

Study on Emulsion and Suspension *In Situ* Polymerization

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ABSTRACT: A novel and simple method of emulsion and suspension *in situ* polymerization was designed for preparing a composite of polystyrene containing core-shell emulsion particles. The advantage of this method was that it did not need a complex process, such as emulsion breaking, washing, drying, and so on, during transforming from emulsion polymerization to suspension polymerization. First, the core-shell particles of poly(styrene/bisphenol A dimethyl methacrylate)/polystyrene [P(St/BPADA)/PS] with crosslinking structure were synthesized by emulsion polymerization. Then the latex was bro-

ken with electrolyte dripping and the emulsion particles became swollen and transformed into the monomer in the suspension polymerization system. Thus the emulsion and suspension *in situ* polymerization could be carried out successfully. The mechanism of the process was investigated in detail.

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Key words: emulsion polymerization; breaking; swelling; suspension polymerization; nanocomposites

INTRODUCTION

It is well known that emulsion polymerization^{1,2} and suspension polymerization^{3–5} are important methods of polymerization in polymer science and technology. Emulsion polymerization offers good control to the process of radical polymerization and the structure of its products.^{6–8} Using the technique of composite emulsion polymerization, we can design polymeric core-shell structures with different components and different crosslinked structures of core or shell and adjust the refractive index of core-shell matching each other, while simultaneously controlling the size of particles, macroscopic physical properties, and so on. For example, people can design a polymer structure and obtain organic^{9–13} or inorganic¹⁴ nanoparticles to modify and functionize polymer materials. There are many researches on the preparation of the composites and hybrids^{15–19} of polymer, in which the core-shell nanoparticles are mostly used as the elastic modifier to plastics.⁶

In general, the composition of polymer and emulsion nanoparticles needs a complex course such as the breaking of emulsion, the washing of emulsion particles, and the drying of products, for example. When emulsion nanoparticles are directly blended with polymer, in fact, it is difficult to remove the impurities adsorbed on the surface of particles and it is likely to lead to coagulation and deformation of particles dur-

ing the handling process from emulsion to dry particles. In view of the above-mentioned unfavorable factors, it is of great realistic significance to find a method to synthesize polymer composites directly with emulsion solution, without further handling of the emulsion nanoparticles.

In contrast, suspension polymerization can overcome the problem of complicated postpreparative treatment of product and is carried out under conditions similar to those of emulsion polymerization. According to these advantages and disadvantages of emulsion and suspension polymerization, a new polymerization method is established in this article, in which emulsion polymerization and suspension polymerization are combined to synthesize a polystyrene composite. The process of emulsion breaking and swelling is studied in detail by spectrophotometry.

EXPERIMENTAL

Materials

Sodium bicarbonate, potassium peroxydisulfate (KPS), calcium chloride, sodium phosphate, and acetone were all analytical grade. Chemical-grade sodium dodecyl benzene sulfonate (SDBS) was used as received. Benzoyl peroxide (BPO) was recrystallized twice in chloroform and methanol, and styrene (St) was distilled under vacuum before use. Hydroxyapatite (HAP) was synthesized as reported.²⁰ Bisphenol A dimethyl methacrylate (BPADA) was used as a crosslinker and synthesized in our laboratory.²¹ Deionized water was used throughout the experiments.

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Synthesis of core-shell nanoparticles by seeded emulsion polymerization

In a 500-mL four-neck flask, 0.2 g of SDBS, 0.24 g of sodium bicarbonate, 22.7 g of styrene, 0.6 g of BPADA, and 90 mL of deionized water were mixed and stirred in an atmosphere of nitrogen and at room temperature for 30 min to preemulsify. The initiator (0.16 g of KPS dissolved in 10 mL of water) was then added. The reaction was carried out for 2–3 h at 75°C, after which the seeded latex of the core emulsion poly(St/BPADA) with 0.24 g/mL of solid content was obtained. In another 500-mL four-neck flask, the seed latex was heated at 78°C; the monomer (22.7 g of styrene) and initiator (0.16 g of KPS dissolved in 25 mL of water) were sequentially introduced by slow dripping over a period of 3–3.5 h. The reaction was continued for 4 h and then the mixture was filtered; the core-shell poly(BPADA)/polystyrene [P(St/BPADA)/PS] emulsion particles were obtained, at a yield of about 89.73%.

