

Morphology and Thermodynamic Analysis of Composite Polymer Particles Prepared by Soap-Free Emulsion Polymerization in the Presence of Poly(Methyl Methacrylate) and Polystyrene as Biseeds

Xingshou Pang, Guoxiang Cheng, Shulai Lu

School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT: Biseeds emulsion polymerization was investigated with poly(methyl methacrylate) (PMMA) and polystyrene (PSt) as biseeds and styrene (St) as second-stage monomer, as well as with thermodynamic analysis; namely, the principle of minimum interfacial free-energy change was utilized to explain the competitiveness of different seeds for second-stage monomer and the final equilibrium morphology of composite polymer particles. The experimental results indicated the polymeric particles prepared had bimodal size distribution and the PMMA seed particles showed a higher chance of obtaining St than that of the PSt seed particles, which was in agreement with the computa-

tional outcome by the principle of minimum interfacial free-energy change. Owing to the kinetic factors, the equilibrium morphology could not be reached in the experiments. However, the results demonstrated that double or multiple seeds emulsion polymerization could be used as a model experiment to study the morphology of polymer particle and the morphological prediction. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2675–2680, 2004

Key words: biseeds emulsion polymerization; equilibrium morphology; interfacial free energy; poly(methyl methacrylate); polystyrene

INTRODUCTION

Composite polymer particles (microspheres) possess excellent physical properties and particular functions and have been applied to many areas, such as plastics, coating, adhesive, membrane separation, and biotechnology. Recently, people lay more and more stress on composite polymer particles, and the research on it is becoming one of the most potential fields of polymer science.

Seeded emulsion polymerization is a typical method used to prepare composite polymer particles.¹ Because of the incompatibility of different polymers, phase separation occurs and a variety of particle morphologies are formed. These morphologies include core-shell, inverted core-shell, hemisphere, raspberry-like, sandwich structure, and confetti-like, and so on. Generally, seeded emulsion polymerization is multi-stage polymerization with a single seed²; however, the emulsion polymerizations with two or more different latex particles as seeds have not yet been reported.

In addition, many studies show that the particle morphology and the structure are the inherent factors, which determine the properties of composite polymer particles.³ Therefore, how to predict and control the composite particle morphology has become the aim of many researchers and some methods have been advanced. Among these, the principle of minimum interfacial free-energy change presented by Sundberg et al.⁴ has been broadly accepted and applied. In terms of this principle, composite particles with well-defined structures have been predicted and prepared^{5–7} and this principle has also been extended,^{8–10} whereas preparation and the morphology prediction of composite polymer particles are almost focused on the emulsion polymerization system with a single seed.

In this article, composite polymer particles were prepared via soap-free emulsion polymerization with poly(methyl methacrylate) (PMMA) and polystyrene (PSt) as biseeds and styrene (St) as second-stage monomer, and the principle of minimum interfacial free-energy change was used to investigate the composite particle morphology.

Correspondence to: G. Cheng (gxcheng@tju.edu.cn).
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EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and St were analytical grade reagents purified by distillation under reduced

TABLE I
Recipes and Results for Soap-Free Emulsion Polymerization

	PMMA seed latex	PSt seed latex
Recipes		
MMA (g)	18.8	—
St (g)	—	22.5
KPS (g)	0.15	0.3
H ₂ O (ml)	180	200
Results		
Average diameter (μ)	0.45	0.35
Final solid contents (g-polymer/g-latex)	0.086 g-PMMA/g-latex	0.095 g-PSt/g-latex
Number of particles	3.06×10^{14}	8.99×10^{14}

pressure. Potassium persulfate (KPS) was an analytical grade reagent (Dongfang Chemical Plant, Tianjin, China) and used without further purification. Deionized water was used throughout.

Soap-free emulsion polymerization

The recipes for preparation of PMMA, PSt seed latices are shown in Table I. The detailed procedure is as follows.

