

Preparation of Polystyrene/Poly(Methyl Methacrylate) Core-Shell Composite Particles by Suspension-Emulsion Combined Polymerization

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ABSTRACT: Suspension-emulsion combined polymerization process, in which methyl methacrylate (MMA) emulsion polymerization constituents (EPC) were drop wise added to styrene (St) suspension polymerization system, was applied to prepare polystyrene/poly(methyl methacrylate) (PS/PMMA) composite particles. The influences of the feeding condition and the composition of EPC on the particle feature of the resulting composite polymer particles were investigated. It was found that PS/PMMA core-shell composite particles with a narrow particle size distribution and a great size would be formed when the EPC was added at the viscous energy dominated particle formation stage of St suspension polymerization with a suitable feeding rate, whereas St-MMA copolymer particles or PS/PMMA composite particles with imperfect core-shell structure would be formed when the EPC was

added at the earlier or later stage of St suspension polymerization, respectively. It was also showed that the EPC composition affected the composite particles formation process. The individual latex particles would exist in the final product when the concentrations of MMA monomer, sodium dodecyl sulfate emulsifier, and potassium persulfate initiator were great in the EPC. Considering the feature of St suspension polymerization and the morphology of PS/PMMA composite particles, the formation mechanism of PS/PMMA particles with core-shell structure was proposed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1659–1669, 2009

Key words: suspension polymerization; emulsion polymerization; particle size distribution; particle morphology; particle formation mechanism

INTRODUCTION

The core-shell structure polymer composite particles have been widely used as the impact modifier of plastics, compatibilizer for polymer blends, adhesives, and so on.^{1–3} They can be prepared by a series of consecutive polymerization sequences with different monomer types, where the second monomer is polymerized in the presence of seed polymer particles of the first monomer. Seed polymer particles can be prepared either in a separate step, or formed *in situ* during one-stage polymerization.

The core-shell polymer composite particles are usually prepared via seeded emulsion polymerization or seeded dispersion polymerization processes. The polymerization mechanism and particle formation process were studied maturely,^{4–11} and the polymer latex particles with a wide variety of morphologies, such as the familiar core-shell, hemispherical and “inverted” core-shell particles, were prepared through the variation of polymerization

conditions. Despite their proven versatility, emulsion or dispersion polymerization-based processes for making composite particles have limitations. The maximum practical particles size is approximately 1 μm .

Special suspension polymerization process has also been applied to prepare larger polymer particles with a core-shell structure (i.e., particle diameter $>50 \mu\text{m}$). Kiatkamjornwong et al.¹² and Sivakumar et al.¹³ prepared core-shell polymer composite particles by suspension polymerization in separate steps, i.e., taking the second monomer swollen in the seed particles and then conducting the polymerization. Obviously, the above polymerization process is complex and the second monomer has its selectivity (i.e., it can be swollen in the seed polymer). It is a sound way to prepare the core-shell particles by adding the second monomer *in situ* during one-stage suspension polymerization, but the particle formation process of suspension polymerization would always be complicated due to the feed of second monomer. Lenzi et al.¹⁴ prepared polystyrene (PS) particles by semibatch suspension polymerizations, with the PS core originating from the suspension polymerization process and the PS shell originating from the emulsion polymerization. However, the core-shell structure was not

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TABLE I
EPC Feeding Conditions in SECP

EPC feeding conditions	REAC 1	REAC 2	REAC 3	REAC 4	REAC 5
Reaction time of St SP before feeding of EPC/min	0	120	200	200	200
Feeding time/min	30	30	30	Batch	60

Typical recipe of EPC for REAC 1 to REAC 5 (in mass): H₂O 0.635, MMA 0.350, SDS 0.005, KPS 0.010. The total mass of EPC fed in REAC 1 to REAC 5 was 14.17 g.

supported and the mechanism of the particle formation process was not investigated.

Suspension-emulsion combined polymerization (SECP), in which the emulsion polymerization constituents (EPC) of the second monomer is fed to the suspension polymerization system of the first monomer during the polymerization process, is a feasible method to prepare core-shell polymer composite particles with a great size by one-stage polymerization. Polymer particles formed through emulsion polymerization mechanism would be coagulated with particles formed through suspension polymerization mechanism, and core-shell structure polymer composite particles can be prepared through controlling of the polymerization conditions of SECP.

In the present work, SECP of styrene (St) and methyl methacrylate (St-MMA) was carried out to prepare polystyrene/poly(methyl methacrylate) (PS/PMMA) composite particles with a core-shell structure. Influences of EPC feeding condition and the composition of EPC on the particle size distribution and morphology of composite particles were investigated, the particle morphology and the particle formation mechanism were also discussed.

EXPERIMENTAL

Materials

St and MMA were distilled under reduced pressure and stored in a refrigerator before use. Benzyl peroxide (BPO) and potassium persulphate (KPS) with analytical purity, were all supplied by No.2 Shanghai Reagent Co., China. BPO were used as initiators for the suspension polymerization, and KPS as the initiator for the emulsion polymerization. Sodium dodecyl sulfate (SDS) with analytical purity, was supplied by

Aijian Chemical Co., Zhejiang, China. Poly(vinyl alcohol) (PVA) suspending agent with trade name PVA1788, was supplied by Guangming Chemical Co., Zhejiang, China. The hydrolysis degree and polymerization degree of PVA1788 are 88% and 1700, respectively. Ethyl glycol dimethyl acrylate (EGDMA) was supplied by Anli Chemical Factory, Suzhou, China.

Polymerization

EPC was prepared in advance at room temperature. The mixture of water, SDS, and MMA was ultrasonic emulsified in the flask for 5 min, then added with KPS solution. A typical recipe of EPC was as follows: 9 g deionized water, 0.07 g SDS, 0.100 g KPS, and 5 g MMA.

