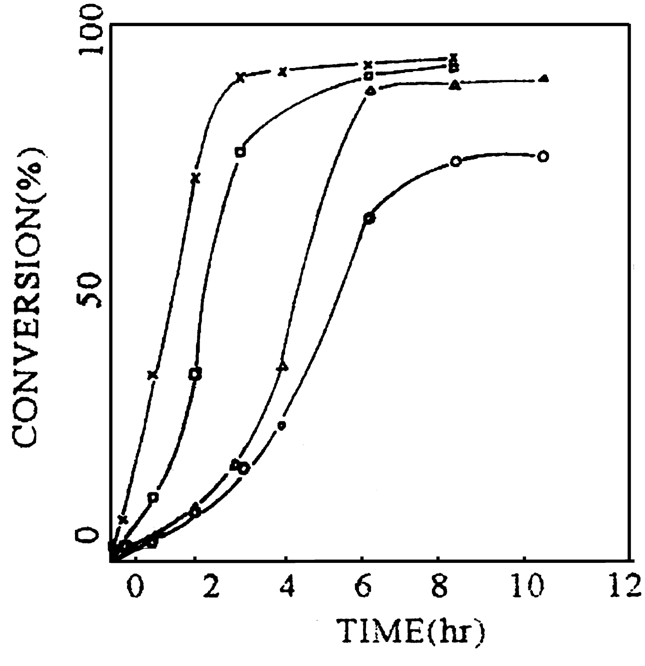

FIGURE 1 Effect of reaction temperature on conversion rate at different temperature (°C): (○) 60; (△) 70; (□) 75; (×) 80.

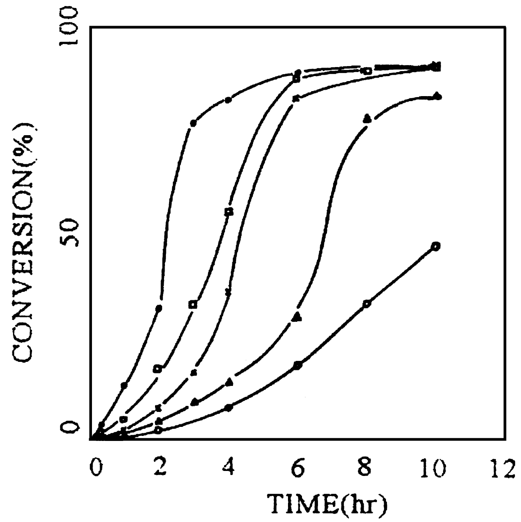

FIGURE 2 Effect of HEA concentration on conversion rate at different [HEA] (mol/l): (○) 0; (△) 0.0529; (×) 0.1059; (□) 0.1589; (•) 0.2119.

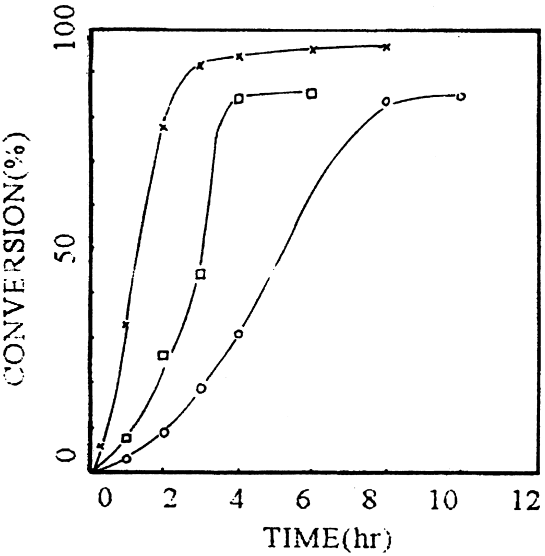

FIGURE 3 Effect of KPS concentration on conversion rate at a constant ion indensity at different [KPS] and [KCl] (mmol/l): (○) 1.281, 11.57; (□) 3.844, 3.855; (×) 5.125, 0.

This is because increasing temperature can improve the decomposition rate of KPS.

The effect of HEA concentration on polymerization rate is shown in Figure 2. As can be seen in it, the conversion rate progressively increased with the increase of HEA concentration due to the initiation rate being speeded up by the increasing the HEA present in the water phase.