By using MMA and St as monomers, KPS as initiator, PMMA seed latex and PSt seed latex were synthesized, respectively. The polymerization was carried out in a 250-mL four-necked flask equipped with a stirrer, a thermostatic water bath, and a nitrogen duct. After N₂ purging, a known amount of monomer and KPS aqueous solution was added to the thermostatic deionized water at 70°C and the reaction was held for 24 h, completing the polymerization. The seed latex was then quenched to room temperature and the unreacted monomer was removed by vacuum distillation. Then, the seed latex was obtained.

Polymerization of St in the presence of PMMA, PSt as biseeds

The recipes for preparation of composite polymer particles by emulsion polymerization with biseeds are shown in Table II. The detailed procedure is as follows.

The seed latices of PMMA, PSt, which had equal total solid content (see in Table II), were first put into the deionized water heated in a water bath at 70°C and the mixture was stirred for 30 min. Then, the second-stage monomer, St, and the KPS aqueous solution were added to the flask. After the reaction went on for 24 h, the latex was quenched to room temperature and the unreacted monomer was removed by vacuum distillation, and the composite particle latex was gained.

Particle morphology

A JEM 100CXII electron microscope (Hitachi Co., Japan) was used for transmission electron microscopy (TEM). A latex sample diluted to about 50 ppm with deionized water was dropped on the colloid-coated copper grid and dried in the vacuum. Thus, the morphology was observed. The particle diameter was denoted with arithmetic average diameter.

Conversion

The conversion rate of polymerization was calculated as

$$C\% = \frac{W_2 - W_3}{(W_1 - W_0) \times M\%} \times 100\%$$

TABLE II
Recipes for Biseeds Emulsion Polymerization and Conversion Rates

	No. 1	No. 2	No. 3	No. 4
PMMA (g, solid content)	0.5	0.5	0.5	0.5
PSt (g, solid content)	0.5	0.5	0.5	0.5
St (g)	1	2	4	8
KPS (g)	0.012	0.024	0.05	0.1
H ₂ O (ml)	60	80	80	100
Conversion rate (%)	94.4	93.6	93.2	93.8

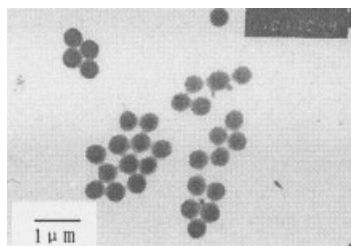


Figure 1 TEM photograph of PMMA seed particles.

where W_0 is the weight of the vessel; W_1 is the total weight of the sample and the vessel; W_2 is the weight of dry polymers obtained from the taken sample; W_3 is the weight of unevaporable components, and $M\%$ is the weight percentage of monomer in the initial reaction mixture.

RESULTS AND DISCUSSION

Morphology of particles prepared by biseeds emulsion polymerization

As we know, latex with uniformly distributed particles can be formed by single-seed emulsion polymerization, because the polymer seeds with smaller diameter have larger specific surface area and second-stage monomer tends to polymerize on the smaller seeds, although when two or more different polymer seeds exist in the reacting system, after the end of second-stage polymerization, uniform particles would not be attained.

The results of Figures 1-3 show the two kinds of polymer seeds had excellent monodispersity when prepared by soap-free emulsion polymerization. In Figure 4, it can be seen that the particles prepared by biseeds emulsion polymerization were spherical and had bimodal size distribution. In Figure 4(A, B), it can be seen that the larger particles clearly demonstrated core-shell structure after exposure to strong electron beams. This phenomenon confirmed that the larger ones were PMMA/PSt composite particles and the smaller ones were PSt. By further increasing the amount of St, the core-shell structure could not be seen [shown in Fig. 4(C-D)]. From Figure 5, we can also see

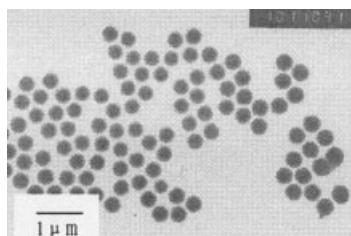


Figure 2 TEM photograph of PSt seed particles.

