



Effect of aqueous phase composition on particle coagulation behavior in batch emulsion polymerization of styrene



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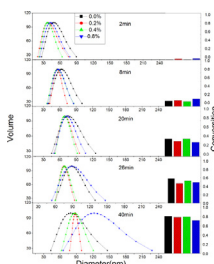
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HIGHLIGHTS

- Particle scale and polydispersity were controlled via adjusting aqueous phase composition.
- Particle coagulation was considered as the dominant particle growth method.
- The relationship between particle coagulation and aqueous phase composition were investigated.

GRAPHICAL ABSTRACT

Effect of electrolyte concentration on the evolution of particle size distribution as a function of time or monomer conversion.



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ABSTRACT

Previously, we studied the latex particle coagulation in the emulsion polymerization of n-butyl acrylate induced by an electrolyte (Colloid Polym Sci 291 (2013) 2385–2398). However, the evolution of particle size distribution vs. monomer conversion and reaction time, and the possibility for the manipulation of particle coagulation to control particle size and polydispersity were not studied. In this study, we investigated the evolution of particle size distribution vs. monomer conversion and reaction time during the emulsion polymerization of styrene. Moreover, the particle coagulation at different aqueous phase compositions was studied in details. The experimental results indicate that the particle size and polydispersity was controlled by particle coagulation, which was adjusted by varying the content of electrolyte or methanol in the aqueous phase. The final latex particle size increased in the range 89.2–265.9 nm with increasing electrolyte or methanol. The effect of aqueous phase composition on the polydispersity index (PDI) of the final latex was also considered. The PDI of the final latex reached 0.005 at an appropriate aqueous phase composition. Interestingly, the demulsification phenomenon easily occurred at electrolyte concentration > 1.2 wt% or methanol/water ratio > 30/70.

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1. Introduction

Polymeric particles with large size and narrow polydispersity index (PDI) are extensively used in many applications such as toner

particles, plastic modifier, catalysis, paint, and medicine [1–5]. In general, these polymeric particles could be prepared by either one-step methods, such as the miniemulsion polymerization and free-soap emulsion polymerization, or multi-step seed emulsion polymerization [6–8]. However, these polymerization methods are carried out at relatively low monomer/water ratios or in the presence of cosurfactant. Moreover, the polymerization reaction time is normally >10h. Therefore, these polymerization methods are

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not suitable for industrial-scale preparation. Hence, manufacturing of polymeric latex particles by a simple approach has been an intensive area of research from the theoretical point of view and industrial production.

In previous study, the latexes of poly (butyl acrylate) with particle size in the range 200–650 nm, narrow particle size distribution (PSD), and high solid content were prepared by the particle coagulation mechanism induced by an electrolyte [9]. The study revealed that the particle coagulation depends on the electrolyte concentration. The final particle size increased with increasing electrolyte concentrations until the demulsification occurred. However, the unaddressed problems of the previous study are: (1) the effect of monomer nature on particle coagulation, (2) the effect of other parameters such as aqueous phase composition on particle coagulation, and (3) the effect of particle coagulation on PDI.

To investigate these problems, the batch emulsion polymerization of styrene was carried out at different aqueous phase composition. The evolution of particle size, distribution, and number vs. monomer conversion was studied to elucidate the particle formation and growth mechanism. The emulsion polymerization of styrene in electrolyte or methanol solution was studied in order to investigate the relationship between the particle coagulation and aqueous phases composition. The particles size and their distribution were studied by transmission electron microscopy (TEM) and dynamic light scattering (DLS), respectively. The zeta potential and surface tension were used to characterize the stability of latex particles.

2. Materials and methods

2.1. Material

The styrene monomer (Jilin, China) was distilled under reduced pressure to remove the inhibitor prior to use. Potassium persulphate (KPS) (>99.5%), sodium dodecyl sulfate (SDS) (>99.0%), potassium carbonate (K_2CO_3) (>99.0%), and methanol (>99.5%) were obtained from Tianjin Fuyu Fine Chemical Factory (Tianjin, China) and used without any further purification. Methanol solution containing 1 wt% hydroquinone was used as the polymerization inhibitor. Deionized water (DI) was used for all experiments.

