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The effect of aqueous medium contains poly(acrylic acid) on the morphology of composite polymer particle produced by two stages soapless seeded emulsion polymerization

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Abstract

The linear composite polymer particles, which contain PMMA and PS components (PMMA/PS composite particle), were synthesized by the method of two stages soapless seeded emulsion polymerization. In this study, the aqueous medium of the emulsion system included poly(acrylic acid) (PAA). In the second stage reaction, the morphology of the PMMA/PS composite particles was changeable under the influence of PAA. In the initial period of second stage reaction, the morphology of the composite particle showed the core(PMMA)–shell(PS) structure, in the middle period of second stage reaction, thermodynamic was the main factor to decide the morphology of the core and two shells, that is, PS as core, PMMA mixed with PS as inner shell, and PS as outer shell. Finally, the PMMA/PS composite particle showed the morphology of core(PS)–shell(PS phase dispersed in PMMA phase). This was in great contrast to the morphology of PMMA/PS composite particles, which were synthesized in the absence of PAA. © 2002 Published by Elsevier Science Ltd.

Keywords: Morphology; Composite particle; Poly(acrylic acid)

1. Introduction

In recent years, the seeded emulsion polymerization (or two-stage emulsion polymerization) was often used to synthesize the polymer/polymer composite particles in industry. The composite particles may include reinforced elastomers, high-impact plastics, toughened plastics, etc.

There were many factors to control the kinetics and morphology of polymer particles, such as the method of the monomer charge into the system [1,2], the sequence of monomers charge into the system, the monomer charge ratio in two stages, the hydrophilicity of the monomers, the surface tension, the molecular weight of the polymers [2–4], the compatibility of the polymer [5], the properties of the initiators [6], and the viscosity of polymerization loci [7–9]. Muroi and Hosoi [10] studied the structure of the core–shell latex particle. They pointed out that the polymer particle formed an inverted core–shell morphology when the hydrophobic monomer of the second stage was polymerized in the presence of hydrophilic seeds.

In the emulsion polymerization system, the surfactant significantly influences the surface properties of the latex particles. Barlioni et al. [11] used the method of ESR spectroscopy of nitroxide probes to study the interfacial properties of a styrene–butadiene–acrylic acid polymeric latex and their variation by the addition of a surfactant, sodium dodecyl sulfate (SDS), able to be adsorbed at the latex interface. They pointed out that the adsorption of SDS at the latex interface led to a decrease in polarity and to an increase in microviscosity of the environment sensed by the probe. The effect occurred only for high latex coverage by SDS monomers. Recently, the polymeric surfactant have been used widely in the pharmaceutical, the use of polymeric surfactant has been suggested as a non-irritant alternative to low molecular weight surfactants by a number of authors [12,13]. The polymeric surfactants have the advantage of low usage level, excellent emulsion stability, simplified emulsion formation procedure. Typical representatives of o/w surfactant are Pemulens® (BF Goodrich, USA), which are the polymers of acrylic acid modified by long chain (C_{10}–C_{30}) alkyl acrylates and cross-linked with allypenthaerythritol [14]. The derivatives of poly(acrylic acid) (PAA) have been used widely as surfactant in the pharmaceutical, but have not been used widely in the emulsion polymerization. There are no investigations about

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the influence of PAA on the emulsion polymerization. Besides, the effect of PAA on the morphology of polymer particles synthesized by emulsion polymerization has not been investigated.

In our previous works [15–21], the method of two stages soapless seeded emulsion polymerization was used to synthesize the PMMA/PS composite polymer particles. The morphology of the PMMA/PS composite particle was core–shell structure, with the PMMA as core and the PS as shell. We proposed a core–shell model to describe the formation of the core–shell composite particle [15,16]. Besides, we indicated that the morphology of the composite particle was largely influenced by the properties of initiator [18]. In our previous works [14–20], the composite polymer particles were always synthesized by the method of soapless emulsion polymerization; there was no surfactant included in the aqueous medium of reaction system.

In this study, the aqueous medium of reaction system consisted of PAA, which was used as a stabilizer in the emulsion polymerization. The method of two stages soapless seeded emulsion polymerization was used to synthesize the PMMA/PS polymer/polymer composite particles in the presence of PAA solution medium. The purpose of this work was to investigate the effect of PAA solution on the morphology of PMMA/PS composite particles.