Synthesis of the composites of polystyrene and core-shell particles through emulsion and suspension *in situ* polymerization

In the continuous experiment, 135 mL of the above core-shell [P(St/BPADA)/PS] emulsion, 120.0 g of styrene, and 200 mL of deionized water were charged to a 1000-mL four-neck flask fitted with a reflux condenser and a stirrer. At first, the suspension system of monomer and emulsion was formed with a suitable stirring speed, after which a 100-mL aqueous solution of calcium chloride (2 wt %) as electrolyte was dripped into the suspension system within 3 h, gradually breaking the emulsion, and then the core-shell particles were swollen by monomer styrene. Finally, the swollen core-shell nanoparticles diffused into the monomer phase. Then the initiator (0.75 g of BPO dissolved in 15.2 g of styrene) and 80 mL of HAP were sequentially added to the reactor. The suspension polymerization was carried out at 82–85°C for 12 h, after which the reaction system was treated with high-pressure steam for 0.5 h to remove the unreacted monomer. The polystyrene composite was washed with hydrochloric acid and water, to remove the dispersant, and then dried under vacuum. Thus the composite beads of polystyrene and core-shell emulsion particles were synthesized through emulsion and suspension *in situ* polymerization.

Characterization

Measurement of solid content of emulsion

A 10-mL sample of core-shell emulsion of P(St/BPADA)/PS was precipitated by adding 4 wt % hydrochloric acid aqueous. The precipitate product was

washed with water to a pH of 7, after which it was filtered and dried. The product was weighed, after which the solid content of emulsion and the yield of emulsion polymerization were then calculated.

Size measurements

The average diameter and size distribution of core-shell emulsion particles were measured by photon-correlation spectroscopy (Zetasizer 1000HS/3000HS, Malvern Instruments, Worcestershire, UK) with a He-Ne laser beam at a wavelength of 633 nm at 25°C (scattering angle of 90°).

Transmittancy measurements

The relationship between the average diameter of emulsion particles and the transmittancy of emulsion during the process of incomplete breaking of the emulsion and breaking-swelling of the core-shell particles was studied by spectrophotometry. Typical measuring steps are as follows: 30 mL of emulsion was charged to a 100-mL conical flask. While the emulsion was maintained at $30 \pm 1^\circ\text{C}$ under constant stirring, it was titrated by 0.6 wt % of electrolyte aqueous at a rate of 0.1 mL/min. Every 5 min, 0.2 mL of mixed solution was accurately transferred from the conical flask into 2 mL of the comparison vessel with a pipette, after which the comparison vessel was filled with deionized water and shaken uniformly. The transmittancy in the process of titration was measured by spectrophotometry.

Measurement of molecular weight and molecular weight distribution

The polystyrene composite beads prepared by emulsion and suspension *in situ* polymerization were placed in chloroform. Then the mixture was filtered to remove the insoluble core synthesized in the emulsion polymerization. The soluble polystyrene was precipitated by methanol, after which it was washed and dried in vacuum. Molecular weight and molecular weight distribution were measured at 35°C by using a Waters 410 GPC instrument (Waters, Milford, MA), equipped with a Waters Styragel HT6E column and a differential refractometer detector. THF was used as eluent at a flow rate of 1.0 mL/min, and the molecular weights were calibrated with polystyrene standards.