St suspension polymerization and St-MMA SECP were carried out in a 500 mL glass jacket reactor equipped with a nitrogen inlet, a condenser, a mechanical agitator, a feeder, and a thermocouple. A semicircular flat blade was used as an impeller. The feeder was linked to the outlet of an analog pump to get an invariable dropping rate of EPC. Hot water was fed into the reactor jacket through a thermostatic bath.

A typical preparation process was as follows: 20 g St, 0.1 g BPO, and 200 g aqueous solution of 0.5 wt % PVA1788 was added into the reactor. The mixture was deoxygenated by bubbling nitrogen gas for 30 min while the agitation rate was kept at 600 rpm, and subsequently heated to the reaction temperature at 353 K. The EPC was pumped into the reactor at a given rate during the different stage of St suspension polymerization. EPC feeding conditions and EPC with different compositions are listed in Tables I and II, respectively. The polymerization was ended 3 h later after the feeding of EPC.

TABLE II
EPC with Different Recipes

Mass fraction of constituent in EPC	REAC 6	REAC 7	REAC 8	REAC 9	REAC 10	REAC 11
H ₂ O	0.740	0.470	0.637	0.629	0.640	0.622
MMA	0.245	0.515	0.351	0.350	0.350	0.346
SDS	0.005	0.005	0.002	0.011	0.005	0.005
KPS	0.010	0.010	0.010	0.010	0.005	0.027

EPC feeding conditions: 120 min for St suspension polymerization before feeding of EPC, feeding time 30 min. The total mass of EPC fed in REAC 6 to REAC 11 was 14.17 g.

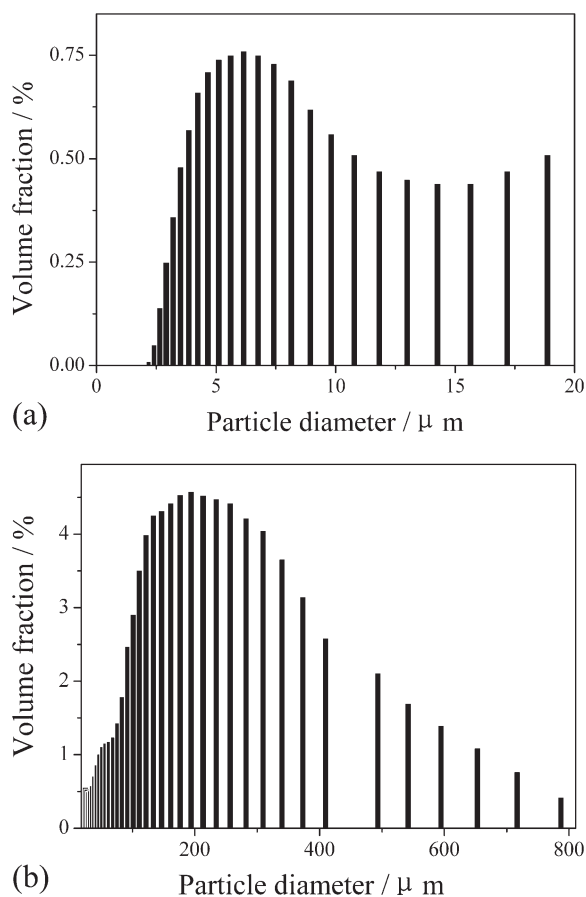


Figure 1 Size distribution of polymer particles prepared by REAC1: (a) latex particles; (b) suspended particles.

Characterization

The conversion of St in suspension polymerization was measured gravimetrically. The viscosity of St dispersed phase (containing PS) with different conversions was measured by using a Hakke RV-20 viscometer at 353 K.

A laser size analyzer (Coulter LS-230) was used for measuring the particle size and particle size distribution (PSD) of polymer particles. Here, the polymer particles with sizes lower than 20 μm were roughly considered as the latex particles and their aggregates, and the polymer particles with sizes greater than 20 μm as the suspended particles. The laser size analyzer program calculates a number of statistical quantities to characterize the particle size distribution, with the volume percent in a certain size channel being analogous to the frequency of occurrence of a certain value. The volume fractions, volume weighted mean diameters (D_v) and the standard deviation (SD) of the latex particles and the suspended particles could be obtained through the measurement. The D_v and SD are defined as follows:

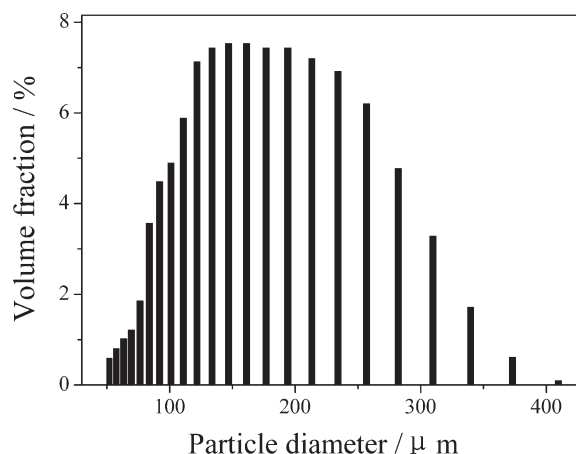


Figure 2 Size distribution of polymer particles prepared by REAC2.

$$D_v = \frac{\sum n_c d_{lc}^4}{\sum n_c d_{lc}^3}$$

$$SD = \text{antilog} \sqrt{\frac{\sum [n_c (\log X_c - \log \bar{X}_g)^2]}{\sum n_c}}$$