2. Experimental

2.1. Material

Methyl methacrylate (MMA), styrene (st) and acrylic acid (AA) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Water was redistilled and deionized. Potassium persulfate and other chemicals were analytical grade and used without further purification.

2.2. Preparation of seed latex

The PAA solution was synthesized by the method of solution polymerization; the reaction conditions were listed in Table 1. Afterwards, the PMMA seed latexes were synthesized in the presence of PAA solution by the method of soapless emulsion polymerization under the condition listed in Table 2. The polymerization was carried out in a 2 l four-necked round-bottom glass reactor with a Teflon paddle operating at 300 rpm. The number-average diameter of the PMMA seed latexes, which were synthesized in the presence of PAA solution, was 207.8 nm.

Table 1
Ingredients for the preparation of PAA solution (N_2; 80 °C; stirring rate, 300 rpm; reaction time, 1.5 h)

Acrylic acid (AA) (g)	50
$K_2S_2O_8$ (KPS) (g)	0.6
Water (g)	500

After the reaction proceeded for 1.5 h, the conversion of the monomer was 99.6%.

Table 2
Ingredients for the production of PMMA seed particles and composite polymer particles in the presence of PAA solution (N_2; 80 °C; stirring rate, 300 rpm)

Ingredients	PMMA seed latexes (first stage)	PMMA/PS composite particles (second stage)
Weight of seed latex emulsion (g)		500
Styrene (g)		96.76
MMA (g)	120	
KPS (g)	0.866	1
Water (g)	900	310
PAA solution[a] (g)	220	

[a] The weight percent of PAA contained in the PAA solution is 9%.

2.3. Production of composite polymer particles

The composite polymer particles were synthesized by the method of multistage soapless seeded emulsion polymerization under the condition listed in Table 2. In the soapless seeded emulsion polymerization, quantitative monomer was poured into the PMMA seed latex emulsion system, and stirred under the atmosphere of nitrogen, and heated in a water bath to 80 °C. At this moment, the styrene monomer swelled into the PMMA seed latex by the process of stirring. After stirring for 50 min, the temperature of the reaction system reached 80 °C, and then the aqueous solution of $K_2S_2O_8$ was added into the reaction system to begin the reaction of soapless seeded emulsion polymerization.

2.4. Conversion

The monomer conversion was determined gravimetrically. The detailed method and the calculation of conversion were stated in our previous work [21].

2.5. Concentration of monomer in polymer particles

The concentration of the monomer in polymer particles was measured by the method that was stated in our previous work in detail [21].

2.6. Observation of ultrathin cross-sections of composite polymer particles

In order to eliminate the influence of PAA during the observation of the morphology of composite polymer particles, the deionized water was used to repeatedly wash the composite polymer particles by the method of centrifugation. Then, the polymer particles were dried, and dispersed in epoxy matrix, cured at 50 °C for 24 h, and then microtomed to form the sections about 900 Å thick. The ultrathin cross-sections were stained with RuO_4 vapor at room temperature for 2 min in the presence of 1% RuO_4 solution. The stained ultrathin cross-sections were observed using the transmission electron microscope (TEM) (JEOL JEM-1200 EX). The RuO_4 can stain PS phase, but cannot stain PMMA phase, so under the observation of TEM, the PS phase shows the dark image, and the PMMA phase shows the bright image.

2.7. Observation and measurement of the diameter of composite polymer particles

The composite polymer particles were observed by using a TEM (JEOL JEM-1200 EX). The number-average diameters of particles were measured from the TEM photographs with image analysis software for Image Map Plus (MPK Technology Inc.)

3. Results and discussion

In this study, the PMMA/PS composite polymer particles were synthesized in the presence of PAA solution by using the method of two stages soapless seeded emulsion polymerization under the conditions listed in Tables 1 and 2. The TEM photographs of PMMA seed particles, PMMA/PS, composite polymer particles are shown in Fig. 1. The photographs show that the composite polymer particles are monodispersed. The diameters of the composite polymer particles are listed in Table 3. The measured diameter of the composite polymer particles approached to the calculated one based on the polymerization recipes. These results indicated that the two stages soapless seeded emulsion polymerization does not generate the second nucleation, and the polymerization proceeded in the corresponding seed particles. The cross-section morphology of PMMA/PS composite polymer particle was core–shell structure, as shown in Fig. 2(a); the core zone is PS phase, and the shell zone is PS phase dispersed in the PMMA phase. This result was in great contrast to the morphology of PMMA/PS composite particle shown in Fig. 2(b) produced under the same conditions except for the existence of the PAA, the ingredients and reaction conditions were listed in Table 4. The morphology of Fig. 2(b) shows that the core zone is PMMA phase, and the shell zone is PS phase. In order to investigate the influence of PAA on the morphology of PMMA/PS composite particles to form the core(PS)–shell(PS dispersed in PMMA) structure, we observed the