RESULTS AND DISCUSSION

All steps of the reaction were completed as shown in Figure 1. First, the core-shell particles were synthesized by the seeded emulsion polymerization. Second, the monomer was added and the electrolyte was dripped into the latex to cause incomplete breaking

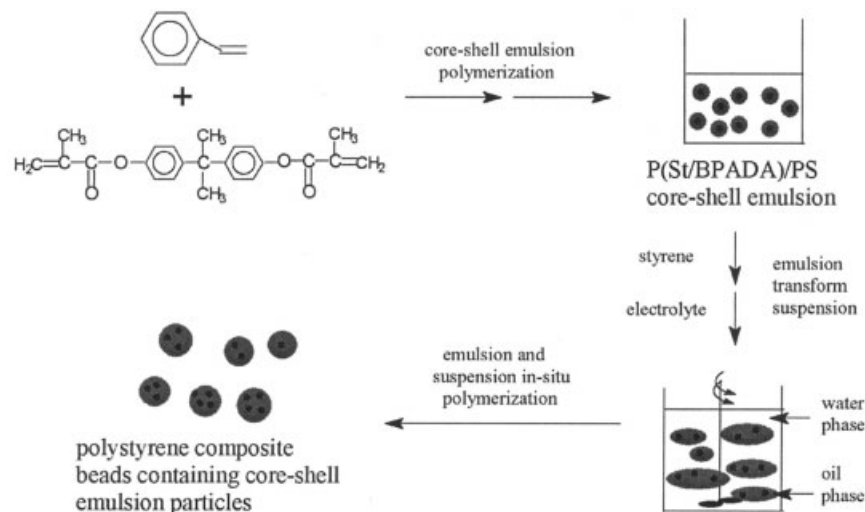


Figure 1 Scheme for emulsion and suspension *in situ* polymerization. The top section illustrates the prepared of P(St/BPADA)/PS core-shell emulsion particles by seed-emulsion polymerization, followed by the process of emulsion transform suspension after the addition of styrene and electrolyte. The bottom section illustrates the preparation of polystyrene composite beads with P(St/BPADA)/PS core-shell emulsion particles by suspension polymerization.

and swelling of the emulsion, and then initiator and dispersant were added to the system. As a result, the dispersant adsorbed with the emulsifier in emulsion polymerization to become a composite dispersant, and a reaction system of suspension polymerization was formed *in situ*. By the new method of emulsion and suspension *in situ* polymerization, the polystyrene composite was prepared with the yield of 97.6%. The polystyrene composite beads containing core-shell emulsion particles are 1–2 mm in diameter, as shown in Figure 2.

The molecular weight of the soluble polystyrene prepared by core-shell emulsion and suspension *in situ* polymerization was determined. The number-average molecular weight was about 66,000; the weight-

average molecular weight was about 380,000; and the polydispersity was about 5.75.

Preparation of core-shell nanoparticles

In the process of emulsion and suspension *in situ* polymerization, some factors can influence either the emulsion polymerization or the suspension polymerization, such as the structure and the concentration of emulsifier, the size, and the solid content of emulsion particles. In emulsion polymerization, SDBS plays an important role in emulsion polymerization and suspension polymerization: it not only acted as an emulsifier, thus guaranteeing the completion of emulsion polymerization, but also can be adsorbed on the HAP particles to form a composite dispersant, which was used in the transforming process from emulsion to suspension polymerization. In the process of core-shell emulsion polymerization, the concentration of emulsifier was controlled at a lower level than the critical micelle concentration (cmc), to make it just cover the surface of emulsion particles completely, while preventing it from forming new micelles in the water phase.^{22,23}

The dropping rate of monomer styrene should be controlled so that the monomer can completely react on the surface of the core particles to become shell, while new core particles are prevented from being formed. With the addition of initiator, a small amount of emulsifier was also dripped into the reactor to stabilize the core-shell particles. Finally, the core-shell emulsion particles, having diameters of 90–110 nm, were obtained, as shown in Figure 3, whose particles size distribution is narrow.

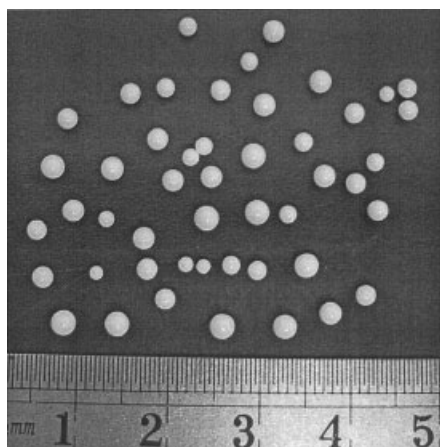


Figure 2 Photograph of polystyrene composite beads synthesized by emulsion and suspension *in situ* polymerization.

