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ORIGINAL CONTRIBUTION

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The morphology of composite polymer particles produced by multistage soapless seeded emulsion polymerization

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Abstract Composite polymer particles which contain poly(methyl methacrylate) (PMMA) and polystyrene (PS) components (PMMA/PS composite particle) were synthesized by the method of multistage soapless seeded emulsion polymerization. In this study, the process of multistage soapless seeded emulsion polymerization included two-stage polymerization, three-stage polymerization or four-stage polymerization. The morphologies of the PMMA/PS composite particles were studied. The kinetic factor was the main force to control the morphology of the linear PMMA–PS composite particles which were synthesized by the method of two-stage reaction. Both the kinetic factor and the thermodynamic factor decide the morphology of the linear composite particles which were synthesized by the method of either three-stage or four-stage reaction. However, the thermodynamic factor cannot influence the morphology of the PMMA/PS composite particles with a cross-linked structure which were synthesized by the method of three-stage reaction. The cross-linked composite polymer particles had the morphology of a multilayer structure, which showed that the polymer layers accumulated in their order of production.

Keywords Morphology · Multistage · Seeded · Emulsion · Composite particle

Introduction

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

There are many factors to control the morphology of polymer particles, such as the method of the monomer addition into the system [1, 2], the sequence of monomer fed into the system, the monomer ratio in the two stages, the hydrophilicity of the monomers, the surface tension, the molecular weight of the polymers [2–4], the compatibility of the polymers [5], and the properties of the initiators [6]. Okubo and coworkers [7–9] pointed out that the morphology of polymer particles could change with the molecular weight of the polymers, the viscosity of the polymerization loci, and the hydrophilicity of the two polymers. Lee and Ishikawa [3] synthesized two kinds of hydrophilic seeds, which had high molecular weight and low molecular weight, respectively, and the morphology of the particles changed with the molecular weight of the polymers.

Moreover, the method of seeded dispersion polymerization was used to successfully synthesize poly(methyl methacrylate) (PMMA)/polystyrene(PS) composite particles which had a PMMA core and PS shell structure. Okubo and coworkers [10–12] suggested that from the viewpoint of thermodynamic equilibrium, such a morphology is difficult to form by usual seeded polymerization in a polar medium. However, in a general seeded dispersion polymerization, almost all the monomers exist in the medium and the viscosity of the seed particles is so high that polymer radicals are unable to diffuse into the inside from the particle surface. So, the polymer formed by the seeded dispersion polymerization seems to accumulate on the PS seed particles. The morphology of the composite particles seems to be controlled kinetically. In our previous work, the method of two-stage soapless seeded emulsion polymerization was used to synthesize core–shell polymer/polymer composite particles [13–17]. We proposed a core–shell model to describe the formation of the core–shell composite particle [13–15]. This core–shell model pointed out the shell was a reaction zone, and in the entire cure of polymerization, the thickness of the shell was not constant. The morphology of the composite particles which were synthesized by the method of soapless seeded emulsion polymerization were largely influenced by the properties of the initiator [17]. In our previous work, the soapless seeded emulsion polymerization, which was used to synthesize the composite particles included two-stage reaction. In this work, multistage soapless seeded emulsion polymerization which included two-stage reaction, three-stage reaction or four-stage reaction was used to synthesize the polymer/polymer composite particles. The purpose of this work was to investigate the morphology of linear PMMA/PS composite particles and cross-linked PMMA/PS composite particles which were synthesized by the method of multistage soapless seeded emulsion polymerization.

Table 1 Preparation of seed latexes by soapless emulsion polymerization (N_2; 80 °C; stirring rate, 300 rpm). *PS*: polystyrene; *PMMA*: poly(methyl methacrylate)

Ingredients	PMMA seed latex	PS seed latex
Methyl methacrylate (g)	120	
Styrene (g)		220
$K_2S_2O_8$ (g)	0.866	3
Water (g)	1,100	1,500
Reaction time (h)	1	5
Conversion of monomer (%)	99.6	99.5

Experimental

Material

Methyl methacrylate (MMA) and styrene (St) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Water was redistilled and deionized. The initiator ($K_2S_2O_8$), the cross-linking agent (ethyl glycol dimethylacrylate, EGDMA) and the other chemicals were analytical grade and were used without further purification.