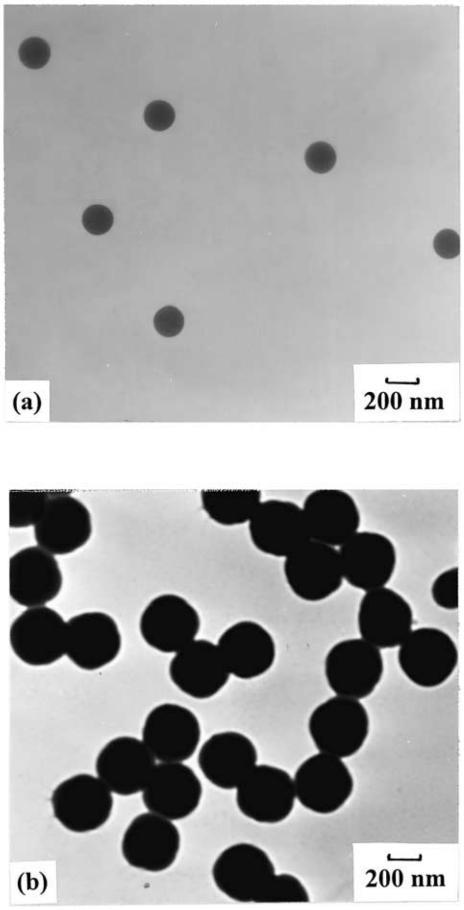


Fig. 1. TEM photographs of (a) PMMA seed, (b) PMMA/PS composite particles produced by two stages soapless seeded emulsion polymerization under the conditions listed in Table 2.

Table 3
The diameters of the seed latex and composite polymer particles

	PMMA seed latex	PMMA/PS composite particles
Calculated diameter (nm)	207.8[a]	306.8
Measured diameter (nm)	207.8	316.6

[a] The measured diameter of PMMA seed latex was used as the calculated diameter of PMMA seed latex.

Table 4
Ingredients for the production of PMMA seed particles and PMMA/PS composite polymer particles in the absence of PAA solution (N_2; 80 °C; stirring rate, 300 rpm)

Ingredients	PMMA seed latex (first stage)	PMMA/PS (second stage)
Weight of seed latex emulsion (g)		500
Styrene (g)		96.76
MMA (g)	120	
KPS (g)	1.2	1
Water (g)	1120	310

The number-average diameter of the PMMA seed latexes produced in the absence of PAA solution was 218.6 nm.

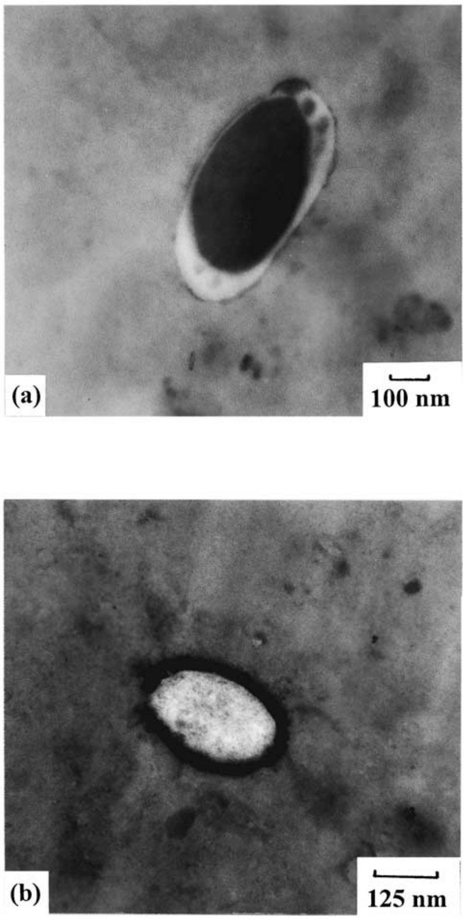


Fig. 2. The morphology of the cross-section of PMMA/PS composite particle that was synthesized by the method of two stages soapless seeded emulsion polymerization (a) in the presence of PAA, (b) in the absence of PAA.