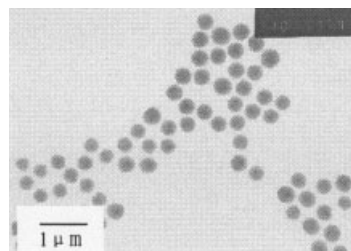


Figure 3 TEM photograph of mixture of PMMA and PSt seed particles.

the polymeric particles prepared had bimodal size distribution.

When biseeds existed in emulsion polymerization, monodisperse particles were not gained. The likely reason, besides the effect of specific surface area of seeds, is because the interfacial free-energy change has a crucial influence on the particle morphology.

Thermodynamic analysis of morphology of composite polymer particles

Thermodynamic considerations

When the second-stage polymerization is finished and the equilibrium morphology is reached in seeded emulsion polymerization, there exist three interfaces: seed polymer1 (p1)/water, second-stage polymer2 (p2)/water, and p1/p2. If p1 and p2 are incompatible, these interfaces can form the possible typical morphologies by phase-separation, namely, core-shell (CS), inverted core-shell (ICS), individual particle (IP), and hemisphere (HS). Considering the process of polymerization roundly in the view of thermodynamic, the morphology development of composite particles should involve polymerization, swelling of monomer and polymer, and the related thermodynamic parameters.¹¹ With respect to the ultimate polymer morphology only, we consider that the driving force will readily be the Gibbs free-energy change of the process. Because the equal thermodynamic parameters can be counteracted in the course of calculation of the Gibbs free energy, by comparing the different parameters, the final morphology can be determined. In such circumstances, the only contribution to the free-energy change is that of the creation of new interfaces.

Sundberg et al.⁴ used encapsulated oil droplets to simulate seeded emulsion polymerization and predicted the final morphology. The prediction principle presented by Sundberg considered only the initial state and the possible stable morphologies. The initial state was considered to be that of seed polymer1 suspended in aqueous phase and bulk phase of polymer2. Accordingly, the total free-energy change for the configurations (CS, ICS, IP, HS) can be expressed as