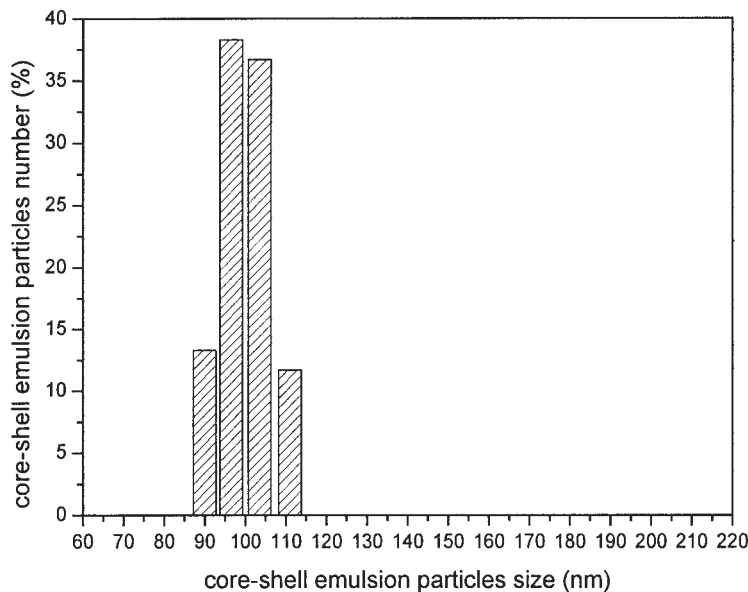


Figure 3 Size distribution histogram of the core-shell emulsion particles determined by Zetasizer.

The solid content of core-shell emulsion was controlled at a high level so that the polystyrene composite beads with high content of core-shell particles can be synthesized after the emulsion was converted into suspension *in situ* polymerization.

Relationship between the transmittancy of emulsion and concentration of electrolyte

As shown in Figure 4, according to the different amounts of core-shell emulsion in the process of

emulsion and suspension *in situ* transformation, the transmittancy of the mixture was measured. We obtained a set of process curves with respect to transmittancy versus electrolyte concentration. The core-shell emulsion is stable in a certain concentration of electrolyte.²⁴ With increasing electrolyte concentration, the extra electrolyte may cause the hydrated electrical double layer around emulsion particles to become thin or be destroyed. In the meanwhile, the extra electrolyte can cause the ζ -potential of the hydrated electrical double layer to decrease, resulting in decreasing sta-

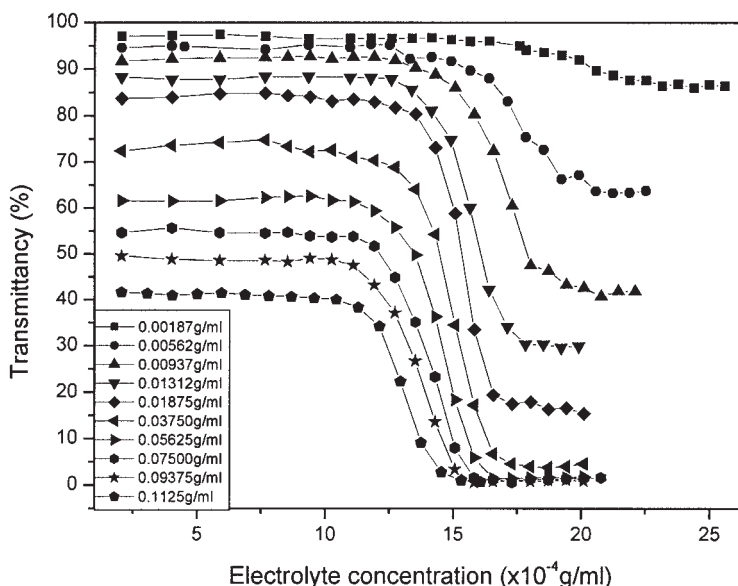


Figure 4 Plot of transmittancy of core-shell emulsion with different solid contents against electrolyte concentration in the process of emulsion breaking under constant stirring and 30°C.