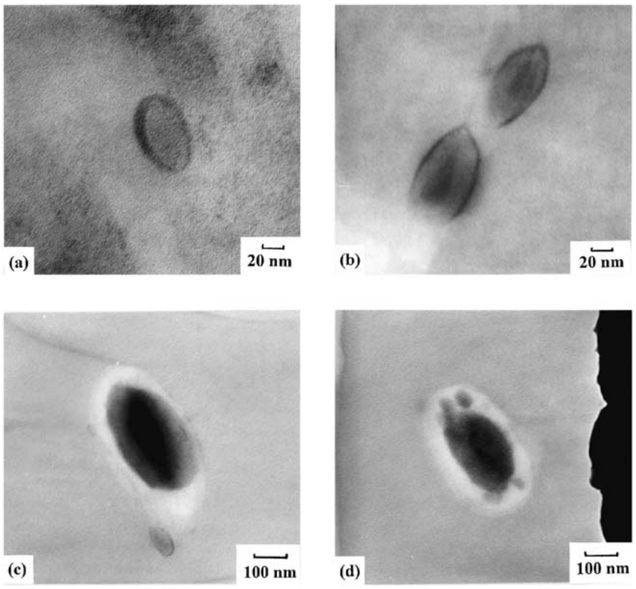


Fig. 3. The morphology of the cross-section of PMMA/PS composite particles that are synthesized by the second stage reaction for (a) 2 min (conversion: 20.5%) (b) 25 min (conversion: 38.4%) (c) 35 min (conversion: 52.6%) (d) 60 min (conversion: 99.8%).

morphology of the cross-section of PMMA/PS composite particles during the process of second stage reaction. We found that the morphology of the PMMA/PS composite polymer particles were changeable during the process of second stage reaction, as shown in Fig. 3(a)–(d). In the initial reaction (conversion of styrene was 0–26%), the PMMA/PS composite polymer particles have the morphology of core–shell structure with PS as shell (black image), PMMA phase mixes with PS phase as core (gray image), as shown in Fig. 3(a). With the increase of conversion (conversion of styrene was 26–38.4%), the morphology of the PMMA/PS composite particles form the core and two shell structure; the core zone was PS (dark image), the inner shell was PMMA phase mixed with PS phase (gray image), and the outer shell was PS (dark image) as shown in Fig. 3(b). In the final reaction (conversion of styrene was 38.4–99.8%), most of the PS diffused from the shell region to the core region, and the shell region gradually showed the PMMA phase. Finally, the PMMA/PS composite particles showed the morphology of core–shell structure, that is, PS as core, PS phases dispersed in PMMA phase as shell, are shown in Fig. 3(c) and (d). The relation between the conversion of styrene and the morphology of the PMMA/PS composite particle is shown in Fig. 4. In addition, the relation between the morphology of the PMMA/PS composite polymer particle and the concentration of monomer included in the polymer particles is also shown in Fig. 5. The figure shows that the morphology of the composite particles was changeable with decreasing concentration of monomer included in polymer particles. In this study, we divided the course of the second stage reaction into three periods to explain the change in the morphology of PMMA/PS composite particle.

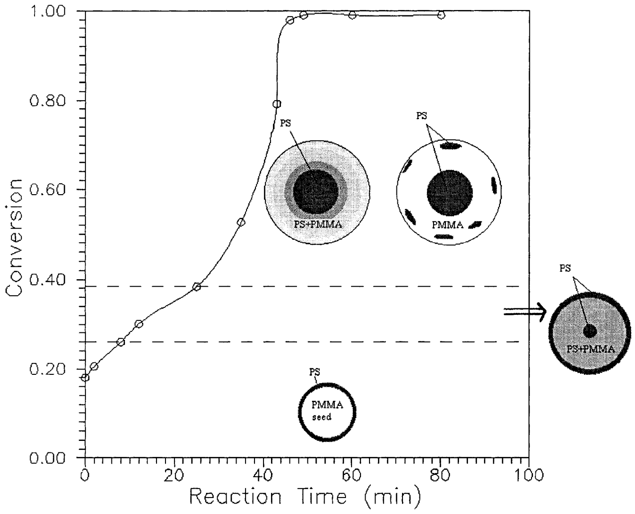


Fig. 4. The relation between the conversion of second stage reaction and the morphology of the cross-section of PMMA/PS composite polymer particle.