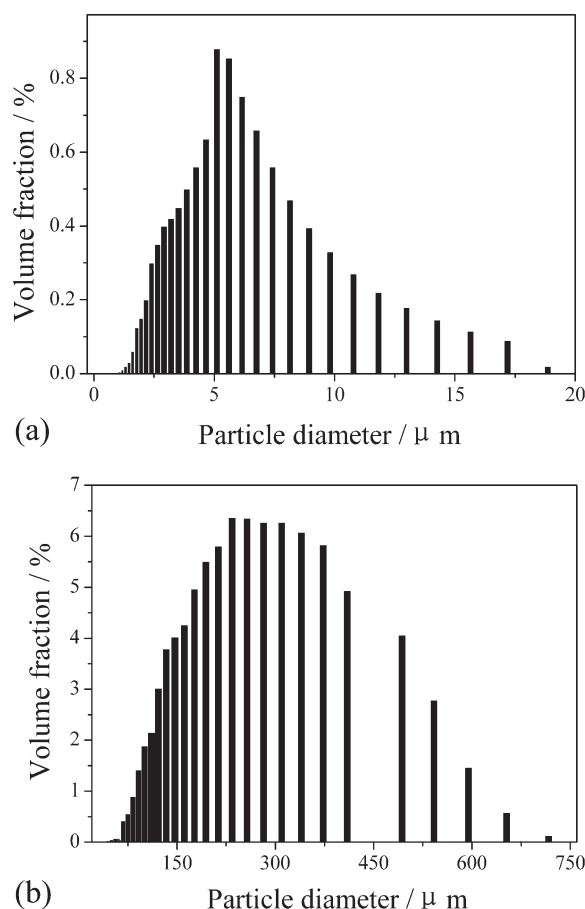


Figure 3 Size distribution of polymer particles prepared REAC3: (a) latex particles; (b) suspended particles.

TABLE III
 D_v and PSD Indexes of Polymer Particles Prepared by SECP

No.	Suspended particles			Latex particles		
	Volume fraction (%)	D_v (μm)	SD	Volume fraction (%)	D_v (μm)	SD
REAC 1	89	178.2	2.12	11	6.95	3.56
REAC 2	100	180.6	1.40	–	–	–
REAC 3	90	238.2	1.40	10	15.2	4.23
REAC 4	87	165.5	1.46	13	4.52	5.26
REAC 5	93	173.4	1.43	7	1.19	1.61
REAC 6	100	168.7	1.41	–	–	–
REAC 7	92	184.5	1.63	8	2.54	1.73
REAC 8	86	171.4	1.67	14	4.05	2.57
REAC 9	93	166.3	1.48	7	0.35	1.23
REAC 10	88	175.2	1.42	12	3.85	2.45
REAC 11	89	173.6	1.58	11	0.52	1.38

in which d_{1c} is the channel center, or diameter of a particle in that channel, n_c the percentage of particles in the c th channel, X_c the weighted center of the c th channel, \bar{X}_g the geometric mean.

The morphology of PS/PMMA composite particles was observed and taken pictures by using an environmental scanning electron microscopy (PHILIPS XL30-ESEM, Holland). Some composite particles were embedded in epoxy resin and the epoxy resin slices with thickness of about 5 μm (containing composite particle) were prepared by slicing the cured epoxy resin using an ultra-microtome (Reichert-Jung ULTRACUT E, Austria). The slice was sandwiched by glass, and then observed and taken pictures using a microscope. FT-IR spectrum of polymer was measured by using FT-IR analyzer (Nicolet 550, Japan). Polymer particles were mixed with KBr and pressed.

RESULTS AND DISCUSSION

Effect of EPC feeding condition on the size distribution of polymer particles

EPC with a fixed composition was started to feed at the different stage of St suspension polymerization. For REAC 1, REAC 2, and REAC 3, EPC started to feed when St suspension polymerization had proceeded for 0, 120, and 200 min, respectively. The size distributions of final polymer particles are shown in Figures 1–3. The volume fractions, D_v and SD of the latex particles and suspended particles are listed in Table III.

For REAC 1, the mean droplet size was 80.6 μm before adding of EPC. When polymerization was finished, the final polymer particles had a multimodal size distribution from 1 to 1000 μm , and could be easily smashed to small particles. For REAC 2, the PSD curve of St/PS dispersed droplets had only one peak and the mean particle size was 153.7 μm before the feeding of EPC. As polymerization was completed, only one peak appeared in the PSD curve

and the size of polymer particles increased to 180.6 μm . It indicates that the latex particles are combined with particles formed through suspension polymerization. For REAC 3, the average particle size of St/PS dispersed droplets was 223.6 μm before the feeding of EPC. As polymerization was brought to an end, the PSD curve of final particles had a bimodal distribution, in which the mean size of suspended particles change no more as EPC fed and the mean

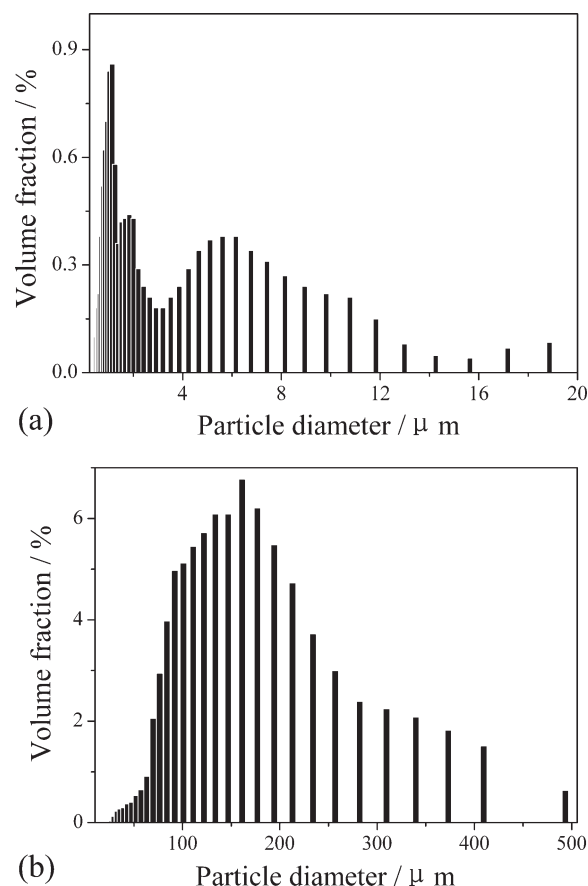


Figure 4 Size distribution of polymer particles prepared by REAC4: (a) latex particles; (b) suspended particles.