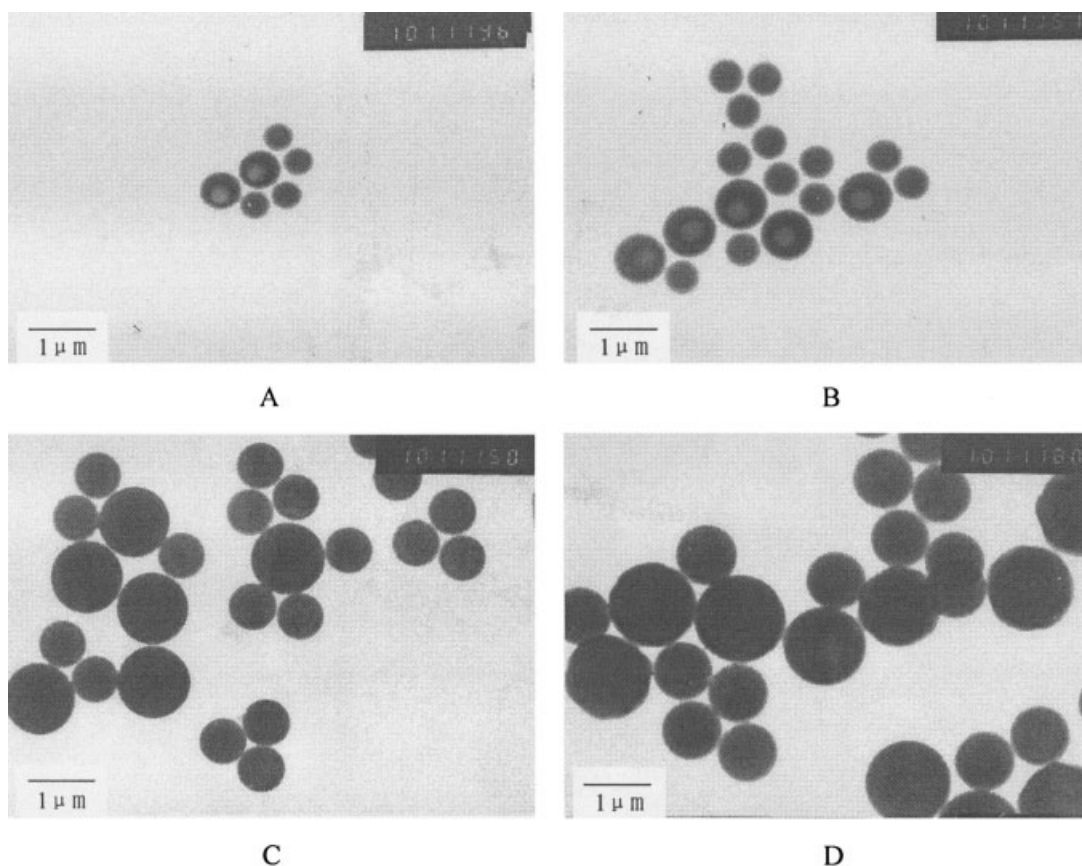


Figure 4 TEM photograph of latices prepared via biseeds emulsion polymerization at different monomer/seed ratios. A: No. 1 latices; B: No. 2 latices; C: No. 3 latices; D: No. 4 latices.

$$\Delta G = \sum \gamma_{ij} A_{ij} - \gamma_{o1w} A_0 \quad (1)$$

where γ_{ij} is the interfacial tension between i and j , and A_{ij} is the corresponding interfacial area. Thus, γ_{o1w} is the interfacial tension between the seed particles of polymer1 suspended in water and A_0 is its interfacial area.

According to the four final morphologies, the values of ΔG can be computed and the equilibrium morphology will be that which has minimum interfacial free-energy change. To calculate conveniently, eq. (1) can be transformed into

$$\Delta \gamma = \Delta G / A_0 = \sum \gamma_{ij} A_{ij} / A_0 - \gamma_{o1w} \quad (2)$$

where $\Delta \gamma$ is the free-energy change per unit surface area of the original polymer1 particle. The formulas describing the free-energy change for different configurations are summarized in Table III.

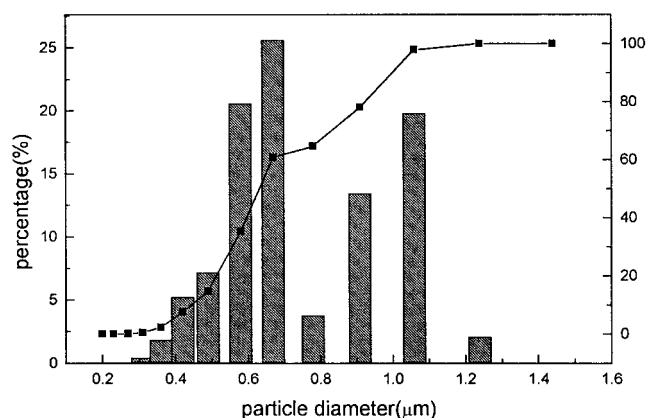


Figure 5 Diameter distribution of No. 3 latices.

Interfacial tension

Polymer–water and polymer–polymer interfacial tensions were proved as key parameters in deciding the thermodynamically preferred morphology, but the measurement of interfacial tension is difficult and polymerization conditions, such as surfactant, initiator, and monomer, can also affect the interfacial tension. To decrease the influence of these parameters, some controlling steps were adopted in this study. The controlling steps were as follows: (1) The polymerizations

TABLE III
The Interfacial Free-Energy Change for Various Morphologies of Composite Polymer