Preparation of seed latex

The PMMA seed latexes and the PS seed latexes were synthesized by the method of soapless emulsion polymerization under the condition listed in Table 1. The polymerization was carried out in a 2-l four-necked round-bottomed glass reactor with a Teflon paddle stirrer operating at 300 rpm. The number-average diameters of the PMMA seed latexes and the PS seed latexes were 303 and 395 nm respectively.

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 added into the seed latex emulsion system, and then the reaction system was heated in a water bath at a temperature of 80 °C, and continuously stirred under the atmosphere of nitrogen, at the moment the monomer swelled into the seed latexes owing to the stirring process. After the temperature of the reaction system had reached 80 °C, the aqueous solution of $K_2S_2O_8$ was added into the reaction system to begin the reaction of soapless seeded emulsion polymerization.

Table 2 Ingredients for the production of various kinds of composite polymer particles (N_2; 80 °C; stirring rate, 300 rpm)

Ingredients	PMMA/PS	PMMA/PS/PMMA	PMMA/PS/PMMA/PS	PMMA/PS(XL)/PMMA(XL)
Seed latexes	PMMA latex	PMMA/PS latex	PMMA/PS/PMMA latex	PMMA/PS(XL) latex
Weight of seed latex emulsion (g)	500	748.86	1,108	1,192
Styrene (g)	98.36		98.36	
Methyl methacrylate (g)		49.18		39.34
$K_2S_2O_8$ (g)	0.5	0.5	0.5	0.7
Water (g)	150	310	310	190
Ethyl glycol dimethylacrylate (g)				0.92
Ingredients	PMMA/PS/PS	PS/PMMA	PS/PMMA/PS	
Seed latexes	PMMA/PS latex	PS latex	PS/PMMA latex	
Weight of seed latex emulsion (g)	700	385	675	
Styrene (g)	49.18		49.18	
Methyl methacrylate (g)		49.18		
$K_2S_2O_8$ (g)	0.5	0.5	0.5	
Water (g)	150	240	240	

Observation of ultrathin cross-sections of composite polymer particles

The composite polymer particles were dried and then dispersed in an epoxy matrix, cured at 50 °C for 24 h, and microtomed to form 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 RuO_4 can stain the PS phase, but cannot stain the PMMA phase. The stained ultrathin cross-sections were observed using a transmission electron microscope (TEM) (Hitachi Co. Japan S-550). Under the TEM, the PS phase shows the dark image and the PMMA phase shows bright image.

Observation and measurement of the diameter of composite polymer particles

The composite polymer particles were observed by using a Hitachi S-550 TEM. The number-average diameters of the particles were measured from the TEM photographs with image analysis software for Image Map Plus (MPK Technology).

Results and discussions

The TEM photographs of the PMMA seed particles, the PMMA/PS, PMMA/PS/PMMA, and PMMA/PS/PMMA/PS composite polymer particles produced by multistage soapless seeded emulsion polymerization under the conditions listed in Tables 1 and 2 are shown in Fig. 1. The photographs show that the composite polymer particles were monodispersed. The diameters of the composite polymer particles are listed in Table 3. The measured diameters of the composite polymer particles approached the ones calculated on the basis of the polymerization recipes. These results indicated that multistage soapless seeded emulsion polymerization does not generate the second nucleation, and the polymerization proceeded in the corresponding seed particles. The cross-section morphology of the PMMA/PS composite polymer particles was a core–shell structure, as shown in Fig. 2a. The core zone is PMMA, and the shell zone is PS. This result was the same as in our previous work (13–17). The PMMA/PS composite polymer particles were synthesized by the method of two-stage reaction. The PMMA seed particles were synthesized in the first stage of the reaction. Then, the St was polymerized in the presence of PMMA seed particles and the PMMA/PS composite particles were formed in the second stage of the reaction. The core–shell morphology of the composite particles formed in this work by using $K_2S_2O_8$ as the initiator could be explained from both the kinetic factor and the thermodynamic factor.