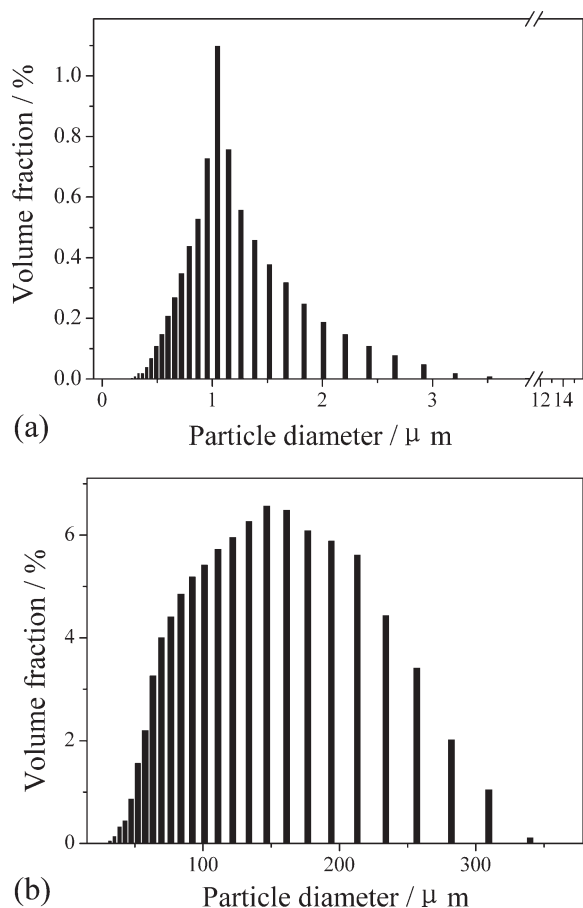


Figure 5 Size distribution of polymer particles prepared by REAC5: (a) latex particles; (b) suspended particles.

size of latex particles were 15.2 μm. It indicates that the latex particles slightly coagulate with suspended polymer particles formed through suspension polymerization mechanism.

According to the above result, PS/PMMA composite particles with a narrow size distribution could

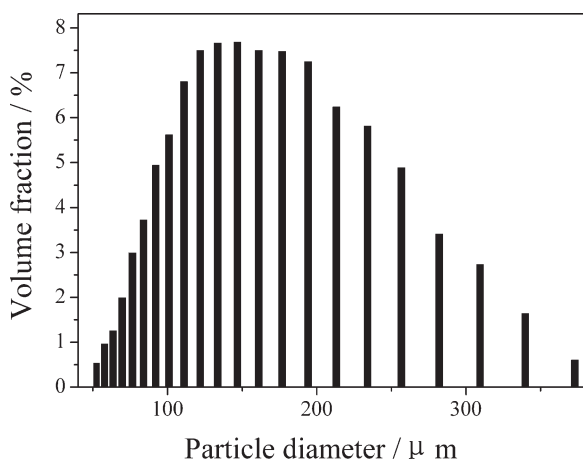


Figure 6 Size distribution of polymer particles prepared REAC6.

be prepared by feeding the EPC into the reactor when St suspension polymerization had proceeded for a suitable time, i.e., 120 min. Thus, the start feeding time of EPC was fixed as St suspension polymerization proceeded for 120 min in the following experiments.

The EPC was fed in a batch way in REAC 4, and fed in a constant rate within 90 min in REAC 5. The size distributions of final polymer particles in REAC 4 and 5 are shown in Figures 4 and 5, respectively. The volume fractions, D_v and SD of the latex particles and the suspended particles are listed in Table III.

It can be seen that PSD curve of final polymer particles prepared by the batch feeding of EPC in REAC 4 shows multip peaks, and the size of suspended particles only increases to 165.5 μm. It indicates that most of latex particles are not combined with particles formed through suspension polymerization. In REAC 5, the PSD curve of final polymer particles exhibited a bimodal distribution. The D_v of the suspended particles increased to 173.4 μm and the D_v of the latex size was 1.19 μm. When the EPC was fed for a long time, the later formed latex particles would be difficult to be coagulated with

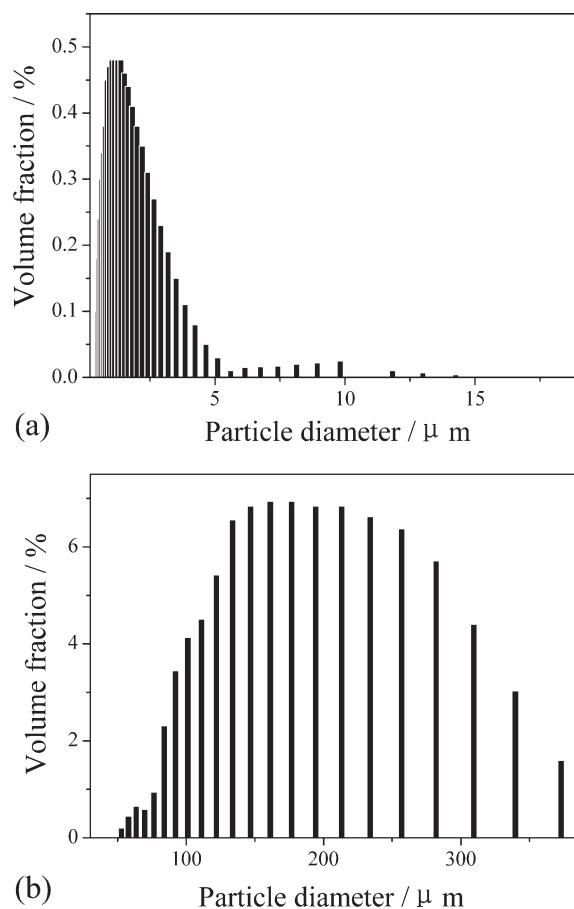


Figure 7 Size distribution of polymer particles prepared by REAC7: (a) latex particles; (b) suspended particles.