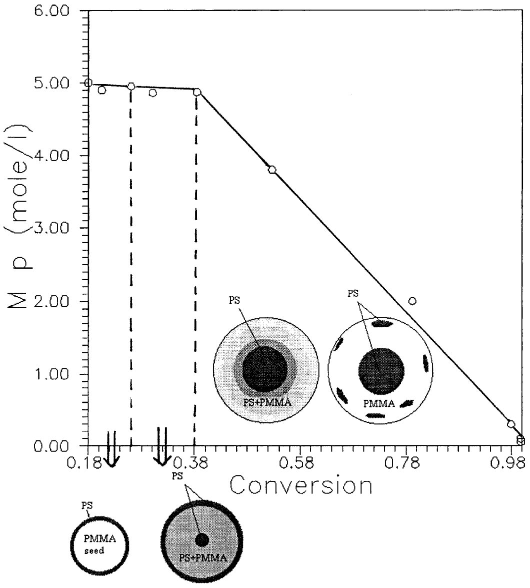


Fig. 5. The relation between the concentration of monomer in the PMMA/PS composite polymer particle and the morphology of the cross-section of the PMMA/PS composite polymer particle.

3.1. The initial period (the monomer drops included in the reaction system)

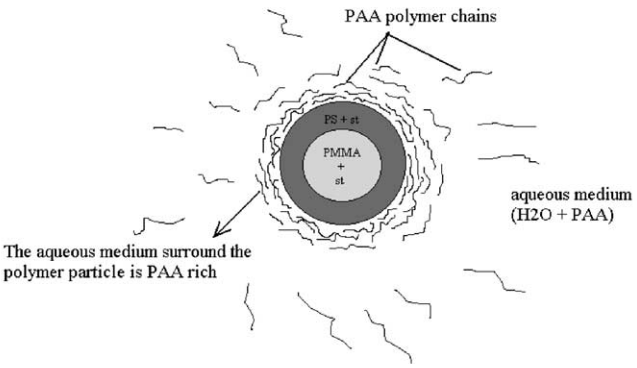
In the initial period of the second stage reaction, the morphology of the PMMA/PS composite particle was core(PMMA mixes with PS)–shell(PS) structure. The reason could be explained as follows: in the second stage reaction, the styrene was polymerized in the presence of PMMA seed latexes. In the reaction system, one part of styrene swollen into the PMMA seed latexes by the stirring process, another part of styrene formed the monomer drops, and dispersed in the aqueous medium. The initiator that was used in the second stage reaction was water soluble $K_2S_2O_8$, so the hydrophilic SO_4^- group, which decomposed from $K_2S_2O_8$, anchored on the surface of latex particle because the hydrophilic SO_4^- group likes to be close to the aqueous medium. Therefore, although the styrene monomer swelled into the inner region of PMMA seed latex during the stirring process, the styrene monomer diffused from the inner region of PMMA seed latex to the shell region to proceed to the second stage reaction. Besides, the styrene, which is included in the monomer drops also diffused to the surface of PMMA seed latex, and polymerized on the surface of PMMA seed latex to form the PS. Both PS and PMMA could dissolve in styrene very well, so the latex particle included the PMMA + st region and PS + st region during the process of second stage reaction. The interfacial tension would control the morphology of the composite polymer particles. Table 5 shows that the interfacial tension of PS + st to the aqueous medium (H_2O + PAA) was slightly higher than that of PMMA + st to the aqueous medium. Theoretically, the PMMA + st region would localize at the shell zone under the effect of thermodynamic factor, while the difference between the interfacial tension of PMMA + st phase to aqueous medium and PS + st phase to aqueous medium was not very significant. Besides, in emulsion polymerization, the latex particle was surrounded by the ionic groups (SO_4^-), which decreased the interfacial tension of the PS shell to aqueous medium significantly [6]. Therefore, the second stage reaction proceeded on the shell region of the PMMA seed latex. Although the PS polymer chains had the hydrophilic SO_4^- group, while the hydrophilic property of the PS polymer chains decreased with increasing polymer chains length. Once the PS polymer chains propagate to form the long chains, the hydrophobic property of the long PS chains was more significant than the hydrophilic property of the chain end SO_4^- group, therefore, the PS polymer chains were not favorable to locate on the surface of polymer particles close to the aqueous medium, but like to diffuse into the hydrophobic core (PMMA + st). Moreover, the aqueous medium of the emulsion system included PAA, which might be close to the surface of the polymer particle (as seen in Scheme 1) due to the fact that PAA behaved as a surfactant, and therefore the aqueous medium, which surrounded the polymer particle, was PAA rich and water poor. The rich PAA might lower the hydrophilic property of the aqueous medium that surrounded the composite particles, so it became possible for the SO_4^- group to leave from the surface of composite polymer particle. At this moment, the monomer droplet is present in the reaction system to support the polymerization and therefore the polymer particle is filled with the styrene monomer to lower the viscosity of the polymer particles. Besides, the styrene monomer was same as plasticizer to lower the glass transition temperature (T_g)