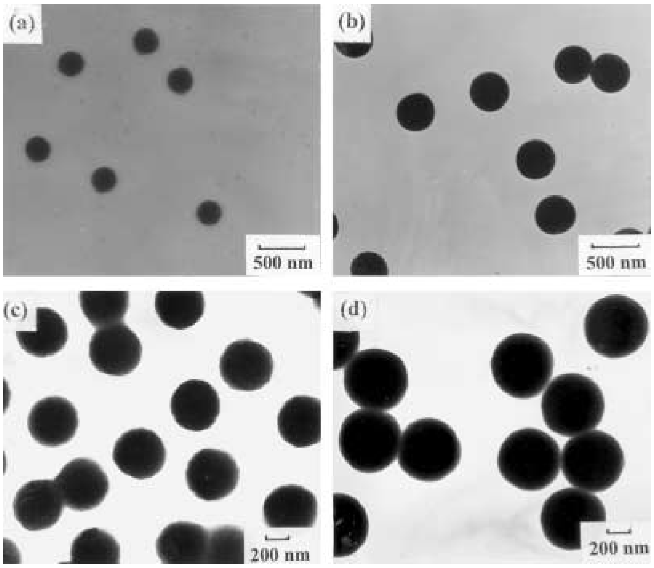


Fig. 1 Transmission electron microscope photographs of **a** poly(methyl methacrylate) (PMMA) seed, **b** PMMA/polystyrene (*PS*), **c** PMMA/PS/PMMA, and **d** PMMA/PS/PMMA/PS composite particles produced by multistage soapless seeded emulsion polymerization under the condition listed in Table 2

Table 3 The diameters of the composite polymer particles

	PMMA seed latex	PMMA/PS	PMMA/PS/PMMA	PMMA/PS/PMMA/PS
Calculated diameter (nm)	303[a]	448	494	566
Measured diameter (nm)	303	439	482	558

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

Kinetic factor

In the second stage of the reaction, the St was polymerized in the presence of PMMA seed latexes. In the reaction system, one part of St swelled into the PMMA seed latexes by the stirring process, another part of St formed the monomer drops and dispersed in the aqueous medium. The initiator that was used in the second stage of the 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 the latex particle owing to the fact that the hydrophilic SO_4^- group likes to be close to the aqueous medium. So although the St monomer swelled into the inner region of the PMMA seed latex during the stirring process, the St monomer diffused from the inner region of the PMMA seed latex to the shell region to proceed to the second stage of the reaction. Besides, the St which was in the monomer drops also diffused to the surface of the PMMA seed latex, and polymerized on the surface of the PMMA seed latex. The polymerization in the second stage proceeded on the surface of the PMMA seed latex and formed the PS shell.

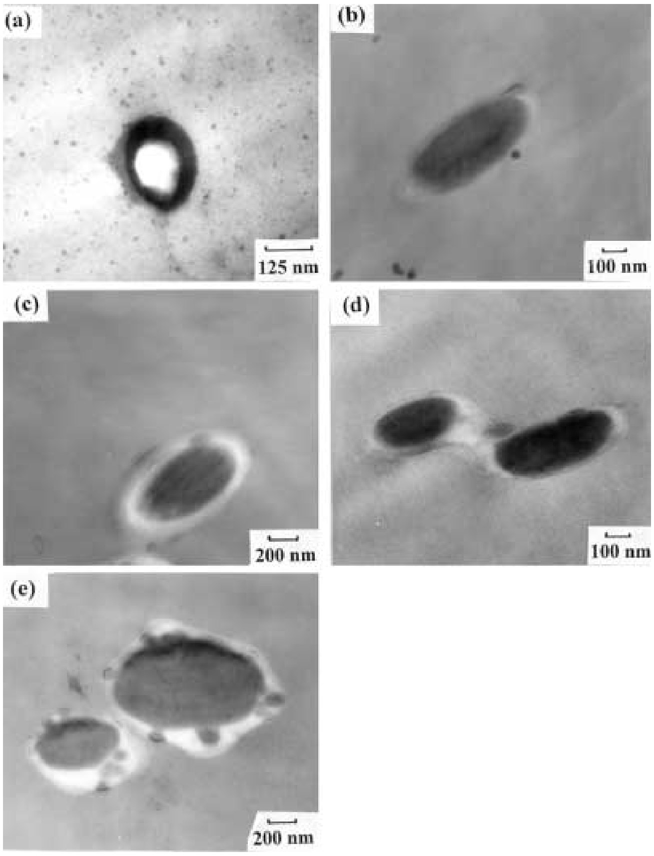
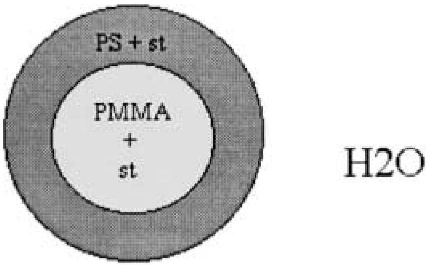