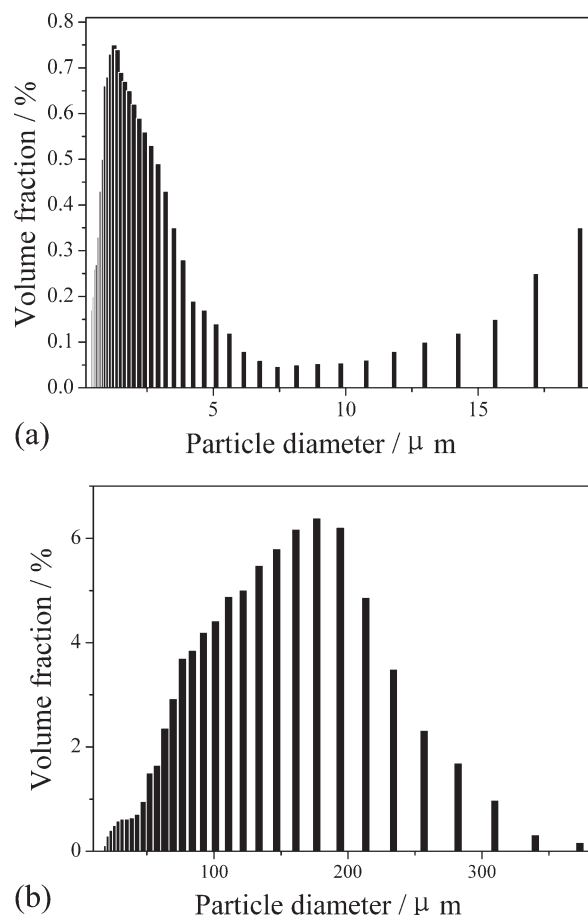


Figure 8 Size distribution of polymer particles prepared by REAC8: (a) latex particles; (b) suspended particles.

suspension polymerization particles due to the high conversion of St and the great viscosity of PS particles. This illustrates that the EPC feeding rate (or emulsion polymerization rate) should be fitted with the St suspension polymerization rate, to prepare PS/PMMA composite particles with a narrow particle size distribution.

Effect of EPC composition on the polymer particle size distribution

In this section, the EPC was started to feed when St suspension polymerization had proceeded for 120 min, and the total feeding time of EPC was fixed at 30 min. The size distributions of final polymer particles prepared by REAC 6 to REAC 11 are shown in Figures 6–11, correspondingly. The volume fraction, D_v , and SD of the latex particles and suspended particles are listed in Table III.

In REAC 2, 6, and 7, the weight fraction of MMA in EPC was varied, whereas other reaction conditions were fixed.

It can be seen that the PSD curve of final polymer particles of REAC 6 was close to that of REAC 2, showing only one distribution peak, but the average size of polymer particles of REAC 6 was less than that of REAC 2. It can also be seen that the PSD of final polymer particles of REAC 7 exhibits a bimodal distribution, with mean size of 184.5 μm and 2.54 μm . Comparison on the result of REAC 2, 6, and 7, it can be concluded that part of latex particles would not be coagulated with suspended particles when the weight fraction of MMA in EPC or MMA/St ratio were too great.

The weight fraction of SDS in EPC was varied in REAC 2, 8, and 9, whereas other reaction conditions were fixed.

It can be seen that the final polymer particles of REAC 8 and REAC 9 exhibit a multimodal distribution in PSD curves, but the distribution peak and the average size of the latex particles were quite different. For REAC 8, the size distribution of the latex particles was wider and the average size was greater (4.05 μm), whereas the size distribution of the latex particles of REAC 9 was narrower and the average

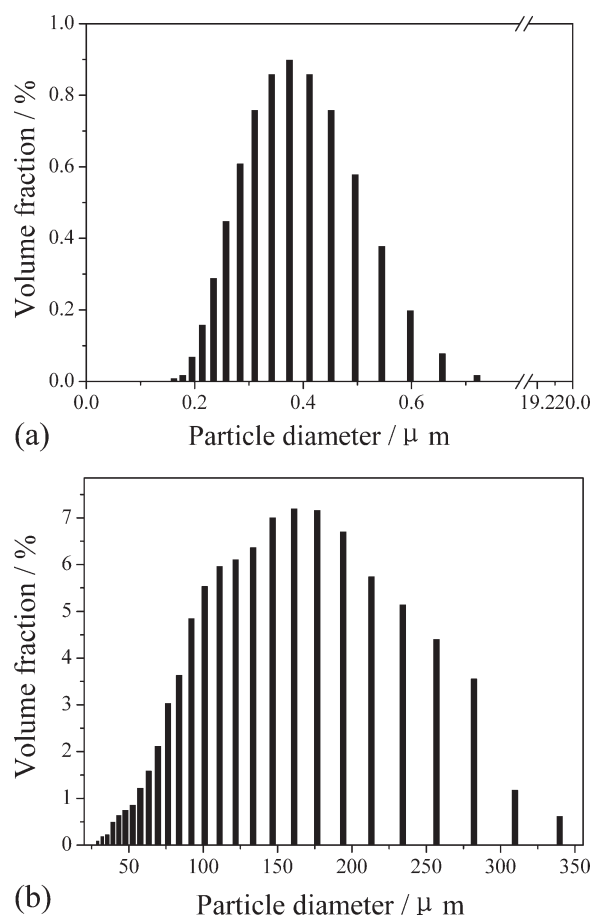


Figure 9 Size distribution of polymer particles prepared by REAC9. (a) latex particles; (b) suspended particles.