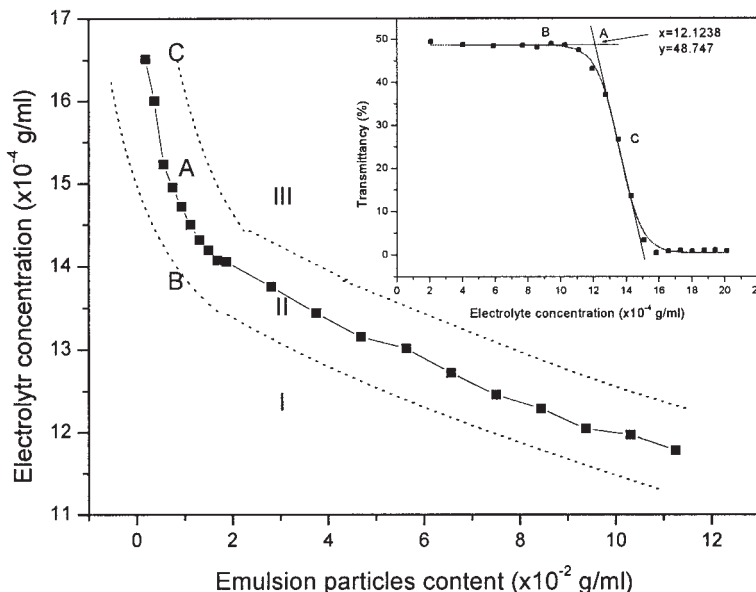


Figure 5 Plot of electrolyte concentration against core-shell emulsion particles content in the process of emulsion breaking under constant stirring at 30°C. Inset: the scheme about mathematical treatment of curve (from Fig. 5) between transmittancy of core-shell emulsion and electrolyte concentration; the emulsion solid content is 0.09375g/mL (A is a inflection point; B and C are tangential points).

bility of the core-shell emulsion. The core-shell emulsion particles would collide with each other to become aggregates. As a result, the transmittancy of emulsion obviously decreased, which was reflected with a sharp inflection that appeared in the curves. With the excessive increase of electrolyte concentration, the core-shell particles freely collided with each other to form flocs and the second sharp inflection once again appeared in the curves, after which the transmittancy of emulsion tended to remain constant.

By studying the first inflection, it is easy to find a transitional region. In this transitional region, a small increase of electrolyte concentration can cause a substantial change of emulsion stability. Considering the fact of second inflection, we can see that emulsion particles collided to form a unit of stable flocs after the electrolyte was added to a constant concentration. To ensure that the above experiment proceeded smoothly, it was important to control the amount of electrolyte. Therefore, the curves in Figure 4 were mathematically treated, respectively, as follows to study the process of emulsion breaking and the relationship between the concentration of electrolyte and the content of core-shell particles in emulsion.

Relationship between the process of core-shell emulsion breaking and the electrolyte concentration

As shown in Figure 5, the process of emulsion breaking was studied through the relationship between the solid content of the emulsion and electrolyte concen-

tration. The result points from the curve in Figure 4 were mathematically treated according to the method as shown in the inset in Figure 5, obtained as the inflection point coordinate A and the tangential point coordinates B and C, respectively. These inflection points and tangential points were drawn as curves in Figure 5. The inflection points were connected to construct an emulsion breaking curve and the tangential points on each side of the emulsion breaking curve were also connected to obtain two theoretical deduction incomplete-breaking curve and complete-breaking curve. Three curves in Figure 5 divided the region of the right-angled coordinates system into three regions. Region I represents the stable state of core-shell emulsion; region II represents the incomplete-breaking state of emulsion, that is, a transitional region between the stable state and the unstable state of core-shell emulsion; and region III represents the formed unit of stable flocs after the core-shell emulsion was broken completely.