2.2. Preparation of PS latex particles

Polymerizations were carried out in a 500-ml three-necked round-bottom flask equipped with a water-bath cauldron, anchor stirrer, and reflux condenser. The initiator and surfactant concentrations were kept at 0.6 and 1.0 wt%, respectively, for the aqueous phases. The electrolyte concentrations were set to 0, 0.2, 0.4, 0.8, and 1.2 wt% for the aqueous phase. The methanol/water ratios were set at 0/100, 10/90, and 30/70. All the experimental conditions are listed in Table 1.

Table 1
Standard recipe for preparation of PS latexes.

Runs	St (g)	DI (g)	Methanol (g)	SDS (g)	KPS (g)	K_2CO_3 (g)
1	100	150	0	1.500	0.900	0
2	100	150	0	1.500	0.900	0.300
3	100	150	0	1.500	0.900	0.600
4	100	150	0	1.500	0.900	1.200
5	100	150	0	1.500	0.900	1.800
6	100	135	15	1.500	0.900	0.600
7	100	105	45	1.500	0.900	0.600

Notes: the polymerization temperature and stirring rate were set as 65 °C and 250 rpm/min, respectively.

2.3. Characterization

The particle size, zeta potential, and distribution of latex particles were characterized using a Brookhaven 90plus particle size analyzer and transmission electron microscope (TEM) (JEOL 1210). The surface tension and contact angle were measured using a drop shape analyzer DSA-30 (KRUSS, Germany). The detailed characterization procedure was followed from our previous report [9].

Conversion: The monomer conversion was defined as the ratio of polymer content in the sample to the monomer content and was calculated using the following equation:

$$X = \frac{\text{residue weight/sample weight} - \text{solid fraction}}{\text{monomer fraction}} \quad (1)$$

where the solid include the initiator, emulsifier, and electrolyte in the sample.

Particle number: The particle number (N_p) was obtained according to the following expression:

$$N_p = \frac{6M_0x}{\pi\rho_p D_p^3} \quad (2)$$

where M_0 is the monomer/water ratio, x is the fractional conversion, ρ_p is the polymer density (1.044 g/cm³), and D_p is the v-average size of particle.

3. Results and discussion

3.1. Effect of electrolyte concentrations

The evolution of particle size vs. monomer conversion at different electrolyte concentrations, as shown in Fig. 1, clearly indicates that the particle size increased with increasing monomer conversion for all the polymerization reactions. Notably, the rate of particle size growth at a high electrolyte concentration (0.8 wt%) was higher than at other concentrations for monomer conversion in the range 0.21–0.45, and the final particle size was 125 nm. However, under all other conditions, the final particle size only reached ~90 nm. Therefore, it was interesting to study the role of the electrolyte on the PSD. Electrolytes may be introduced in the emulsion polymerization either as a buffer to stabilize the pH of the latex systems or as an antifreezing agent to reduce the freezing point of the aqueous phase (or reducing viscosity of latex) [10,11]. The effect of electrolyte concentrations on the particle formation and growth was not taken into account in the theory of emulsion polymerization, although many investigators have found that the electrolytes

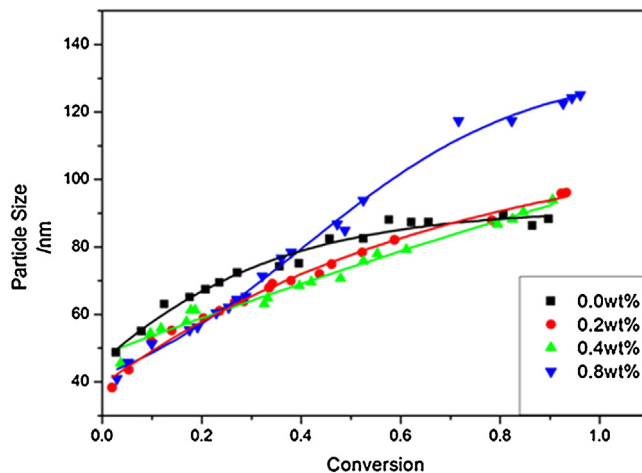


Fig. 1. The evolution of particle size as a function of monomer conversion for emulsion polymerization of St at different electrolyte concentrations.

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