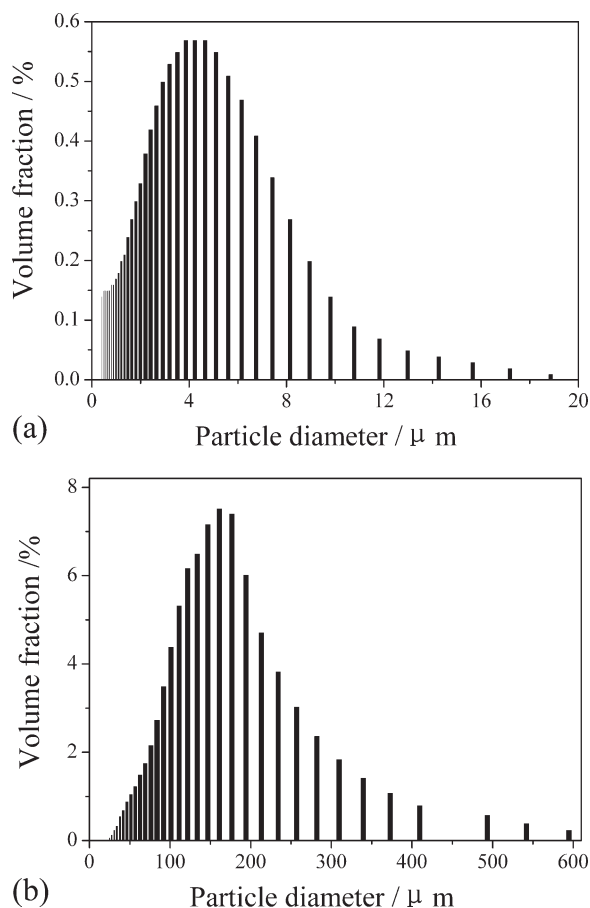


Figure 10 Size distribution of polymer particles prepared by REAC10: (a) latex particles; (b) suspended particles.

size was lower (0.35 μm). The emulsion polymerization rate was lower in REAC 8 due to the lower weight fraction of SDS in EPC (and in the whole reaction system), and the later formed latex particles would be difficult to coagulate with suspension polymerization particles. On the other hand, the colloid protection to latex particles was poor, and latex particles tended to coagulate each other to form aggregates. For REAC 9, the colloid protection to formed latex particles was greater due to the greater concentration of SDS in the reaction system, thus a part of latex particles would stably exist at the end of SECP.

The weight fraction of KPS in EPC was varied in REAC 2, 10, and 11, whereas other reaction conditions were fixed.

It can be seen that only one peak appeared in the PSD curve of final particles of REAC 10. The D_v of suspended particles size increased from 153.7 to 175.2 μm and D_v of latex particles size 3.85 μm. For REAC 11, it can be seen that a bimodal distribution in the PSD curve of final polymer particles, with D_v of the suspended particles of 173.6 μm and the D_v of latex particles of 0.52 μm. In this case, the emulsion polymerization rate was increased, and the forma-

tion rate of latex particles was faster than the coagulation rate of latex particles with suspension polymerization particles.

Structure of core-shell composite particle

The above results illustrate that both the feeding condition and the EPC composition has great influences on the size distribution of final polymer particles. It can be inferred that the morphology of polymer particles would also be affected by the feeding condition and the composition of EPC, and PS/PMMA composite particles with a perfect core-shell structure would be formed in SECP process when no latex particles was detected in the final product of polymerization.

Taking the final product of REAC 2 as the example, the morphology of polymer particle is shown in Figure 12. From Figure 12(a), it can be seen that the composite particles with size of about 200 μm were formed. From Figure 12(b), it can be seen that the composite particle had a near round shape, and the particle surface was coarse. From Figure 12(c), it can be seen that the composite polymer particle had a

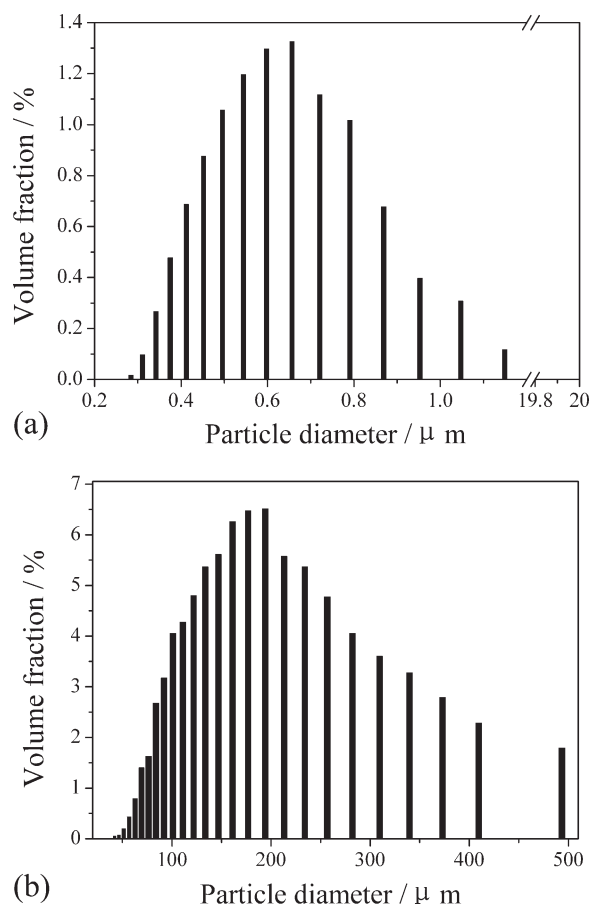


Figure 11 Size distribution of polymer particles prepared by REAC11: (a) latex particles; (b) suspended particles.