In this test, region II is the key area to the transformation from emulsion to suspension. When the electrolyte concentration gradually increased, the hydrated electrical double layer outside the emulsion particles became thin; thus the monomer was easier to diffuse into the surface of core-shell particles. By determining this transitional region in the process of incomplete-breaking emulsion, the content of the electrolyte must be controlled to cause incomplete breaking and swelling of emulsion to occur steadily without aggregates, so emulsion particles can be smoothly

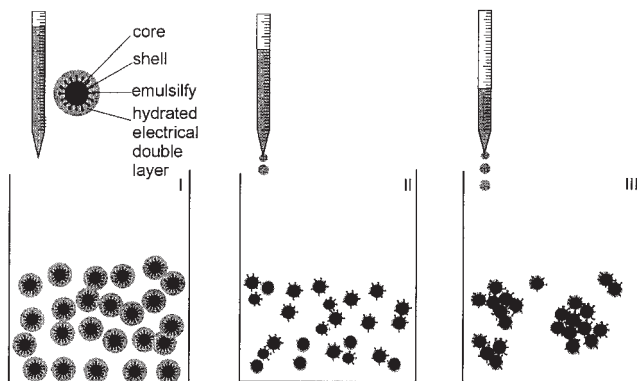


Figure 6 Scheme for the breaking process of core-shell emulsion under the condition of adding different amounts of electrolyte. (I) The core-shell emulsion particles in this system are characterized by irregular movements without electrolyte. (II) The hydrated electrical double layer of core-shell emulsion particles become thin and the particles form an unstable aggregate in this system with proper quantity of electrolyte. (III) Most hydrated electrical double layers around core-shell emulsion particles are completely destroyed and those particles form a unit of stable flocs with an excess quantity of electrolyte.

transferred from the emulsion phase to the oil phase. The process of emulsion breaking with different concentrations of electrolyte is summarized in Figure 6.

Swelling of the core-shell particles with monomer and process of transformation from emulsion to suspension

In the emulsion phase, the distribution of particle size was measured and the results are drawn as shown in

Figure 7. Compared with Figure 3, the size of core-shell emulsion particles became larger and its distribution became wider. If the monomer was not added to the emulsion system, we found that the size distribution was similar to that in Figure 3, which indicated that with electrolyte dripping the hydrated electrical double layer became thin. The monomer can go through the hydrated electrical double layer and swell the emulsion particles. The swelling mechanism was thought to be explained by the fact that the monomer has a definite solubility in the water phase, and the monomer could thus more easily infiltrate into the emulsion particles as the hydrated electrical double layer gradually became thinner, so that the emulsion particles were swollen and their size increased.

Behavior of core-shell nanoparticles in the process of incomplete breaking and swelling of emulsion and *in situ* suspension polymerization

In the process of incomplete breaking of emulsion with electrolyte and swelling with monomer, electrolyte and monomer played an important and dual role. To simulate the test of core-shell emulsion transforming into suspension polymerization, styrene was added to the core-shell emulsion with stirring, and the electrolyte solution was dripped into the core-shell emulsion. Thus the core-shell emulsion was incompletely broken by electrolyte and the monomer could go through the hydrated electrical double layer and swell the core-shell particles. With the electrolyte dripping into the emulsion, the transmittancy of the mixture changed, as shown in Figure 8 (upper). This state variation was considered as the process of emul-