To eliminate the effect of different ion intensity on polymerization, potassium chloride (KCl) was added to the system which was used to study the effect of KPS concentration on the conversion rate. The conversion rate curves obtained from the experiments of different KPS concentrations are shown in Figure 3. The conversion rates were increased by increasing the initiator concentration.

To investigate the effect of solvent- methanol on the St-BA-HEA polymerization, different amounts of methanol were introduced into the system while keeping other variables constant. The experimental results are shown in Figure 4. In the system, the function of methanol is rather complicated. In the initial period, the addition of methanol can speed up the polymerization rate, but during the linear and accelerating period, the conversion rate was decreased as the methanol content was increased.

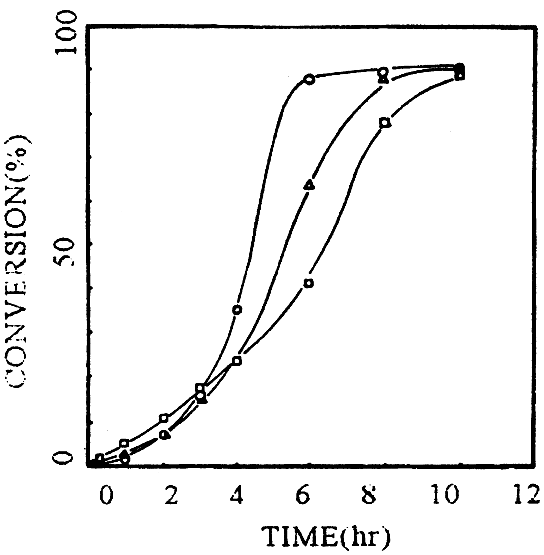

FIGURE 4 Effect of methanol amount on conversion rate, at different methanol amount (% vol, in water): (○) 0; (△) 13.3; (□) 24.4.

TABLE 1 Effect of different polymerization condition on particle size and uniformity

Latex code	*Reaction temperature* (°*C*)	[*HEA*] (*mol*/*l*)	[*KPS*] (*mmol*/*l*)	[*KCl*] (*mmol*/*l*)	*Methanol content*(%.*v*/*v*)	$D_n(\mu m)$	$D_w(\mu m)$	*U*
P1	60	0.1059	3.844	–	–	0.295	0.300	1.02
P2	70	0.1059	3.844	–	–	0.298	0.301	1.01
P3	75	0.1059	3.844	–	–	0.279	0.283	1.02
P4	80	0.1059	3.844	–	–	0.233	0.243	1.04
P5	70	0.05297	3.844	–	–	0.713	0.718	1.01
P6	70	0.2119	3.844	–	–	0.217	0.222	1.02
P7[a]	70	0.1059	1.281	11.57	–	0.306	0.310	1.01
P8[a]	70	0.1059	3.844	3.855	–	0.290	0.297	1.02
P9[a]	70	0.1059	5.125	–	–	0.286	0.297	1.04
P10	70	0.1059	3.844	–	13.3	0.648	0.650	1.00
P11	70	0.1059	3.844	–	24.2	0.766	0.770	1.00

[a] P7, P8, and P9 have the same ion intensity.

Particle Size

In order to obtain mono-dispersed particles and gain control over the final particle diameter, the influence of different polymerization variables were studied.

The influence of reaction temperature on the particle size is shown in Table 1. Increasing the reaction temperature caused a decrease of particle diameter. The reason was that increasing temperature hastened the decomposition rate of KPS, therefore increasing the particle concentration and decreasing the particle size.

In Table 1, the results of experiments in different HEA concentration are also listed. As the concentration of HEA was increased, the particle size