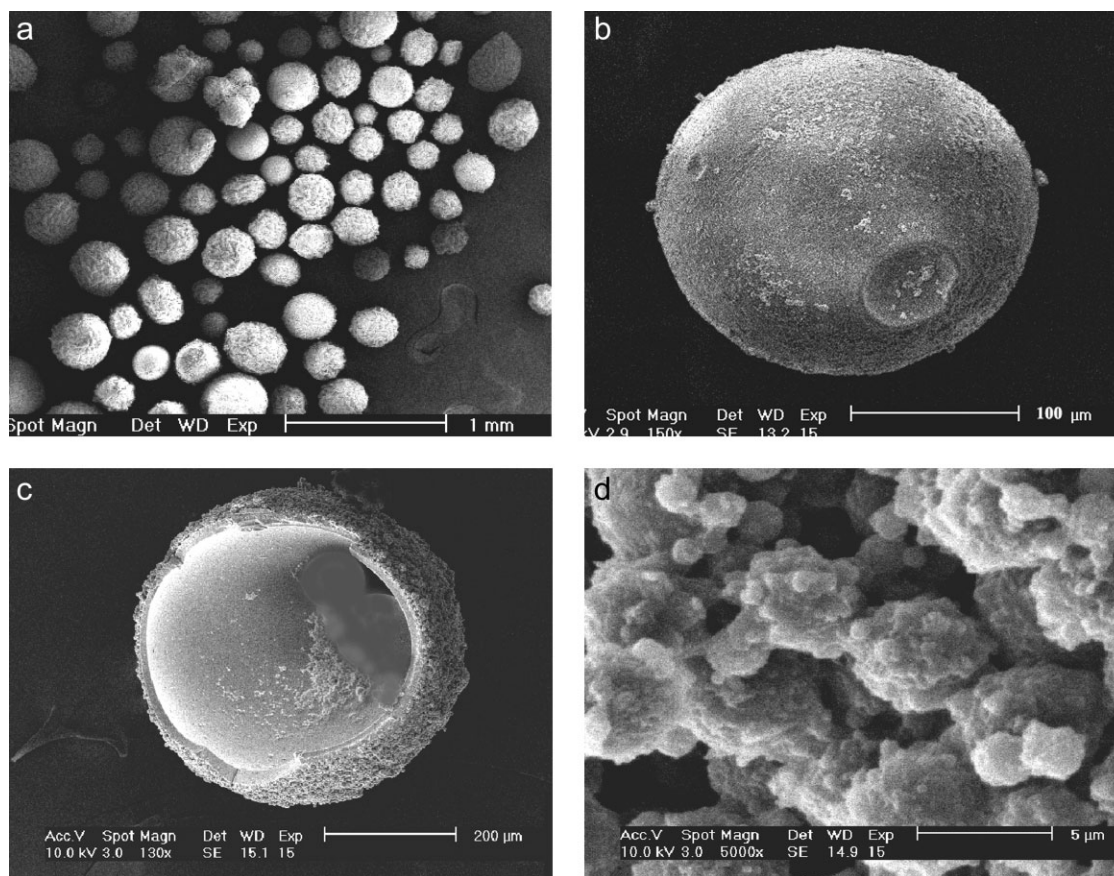


Figure 12 SEM micrographs of polymer particle prepared by REAC 2. a: Particles (top left); b: Whole view of particle (top right); c: Cross-sectioned particle (bottom left); d: Surface of shell (bottom right).

perfect core-shell structure. From the amplified shell structure shown in Figure 12(d), it can be seen that the shell was composed with many berry-shape aggregates of primary particles. The diameter of berry-shape aggregates range from 2.0 to 5.0 μm , and the size of primary particle was less than 0.5 μm .

The microscope picture of the sectioned composite polymer particle is seen in. It can also be seen that the composite particles exhibit a core-shell structure (Fig. 13).

To confirm the chemical composition of the core and the shell of composite polymer particles prepared by REAC 2, a small amount of EGDMA cross-linking agent was added in the EPC and core-shell polymer particles with crosslinked shell was obtained. After extraction with trichloromethane for 72 h, the sol and gel fractions of polymer were obtained. FT-IR spectra of the sol and gel fraction are shown in Figure 14.

It can be seen that a strong absorption located at 1737.63 cm^{-1} appears in the IR spectrum of the gel fraction, whereas it does not appear in the spectrum of the sol fraction. The absorption located at 1737.63 cm^{-1} is the symbol of carbonyl.¹⁵ In the spectrum of

the sol fraction, some strong absorption located at 900–650 cm^{-1} and some weak but sharp absorption located at 1650–1400 cm^{-1} identified the existence of phenyl group in the sol fraction.¹⁴ According to the above analysis, it can be concluded that the gel (shell) was composed of PMMA, whereas the sol (core) was mainly composed of PS.