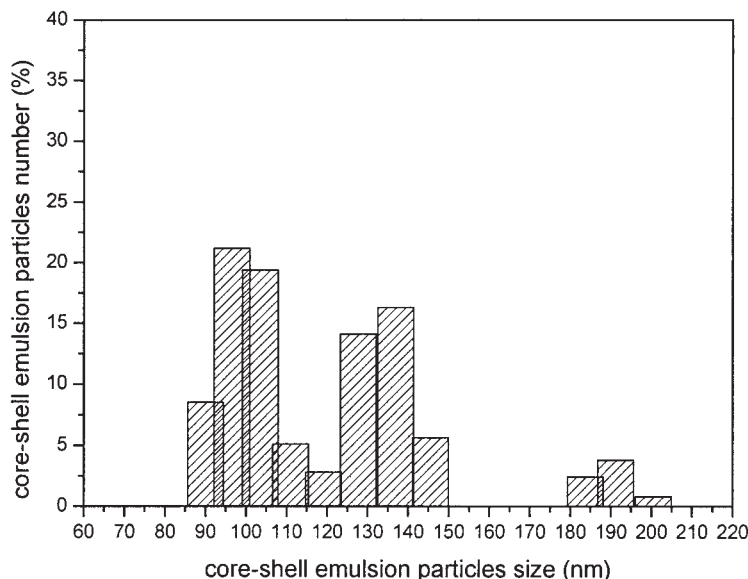
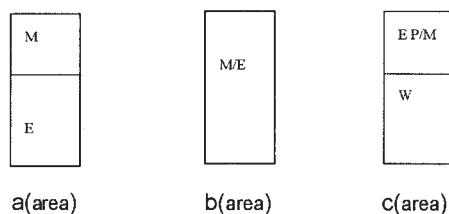
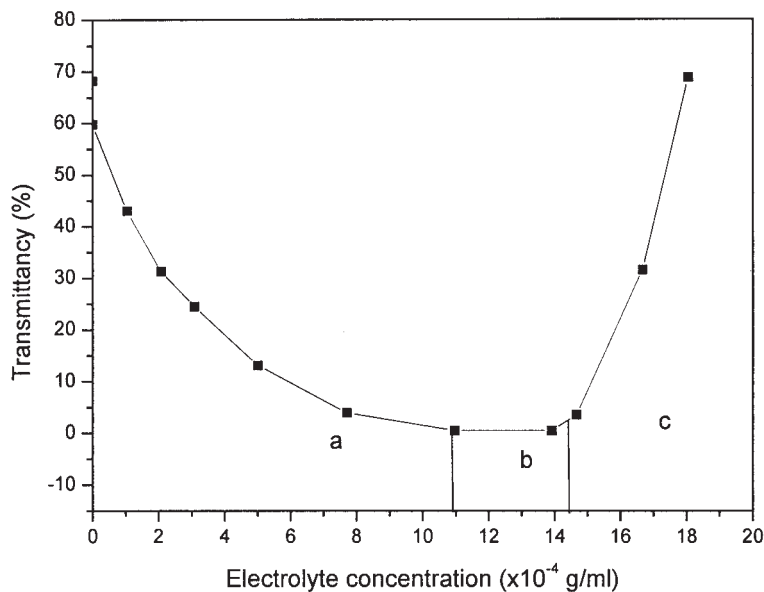


Figure 7 Size distribution histogram of the core-shell emulsion particles swollen by monomer with gradually dripping electrolyte.



M: Monomer E: Emulsion EP: Emulsion Particles W: Water

Figure 8 Upper: plot of the transmittancy of core-shell emulsion against the electrolyte concentration in the process of emulsion breaking-swelling under the constant stirring rate at 30°C, with the existence of monomer and dripping electrolyte into the system. Lower: scheme for different static state of core-shell emulsion with the existence of monomer and dripping electrolyte into the system. (a) Two phases of monomer and emulsion. (b) The metastable state phase of the water and oil inter-dissolution. (c) Two phases of oil and water.

sion breaking and core-shell particles swelling with electrolyte and monomer, which is shown in Figure 8 (lower). So we divided the curve into regions (a), (b), and (c). In region (a), the mixture consisted of two phases of monomer and emulsion. At first, without the titration of electrolyte, the transmittancy of the emulsion mixture was constant after a prescribed amount of monomer was added. Because there was emulsifier in emulsion, the monomer solubility in emulsion was increased, and thus the transmittancy of emulsion decreased. When the electrolyte was gradually added to the emulsion, the hydrated electrical double layer be-

came thinner, and the monomer was more easily able to transform into preemulsified liquid in this system. The monomer infiltrated into the core-shell particles through the hydrated electrical double layer and caused core-shell particles to swell, which further caused the transmittancy of emulsion to decrease. There were still two phases of oil and emulsion at this very moment, but as more monomer infiltrated into the water phase with the addition of electrolyte, the system was close to the metastable state.