Fig. 2 The morphology of the cross-section of a PMMA/PS composite particlse, **b** PMMA/PS composite particles which swell with methyl methacrylate (*MMA*) monomer before the beginning of the third stage of the reaction, **c** PMMA/PS/PMMA composite particles, **d** PMMA/PS/PMMA composite particles which swell with styrene monomer before the fourth stage of the reaction, and (**e**) PMMA/PS/PMMA/PS composite particles

Thermodynamic factor

During the second stage of the reaction, the St diffused into the PMMA seed and was polymerized to form PS. Both PS and PMMA could dissolve in St very well, so the latex particle included the PMMA and St region and the PS and St region during the process of the second stage of the reaction. In the reaction system, the latex particle was surrounded by water as seen in Scheme 1. The interfacial tension would control the morphology of the composite polymer particles. The interfacial tension of PS and St to water was slightly higher than that of PMMA and St to water as seen in Table 4. Theoretically, the PMMA and St region would localize at the shell zone under the effect of the thermodynamic factor; however, during the second stage of the polymerization, the St monomer quickly diffused from the inner region of the PMMA seed particles to the shell region to continue the reaction, so the PS and St phase did not have enough time to transfer into the core region of the polymer particles. Moreover, the difference between the interfacial tension of the PMMA and St phase to water and the PS and St phase to water was not very significant. The effect of the kinetic factor on the morphology of the composite particles was more significant than the effect of the thermodynamic factor on the morphology of the composite particle. The kinetic factor was the main factor to decide the morphology of the PMMA/PS composite particles which were synthesized by two-stage reaction.



Scheme 1 The latex particle surrounded by water

Table 4 Interfacial tension values of polymer solution to water at 27 °C

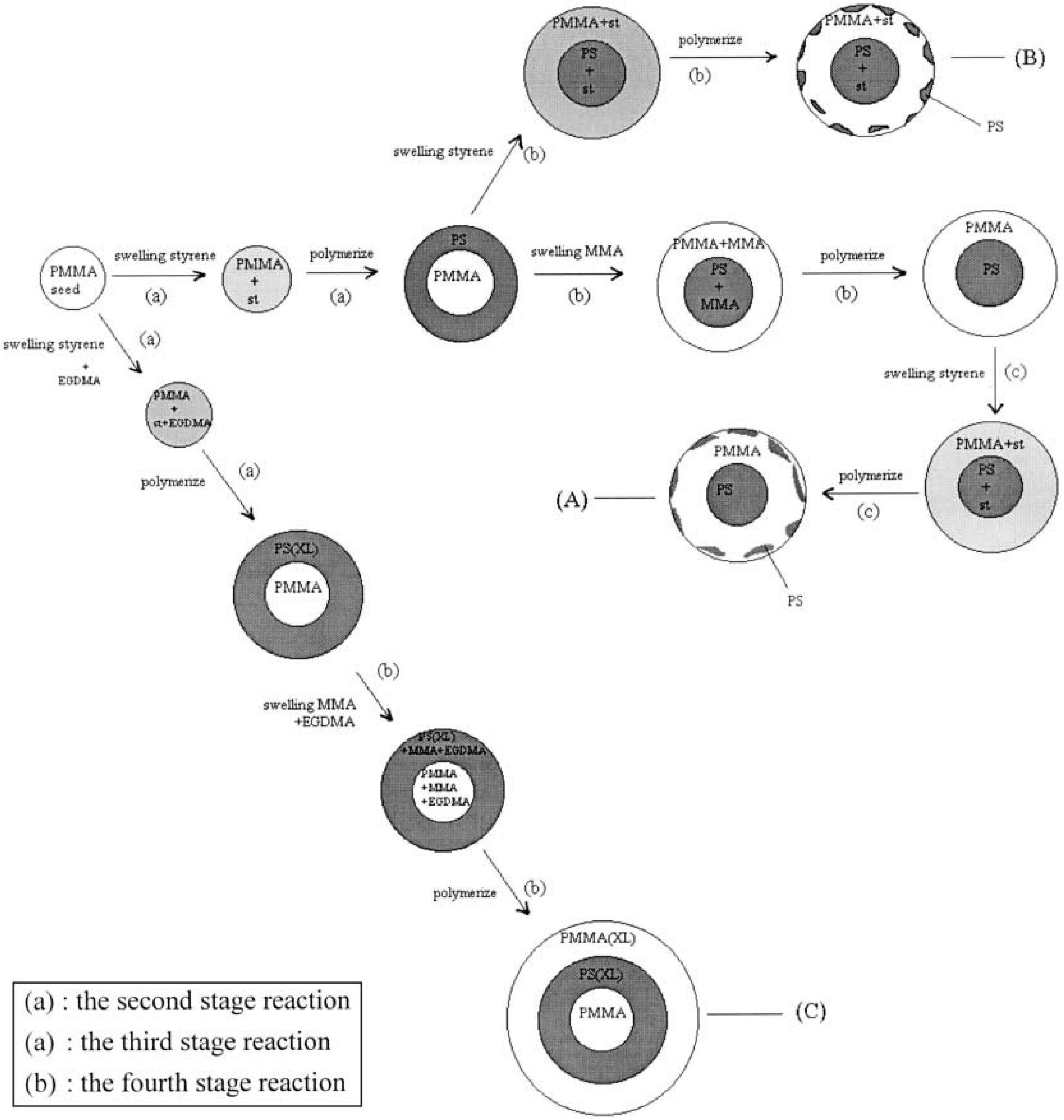
Polymer solution	Interfacial tension (dyne/cm)
PMMA + methyl methacrylate	22.4[a]
PS + methyl methacrylate	23.8[b]
PMMA + styrene	23.2[a]
PS + styrene	24.2[b]