Table 5
Interfacial tension values of polymer solution to aqueous medium (water + PAA) at 27 °C

Polymer solution	Interfacial tension (dyne/cm)
PMMA + styrene	11.6[a]
PS + styrene	13.8[b]

[a] Soapless emulsion polymerized PMMA was used (concentration 2.0 wt%).

[b] Soapless emulsion polymerized PS was used (concentration 2.0 wt%).



Scheme 1. The latex particle was surrounded by the PAA solution.

of the polymer particles, so the PS polymer chains were able to move to the center. Moreover, the polymerization proceed at high temperature (80 °C), so as to increase the movability of the PS polymer chains. In the initial period of second stage reaction, the conversion of styrene was low, so only a little of hydrophobic long PS polymer chains diffused from the shell zone across the PMMA phase to the core zone. Because the amount of hydrophobic long PS polymer chains was not large, so as to accumulate significantly on the core zone, the core zone only showed the gray image (PS phase mixes with PMMA phase). Therefore, the particles showed the stable core(PMMA mixed with PS)–shell(PS) structure in the initial period of reaction as shown in Fig. 3(a).

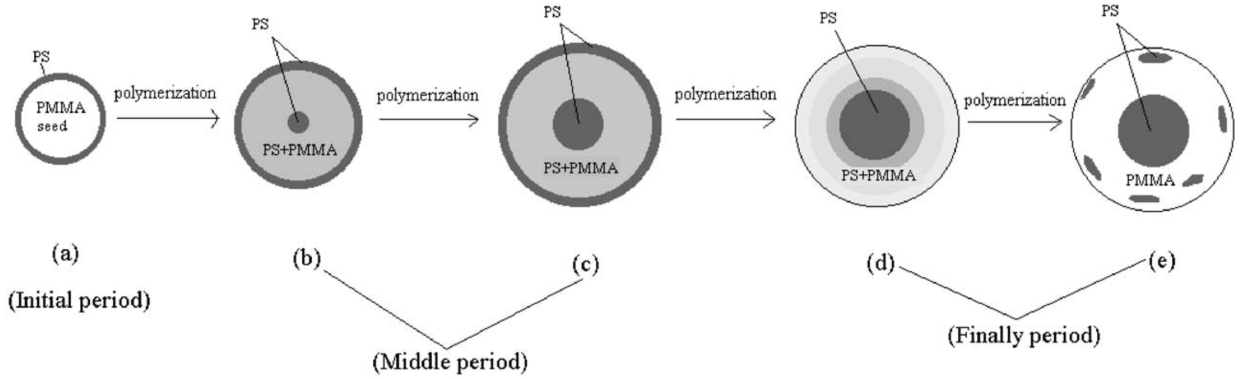
3.2. The middle period (the monomer drops included in the reaction system)

In the middle period of second stage reaction, the polymer particle showed the morphology of core and two shell, that is, PS as core (dark image), PMMA phase mixed with the PS phase as inner shell (gray image), PS as outer shell (dark image) as shown in Fig. 3(b). The reason could be explained as follow.

In the middle period of second stage reaction, the monomer still included in the polymer particles as shown in Fig. 5, so the viscosity and T_g of the polymer particles was low as usual. The styrene monomer diffused continuously from the monomer drops to the surface of the polymer particle to support the synthesis of the PS polymer chains, and then once the PS polymer chains were so long as to increase the hydrophobic property, the PS polymer chains diffused continuously from the shell region across the PMMA region to the core zone, and accumulated on the core zone. In the middle period of reaction, the conversion of styrene was high, so a large amount of PS polymer chains accumulated on the core zone to show the significant black image. The morphology of the composite polymer particles shows that the outer shell and core zones were PS phases (black image), and the inner shell was PMMA phase mixed with the PS phases (gray image) due to the fact that the PS chains diffused across the PMMA region to the core zone.