Morphology	$\Delta\gamma$
Core-shell (CS)	$\gamma_{12} + \gamma_{2w} (1-\phi)^{-2/3} - \gamma_{1w}$ (3)
Inverted core-shell (ICS)	$(\gamma_{1w} + \gamma_{12}\phi^{2/3})(1-\phi)^{-2/3} - \gamma_{1w}$ (4)
Individual particles (IP)	$\gamma_{2w}[\phi/(1-\phi)]^{2/3}$ (5)
Hemisphere (HS)	$(1-\phi)^{-2/3}\{\gamma_{2w}f + \gamma_{12}f(1-f) + \gamma_{1w}[1-f-(1-\phi)^{2/3}]\}$ (6)

Where $f = h/(2R)$, R is radius of the simple hemisphere, h is height of cap of sphere of polymer 2, and ϕ is the volume fraction of polymer 2 in the final particle.

were all carried out without surfactant; (2) The same initiator was used in the course of two-stage polymerizations; (3) The conversion rate should be over 90% and the unreacted monomers were removed by vacuum distillation.

In this article, in terms of some basic surface tensions (see Table IV) reported in literature,¹² the interfacial tensions can be simply predicted by use of the harmonic mean equation. The harmonic mean equation is defined as

$$\gamma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}$$

where γ^d and γ^p are the dispersive components of the surface tension and the polar components, respectively. These two components are related as $\gamma = \gamma^d + \gamma^p$. The interfacial tensions computed by the above equation were as such,

$$\gamma(\text{PMMA}/W) = 26.1 \text{ mN/m};$$

$$\gamma(\text{PSt}/W) = 36.4 \text{ mN/m};$$

$$\gamma(\text{PMMA}/\text{PSt}) = 1.5 \text{ mN/m}$$

The interfacial free-energy change ($\Delta\gamma$)

The interfacial free-energy change of the four typical equilibrium morphologies of PMMA/PSt composite particles and PSt particles can be calculated by using eqs. (3)-(6). By comparing the values of $\Delta\gamma$ for different morphologies in Figure 6, the morphology that has the lowest computed interfacial energy change should be the preferred equilibrium morphology. Because of the existence of biseeds in reacting system, in respect to the interfacial free energy, the polymer seeds that

formed the morphology with minimum $\Delta\gamma$ would compete for more St in the process of polymerization.

Experimental results and thermodynamic analysis

The results depicted in Figure 6 indicate the ICS structure of PMMA/PSt has the minimum computed interfacial energy and is thus the ultimate equilibrium morphology. Regardless of the final particle morphology, by only considering the reduced free energy, PMMA seed particles would show a higher chance of obtaining more St than PSt seed particles and the experimental results confirmed this computation.

The TEM photographs given in Figure 4 show that, at different monomer/seed ratios, the polymer particles had different diameters and the volumes of PMMA seeds increased to a greater extent. The average diameters of small and large particles after the seed polymerization are shown in Table V. For the sake of characterizing the ability of different seeds in competing for second-stage monomer, the volume change ratio was defined as

$$\Delta V = \frac{(V_1 - V_{o1})n_{o1}}{(V_2 - V_{o2})n_{o2}}$$

TABLE IV
Surface Tensions¹²

	PMMA	PSt	H ₂ O
γ (mN/m)	41.1	40.7	72.8
γ^d (mN/m)	29.6	33.9	21.8
γ^p (mN/m)	11.5	6.8	51

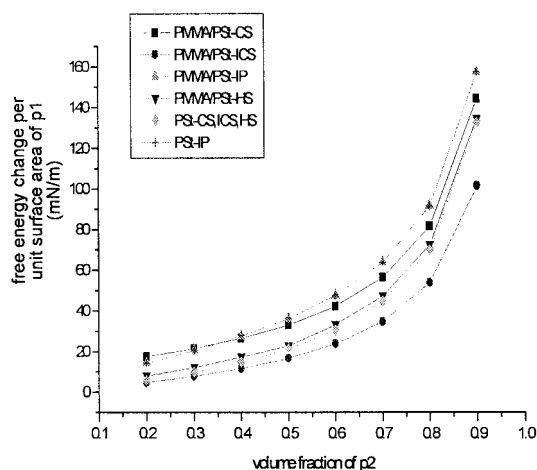


Figure 6 Interfacial free-energy change ($\Delta\gamma$) curve for bi-seeds emulsion polymerization system.