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

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

Afterward, the core–shell PMMA/PS composite polymer particles were used as seeds for the third stage of the reaction. In the third-stage of the reaction, the MMA monomer was added into the PMMA/PS seed latex emulsion system and then stirred before the addition of the initiator into the reaction system. So the MMA monomer had enough time to diffuse into the PMMA/PS composite seed latexes, and formed the PMMA and MMA region and the PS and MMA region. The interfacial tension of PS and MMA to water was higher than that of PMMA and MMA to water as seen in Table 4, so the PS and MMA region transfers from the shell region into the core zone and the PMMA and MMA region transfers from the core region out to the shell zone owing to the thermodynamic equilibrium, as shown in Fig. 2b. After $K_2S_2O_8$ had been added into the reaction system, the hydrophilic SO_4^- group anchored on the surface of the PMMA/PS composite seed latex to continue the polymerization of MMA and PMMA/PS/PMMA composite polymer particles were formed. The morphology of the PMMA/PS/PMMA composite polymer particles was a core–shell structure with PS as the core and PMMA as the shell is shown in Fig. 2c. Scheme 2(A), reactions a and b, shows the process of three-stage reaction for the synthesis of PMMA/PS/PMMA composite polymer particles. The results show that both the kinetic factor and the thermodynamic factor control the morphology of the PMMA/PS/PMMA composite polymer particles. Moreover, the PMMA/PS/PMMA composite polymer particles were used as seeds to continue the fourth stage of the reaction and to synthesize the PMMA/PS/PMMA/PS composite

Scheme 2 The process of (**A**) four-stage reaction for the synthsesis of poly(methyl methacrylate) (*PMMA*)/polystyrene (*PS*)/PMMA/PS composite polymer particles, (**B**) three-stage reaction for the synthesis of PMMA/PS/PS composite polymer particles, and (**C**) three-stage-reaction for the synthesis of PMMA/PS(XL)/PMMA(XL) composite polymer particles