3.3. The final period (the monomer drops had been consumed)

After the monomer drops were consumed by the polymerization, only the styrene, which remained in the polymer particle, supported the reaction. In the beginning of the final period of reaction, styrene monomer still remained in the polymer particle to lower the viscosity and T_g of the polymer particle, and in addition, the reaction proceeded at high temperature (80 °C), and hence the PS polymer chains still had the ability to move to the center. The long PS chains, which were synthesized on the shell zone, diffused gradually into the core zone due to the hydrophobic property of the long PS chains and the poor hydrophilic property of the aqueous medium surrounding the polymer particle. In the final period of reaction, there was no styrene monomer, which came from the monomer drops, supporting the synthesis of PS on the shell zone continuously, so the shell zone did not show the PS phase gradually, as shown in Fig. 3(c). The increase in conversion might decrease the concentration of styrene included in the polymer particle, so the viscosity and T_g of the polymer particle seemed to be high gradually. At this moment, the PS polymer chains were difficult to diffuse from the shell zone to the core zone, while located on the shell zone due to the high viscosity of the polymer particle. At the end of second stage reaction, the PMMA/PS composite polymer particles showed the morphology of core–shell structure with PS as core, PS phase dispersed in PMMA phase as shell, as shown in Fig. 3(d). The above results clearly show that thermodynamic factor was the main factor to decide the morphology of the PMMA/PS composite particle, which was synthesized in the presence of PAA solution. The process of the second stage reaction to synthesize the PMMA/PS composite polymer particle is shown in Scheme 2.



Scheme 2. The process of second stage reaction for the synthesis of PMMA/PS composite polymer particles. (a) The morphology of the PMMA/PS composite particle, which was synthesized in the initial period of reaction. (b,c) The morphology of the PMMA/PS composite particle, which was synthesized in the middle period of reaction. (d,e) The morphology of the PMMA/PS composite particle, which was synthesized in the final period of reaction.

4. Conclusion

In this present work, the method of two stages soapless seeded emulsion polymerization was used to synthesize the PMMA/PS polymer/polymer composite polymer particles in the presence of PAA solution. The PAA solution was the important factor to decide the morphology of the PMMA/PS composite particles. All over the course of second stage reaction, the morphology of the PMMA/PS composite polymer particles was changeable; in the initial period of reaction, the morphology of the PMMA/PS composite particles showed the core(PS phase mixes with PMMA phase)–shell(PS) structure, in the middle period of reaction, thermodynamic factor was the main factor to decide the morphology of the core and two shells, with PS as core, PMMA mixed with PS as inner shell, and PS as outer shell. Finally, the PMMA/PS composite particle showed the core–shell structure with the PS as core, and the PS phase dispersed in PMMA phase as shell. The morphology of the PMMA/PS composite particle synthesized in the presence of PAA was different from that synthesized in the absence of PAA, the reasons may be concluded as follow.

The PAA that included in the emulsion system might be close to the surface of the polymer particle due to the fact that the PAA behaved as a surfactant. The PAA might lower the hydrophilic property of the aqueous medium that surrounded the composite particles, and so it became possible for the SO_4^- group to leave from the surface of composite polymer particle. Once the PS polymer chain propagate to form the hydrophobic long chain, the PS polymer chains with the SO_4^- groups tend to leave from the shell zone to the hydrophobic core zone. Moreover, although the difference between the interfacial tensions of PMMA + st phase to aqueous medium and PS + st phase to aqueous medium was not very significant, the difference during the presence of PAA was larger than that during the absence of PAA as shown in our previous work [22], so the PS + st phase was more likely to move to the core zone in the presence of PAA than that in the absence of PAA. In addition, lower interfacial tensions in the presence of the PAA than those in the absence of the PAA seem to lead the amount of monomer absorbed in seed particle to be larger, that is, the viscosity and T_g of the PMMA seed particle to be lower in the presence of PAA. Therefore, the PS polymer chains were easier to move from shell zone to core zone than that in the absence of PAA. The above reasons describe why the thermodynamically stable morphology was obtained in the presence of PAA.

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