Region (b) represents the mutually dissolved single phase of water and monomer. In this region, the

monomer phase was completely "interdissolved" in the water phase and the hydrated electrical double layer of core-shell particles was substantially destroyed. An increasing amount of monomer penetrated into emulsion particles to cause them to swell and thus the system became viscous. We found that, to ensure that the emulsion and suspension *in situ* polymerization proceeded smoothly, this reaction system was required to have a proper ratio of monomer to water [monomer : water (*v/v*) = 1 : 4–6], which could ensure the breaking and swelling of the emulsion in the system, thus allowing these core-shell particles to disperse thoroughly in the monomer.

Region (c) represents two phases of organic and water. Under the twofold factors—action of incomplete breaking of emulsion by the electrolyte and swelling of core-shell particles by the monomer—the hydrated electrical double layer of core-shell emulsion particles was destroyed and core-shell emulsion particles that separated out from the water phase were completely dissolved in the monomer, upon which the water phase became clear. After adding the inorganic dispersant HAP, HAP and SDBS were considered to form a composite dispersant (HAP/SDBS), which can be adsorbed on the surface of droplets and make them stable. All these factors guaranteed that suspension polymerization would proceed smoothly.

According to the above experimental facts, the schematic illustration from the core-shell emulsion and suspension *in situ* transformation is described in Figure 9. In step I, without electrolyte, the state of monomer and emulsion particles was characterized by irregular movement. In step II, after dripping the proper quantity of electrolyte, the core-shell particles were incompletely broken and swollen, and then were transferred into the monomer phase: this is the key step to control the emulsion and suspension *in situ* transformation. In step III, an excess quantity of electrolyte caused the core-shell particles to be completely broken in the monomer. The system of suspension was formed through quick stirring, and the suspension polymerization was carried out smoothly.

CONCLUSIONS

Emulsion and suspension *in situ* polymerization was successfully completed without complex emulsion breaking, washing, drying, and so on, and a composite of the core-shell emulsion particles and polystyrene was simply prepared by this polymerization. Two key points for this polymerization are: (1) the structure of the emulsifier and its combination with the HAP to form a composite dispersant, and (2) the concentration and dripping rate of electrolyte. The breaking of core-

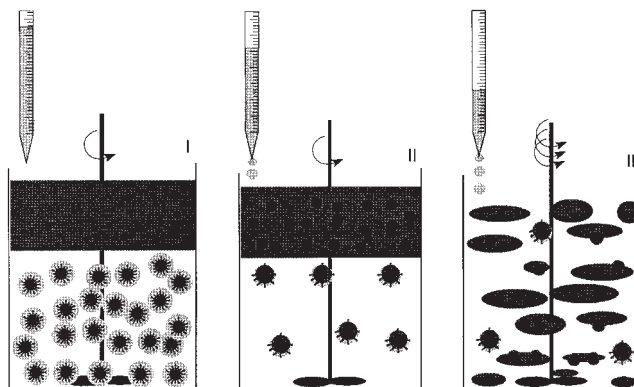


Figure 9 Scheme for breaking and swelling process of core-shell emulsion with monomer by adding different amounts of electrolyte. (I) Without electrolyte, the monomer in the emulsion has a definite solubility and cannot cause swelling of the core-shell emulsion particles. These molecules of monomer and particles of emulsion in this system are characterized by irregular movement. (II) Under gradual addition of the proper quantity of electrolyte, the hydrated electrical double layer of the core-shell emulsion particles become thin and the monomer dissolved in this system can cause swelling of the core-shell emulsion particles. (III) Under the condition of excess quantity of electrolyte, the core-shell emulsion particles are broken and swollen and transferred into the monomer phase. The stirring speed is quickened.

shell emulsion with electrolyte and its swelling with monomer are the important steps during the transforming process from emulsion to the suspension system. The emulsion breaking and swelling process could be divided into three states: monomer and emulsion separated two phases; the mutually dissolved single-phase of water and monomer; organic and water separated two phases. The process mechanism was investigated through monitoring the variation of the transparency of system. This emulsion and suspension *in situ* polymerization method can also be applicable to other monomers. If some functional inorganic particles are introduced as a core during the emulsion polymerization, some kinds of inorganic/polymer composites can be obtained by this polymerization approach.

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