polymer particles. In the fourth stage of the reaction, the St monomer was added into the reaction system and then stirred before the addition of the initiator into the reaction system. The St monomer diffused into the PMMA/PS/PMMA composite seed particles, so the composite polymer particles contained the PS and St region and the PMMA and St region. The PS and St region located at the core region and the PMMA and St region located at the shell region under the effect of the thermodynamic factor, as shown in Fig. 2d. $K_2S_2O_8$ was added into the reaction system to begin the fourth stage of the reaction. The hydrophilic SO_4^- groups anchored on the surface of the composite seed particles to polymerize the St monomer and the PMMA/PS/PMMA/PS composite polymer particles were formed. The morphology of the PMMA/PS/PMMA/PS composite polymer particles showed that the core region was a PS phase and the shell region was PS dispersed in the PMMA phase, as shown in Fig. 2e. The process of the synthesis of the PMMA/PS/PMMA/PS composite particles is shown in Scheme 2(A), reactions a–c. The morphology of the PMMA/PS/PMMA/PS composite particles which were synthesized by the method of four-stage reaction was decided by both the kinetic factor and the thermodynamic factor.

From these results, it is clear that the morphology of the composite polymer particles which were synthesized by two-stages reaction was decided only by the kinetic factor, however, the morphology of the composite polymer particles which were synthesized by either three-stage reaction or four-stage reaction,was decided by both the kinetic factor and the thermodynamic factor. Moreover, the morphology of the PS/PMMA/PS composite polymer particles was studied in order to investigate whether both the thermodynamic factor and the kinetic factor controlled the morphology of every kind of composite polymer particle or not. The method of three-stage reaction was used to synthesize the PS/PMMA/PS composite polymer particles. The first stage of the reaction was to synthesize the PS seed latexes. The second stage of the reaction was to polymerize MMA in the presence of PS seed latexes to form the PS/PMMA composite polymer particles. Under the influence of the kinetic factor, the morphology of the PS/PMMA composite particle was a core–shell structure with PS as a core and PMMA as a shell, as shown in Fig. 3a. Afterward, the PS/PMMA composite polymer particles were used as seeds to continue the third stage of the reaction. Once St had been added into the reaction system before the beginning of the third stage of the reaction, the St monomer diffused into the PS/PMMA composite particles immediately and formed the PS and St region and the PMMA and St region. Under the effect of the thermodynamic factor, the PS and St region located at the core zone and the PMMA and St region located at the shell zone, as shown in Fig. 3b. In the third stage of the reaction, the St was polymerized on the surface of the PS/PMMA composite seed particles by the hydrophilic SO_4^- groups which anchored on the surface of the PS/PMMA composite seed particles. The morphology of the PS/PMMA/PS composite particles showed that the core region was PS and the shell region was a PS phase dispersed in the PMMA phase, as shown in Fig. 3c. The process of the three-stage reaction to synthesize the PS/PMMA/PS composite polymer particles is shown in Scheme 3. Besides, the PMMA/PS/PS composite polymer particles did not show the morphology of a core(PMMA)–shell(PS) structure, but showed that the core region was PS and the shell region was PS dispersed in the PMMA phase. The PMMA/PS/PS composite polymer particles were synthesized by using PMMA/PS composite polymer particles as seeds. Once the St monomer was added into the PMMA/PS seed latex emulsion system, the St monomer diffused into the PMMA/PS composite particles and formed the PMMA and St region and the PS and St region. Under the influence of the thermodynamic factor, the PMMA and St phase transferred out to the shell zone and the PS and St phase transferred into the core zone, as shown in Fig. 4a. After $K_2S_2O_8$ had been added into the reaction system, the St was polymerized on the shell region to form a PS phase dispersed in the PMMA phase as shown in Fig. 4b. The process of the synthesis of the PMMA/PS/PS composite latex is shown in Scheme 2(B). These results once more clarify that although the polymer of the composite polymer particles was