where V_{o1} , V_{o2} were the initial volumes of PMMA particle and PSt particle, respectively; V_1 , V_2 were the final volumes, accordingly; and n_{o1} , n_{o2} were the initial numbers of PMMA and PSt particles, respectively. In our experiments, n_{o1} is 8.96×10^{12} and n_{o2} is 21.28×10^{12} .

It can be seen in Figure 7 that $\Delta V > 1$ at different monomer/seed ratios, which demonstrates that PMMA seeds had the advantage of obtaining more St than PSt seeds. The reason was because the interfacial free-energy change had a higher influence in the morphology development than specific surface area during the second-stage polymerization. This result was in agreement with the theoretical prediction. From the curve tendency in Figure 6, we can see, in the case of less St, the effect of interfacial free-energy change was more distinct. Further increasing the amount of St, ΔV decreased and the extreme case would be $\Delta V < 1$. When $\Delta V < 1$, it is suggested that the specific surface area has a greater effect on distribution of St between PMMA and PSt. The likely explanation is, when the amount of St was small or during the initial state of reaction, the surface of PMMA seeds did not vary too much; therefore, the interfacial free-energy change had higher influence on the development of seed polymer than specific surface area. With the increase of St, when the surfaces of PMMA particles were completely covered by PSt, the surface states of the PMMA and the PSt were identical. Thus, the smaller particles would increase more quickly.

It can also be seen in Figure 4 that the theoretically computed morphology of ICS structure cannot be found. This result suggests, besides thermodynamic factors, the kinetic factors, such as viscosity of polymerization loci and mode of second-stage monomer addition, have key effects on the final morphology. Because the T_g of PMMA was above the reacting temperature, the viscosity was high within the PMMA particle, which prevents the movement of PSt chains. Furthermore, the anchoring of hydrophilic end group of the growing polymer chains on the surface of the particles had also prevented the development of ICS structure.

TABLE V
Average Diameters of PMMA/PSt Composite Latics and PSt Latics Under Different Monomer/Ratios

Monomer/seed ratios	PMMA/PSt (large particles) (μ)	PSt (small particle) (μ)
1/1	0.59	0.42
2/1	0.78	0.50
4/1	1.10	0.68
8/1	1.36	0.91

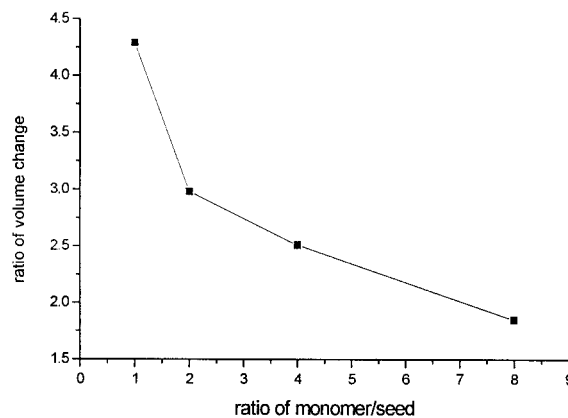


Figure 7 ΔV against monomer/seed ratios curve.

CONCLUSION

The composite polymer particles were prepared in the presence of biseeds and the morphology was researched. The TEM photographs show that the composite polymer particles had bimodal size distribution. The principle of minimum interfacial free-energy change was used to interpret the ability of competing for second-stage monomer of different polymer seeds and the final equilibrium morphology. The experimental results demonstrate, when the amount of St was small, the PMMA seeds with lower free-energy change had a higher chance for obtaining more St; when increasing the amount of St, the influence of free-energy change decreased. Moreover, because of the effect of kinetic factors, the theoretically computed equilibrium morphology was not gained during the process.

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