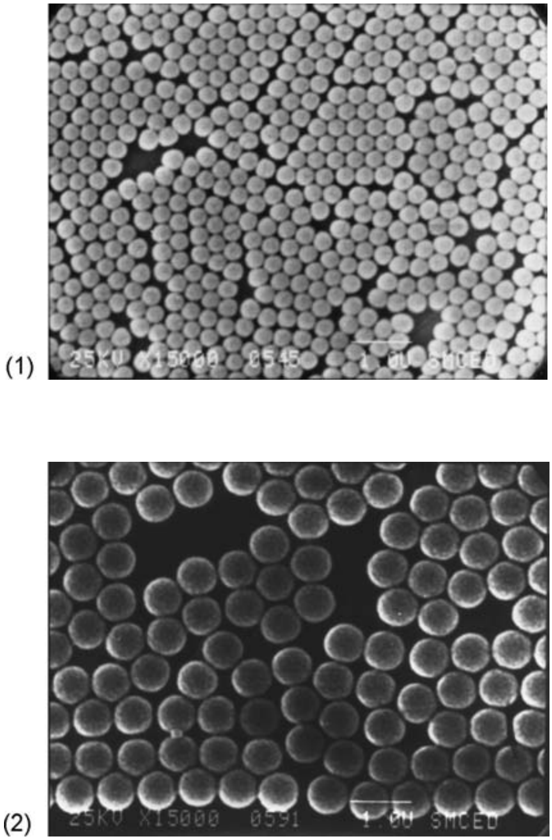

FIGURE 5 SEM photographs of particles (magnified by 15,000 times): (1) without methanol, (2) with 13.3% methanol.

TABLE 2 Influence of reaction temperature and HEA concentration on element content

Latex	*Reaction*	[*HEA*]	*Element content* (%)			*Element*	*Surface element content* (%)		*Element*
code	*temperature* (°*C*)	(*mol*/*l*)	*C*	*H*	*O*	*ratio* (*C*/*O*)[a]	*C*	*O*	*ratio* (*C*/*O*)[b]
P2	70	0.1059	86.99	7.876	4.942	17.60	–	–	–
P4	80	0.1059	84.83	7.825	7.169	11.83	–	–	–
P5	70	0.05297	87.97	7.933	3.922	22.43	79.00	20.92	3.766
P12	70	0.1589	86.08	7.849	5.863	14.68	–	–	–

[a] These values are the ratios of elements in the whole polymer.
[b] This value is the ratio of element only on the particle surface.

decreased, obviously because more hydrophilic monomer combined on the surface of particle and then smaller particles were obtained.

The effect of KPS concentration on particle size is also shown in Table 1. Increasing concentration of initiator at constant ion intensity decreases the particle diameter and the uniformity.

As can be seen from Table 1, the effect of added methanol on particle size is clearly shown. The particle diameter was greatly increased. It was suggested that the hydrated layer of primary particles was rather thin and the primary particles coagulated to form bigger particles when methanol was added. The SEM photographs are shown in Figure 5.

Element Content

The purpose of investigating the element content of polymers in this work was to learn about copolymerization among the monomers. In order to learn about the distribution of hydroxyl groups on the surface of particles, the element contents on the particle surface were also determined.

The effect of reaction temperature on element contents is shown in Table 2. Increasing temperature of polymerization can increase oxygen element content. It was suggested that raising reaction temperature favored the copolymerization.

The effect of the concentration of HEA on element contents is also shown in Table 2. Oxygen element content increased with the increasing HEA concentration. The surface oxygen element content was higher than that in the whole polymers. This indicated that hydroxyl groups bound mostly on the surface of particles. It was suggested that reactive polymer microspheres were synthesized.

Particle Nucleation Mechanism

The comonomer HEA used in the polymerization is a strong hydrophilic monomer. Styrene is a strong hydrophobic one. To determine the particle nucleation mechanism, the molecular weight of particles in the initial period of polymerization was measured and listed in Table 3. From Table 3, we can see that the molecular weight has reached 2790 when the conversion is only

TABLE 3 Relation of molecular weight and conversion in the initial period of polymerization

Conversion (%)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n
0.0420	0.02790	0.06212	2.227
7.26	0.3084	1.523	4.939
15.8	0.5718	5.354	9.313

0.042%. However, in the oligomer micelle nucleation mechanism, only the oligomer which has the molecular weight less than 1000 can act as critical micelle [10]. So it was suggested that the particle nucleation mechanism of the system is not the oligomer micelle nucleation mechanism.

CONCLUSIONS

The microspheres prepared in this work have monodisperse diameter and their surface is occupied by hydrophilic functional monomer. Increasing the concentration of monomer HEA or initiator KPS, and increasing the reaction temperature can increase the reaction rate and decrease the particle diameter. At the same time, the particle diameter can be greatly increased by adding methanol to the polymerization system. The particle nucleation mechanism is not the oligomer micelle nucleation mechanism.

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