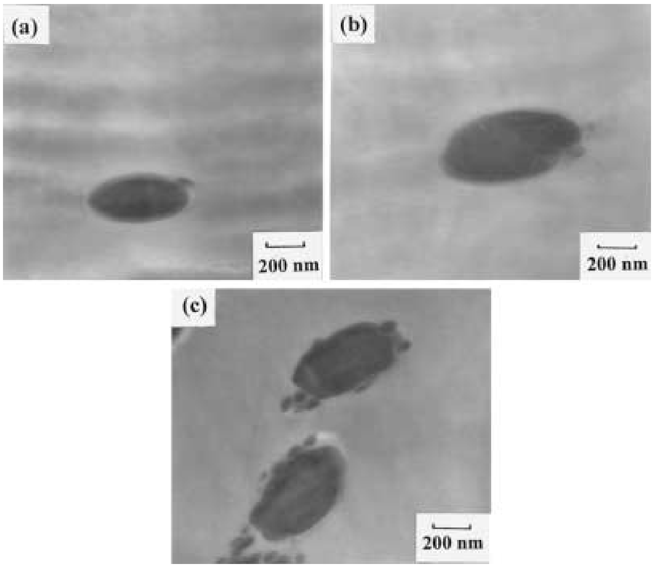
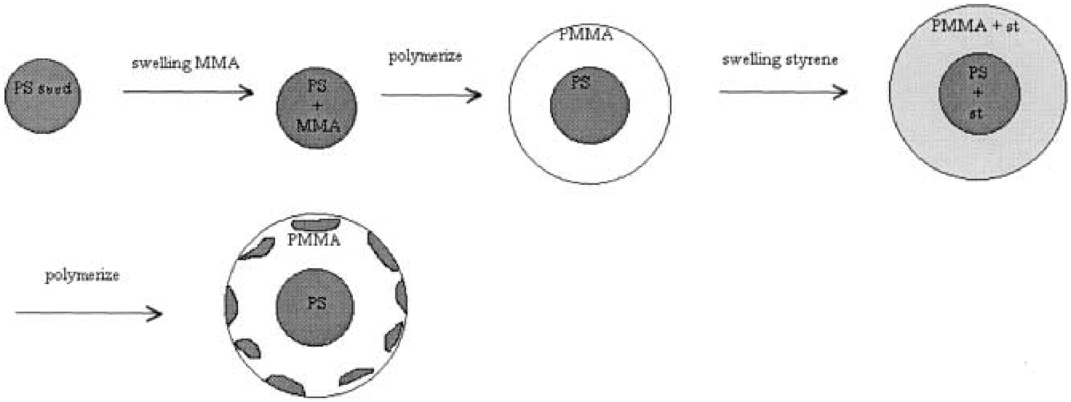


Fig. 3 The morphology of the cross-section of **a** PS/PMMA composite particles, **b** PS/PMMA composite particles which swell with styrene monomer before the third stage of the reaction, and **c** PS/PMMA/PS composite particles



Scheme 3 The process of the three-stage reaction for the synthesis of PS/PMMA/PS composite polymer particles

synthesized in order, the composite polymer particles did not show the morphology of polymer layers accumulated in their order of production.

The morphology of the composite polymer particles which were synthesized by the method of multistage soapless seeded emulsion polymerization was decided by both the kinetic factor and the thermodynamic factor but not by the order of polymerization. However, the

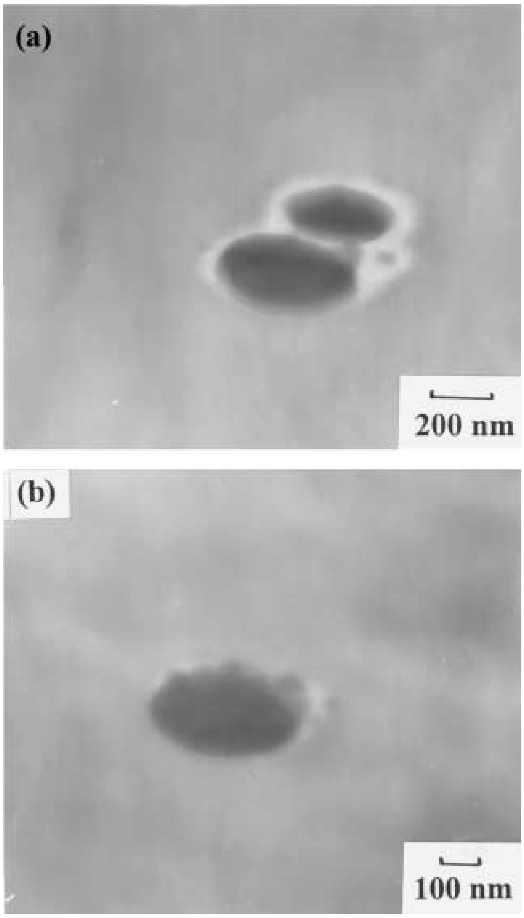


Fig. 4 The morphology of the cross-section of **a** PMMA/PS composite particles which swell with styrene monomer before the third stage of the reaction and **b** PMMA/PS/PS composite particles

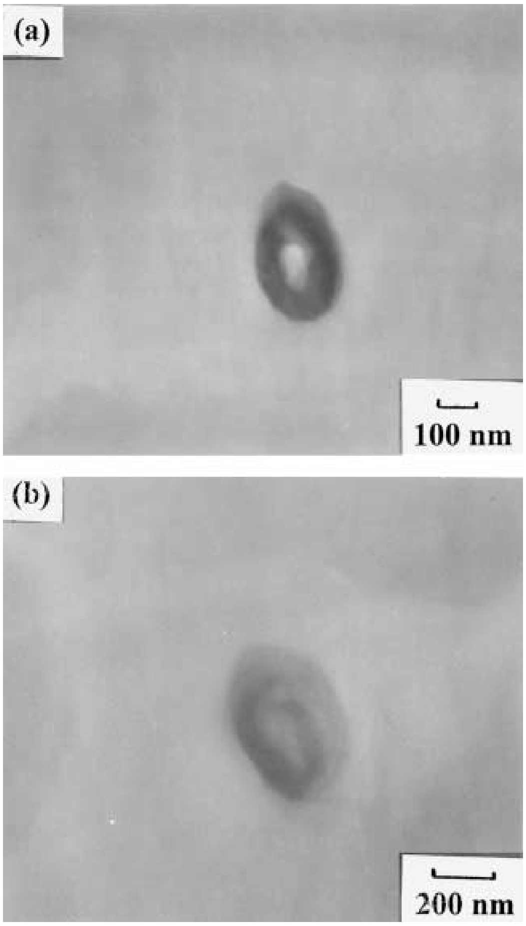


Fig. 5 The morphology of the cross-section of **a** PMMA/PS(XL) composite particles which swell with MMA monomer and ethyl glycol dimethylacrylate before the third stage of the reaction and **b** PMMA/PS(XL)/PMMA(XL) composite particles

PMMA/PS(XL)/PMMA(XL) composite polymer particles showed the morphology of polymer layers accumulate in their order of production, as shown in Fig. 5b. The PMMA/PS(XL)/PMMA(XL) composite polymer particles were synthesized by the method of three-stage reaction. Before the beginning of the third stage of the reaction, the MMA monomer and the cross-linking agent (EGDMA) diffused into the PMMA(core)/PS(XL)(shell) composite seed particles to form the PMMA and MMA region and the PS(XL) and MMA region. Although the interfacial tension of the PMMA and MMA phase to water is smaller than that of the PS(XL) and MMA phase to water, the PMMA and MMA phase located at the core region and the PS(XL) and MMA phase located at the shell region, as shown in Fig. 5a, owing to the cross-linked structure of the PS(XL) phase being immovable. After the initiator had been added into the reaction system, the hydrophilic SO_4^- group anchored on the surface of the PMMA/PS(XL) seed latex and polymerized MMA and EGDMA to form PMMA/PS(XL)/PMMA(XL) composite particles. The morphology of the PMMA/PS(XL)/PMMA(XL) composite particles showed a core and multishell structure. The first core zone was a PMMA phase, the second shell was a cross-linked PS phase, and the third shell was a cross-linked PMMA phase. The process of the synthesis of the PMMA/PS(XL)/PMMA(XL) composite particles is shown in Scheme 2(C). The morphology of the PMMA/PS(XL)/PMMA(XL) composite polymer particles was decided by the order of polymerization, but not by the thermodynamic factor.

Conclusion

The results clarify that the morphology of the linear composite polymer particles which were synthesized by two-stage reaction was decided by the kinetic factor only. Both the thermodynamic factor and the kinetic factor influenced the morphology of the linear composite polymer particles which were synthesized by the method of either three-stage reaction or four-stage reaction; however, the thermodynamic factor cannot influence the morphology of composite polymer particles with cross-linked structures. The method of multistage soapless seeded emulsion polymerization can be used to synthesize cross-linked composite polymer particles which have the morphology of polymer layers accumulated in their order of production.

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