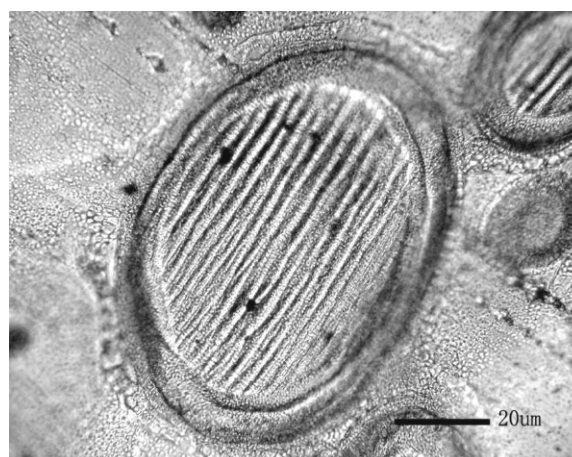


Figure 13 Microscope morphology of PS/PMMA composite particles slice showing their core-shell structure.

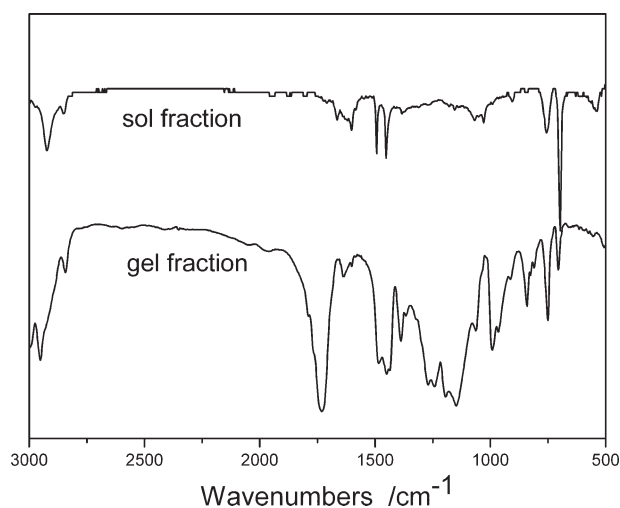


Figure 14 FTIR spectra of the sol and gel fractions of composite polymer particles.

Formation mechanism of core-shell composite particles in SECP

Obviously, the formation of core-shell structure composite particles in SECP process is related with the feature of St suspension polymerization, and the feeding condition and the composition of EPC. St suspension polymerization process can be divided into three stages, in which interfacial energy, viscous energy, and viscoelastic energy is dominant in the particle formation process, respectively.^{16–18} Figure 15 shows the variations of the particle size and the viscosity of PS (containing St) with the conversion. It can be seen that the viscosity of PS dispersed phase increases rapidly as the conversion increases. The particle size of PS dispersed phase varies slowly in the lower conversion stage (0–30%), and increases

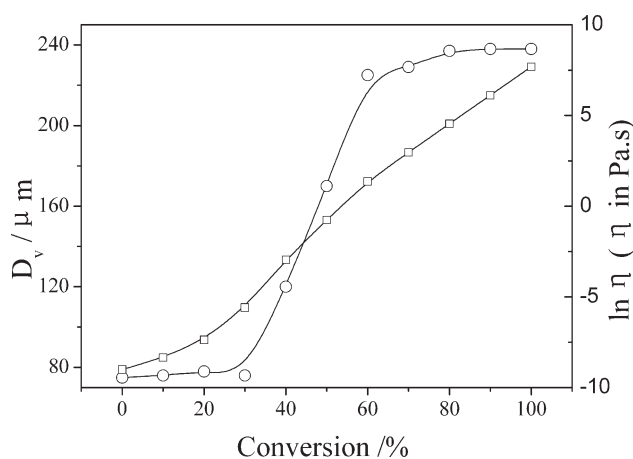


Figure 15 Variation of diameter and viscosity of dispersed PS with conversion (○) Diameter (D_v); (□) Viscosity (η).

TABLE IV
Conversion, Viscous, and D_v of PS/St Dispersed Droplets in REAC 1, 2, and 3 at Time of Starting EPC Addition

No.	Conversion (%)	Viscosity (Pa·s)	D_v (μm)	Suspension polymerization stage
REAC 1	0	0.5×10^{-3}	80.6	Interfacial stage
REAC 2	45	0.34	153.7	Viscous stage
REAC 3	72	19.2	223.6	Elastic stage

rapidly in the mid conversion stage (30–60%) and levels off in the higher conversion stage (>60%).

The conversion of St, the viscosity and the mean size of PS dispersed particles corresponding to the start adding time of EPC in REAC 1, 2, and 3; were determined and shown in Table IV. It can be seen that St suspension polymerization proceeded in the interfacial energy, viscous energy, and viscoelastic energy dominated particle formation stages when the EPC was started to feed in REAC 1, 2, and 3, respectively.

When EPC is started to add at the initial (interfacial energy dominated) stage of St suspension polymerization, the liquid-liquid dispersion equilibrium is achieved and the mean size of dispersed phase keeps constant before the feeding of EPC. As EPC added, the interfacial tension between oil and water phases would be reduced owing to the added emulsifier in the EPC, and the original equilibrium would be broken up. St/MMA droplets would be dispersed again under the agitation and the average size of dispersed phase decreases significantly. The primary polymer particles formed would be aggregated due to the increase of specific surface area of dispersed phase and the decreased colloid protection to the primary particles. Obviously, the obtained polymer particles would not exhibit core-shell structure in this case.

When EPC is started to add at the later (viscoelasticity dominated) stage of St suspension polymerization, the viscosity of PS dispersed droplets become too high. Therefore, MMA is difficult to diffuse deeply into PS particles and PMMA latex particles formed are difficult to coalesce with PS particles. As a result, PS/PMMA particles with an imperfect core-shell structure would be formed, and some PMMA latex particles would exist in the individual or aggregated forms. The resulting polymer particles become a bimodal distribution and the particle size distribution is wider. This is the case for REAC 3.

For SECP in which EPC is added at the mid (viscous energy dominated) stage of St suspension polymerization, PS dispersed particles is sticky and easy to coalesce. As the EPC added, a part of MMA monomer would diffuse to the surface of PS

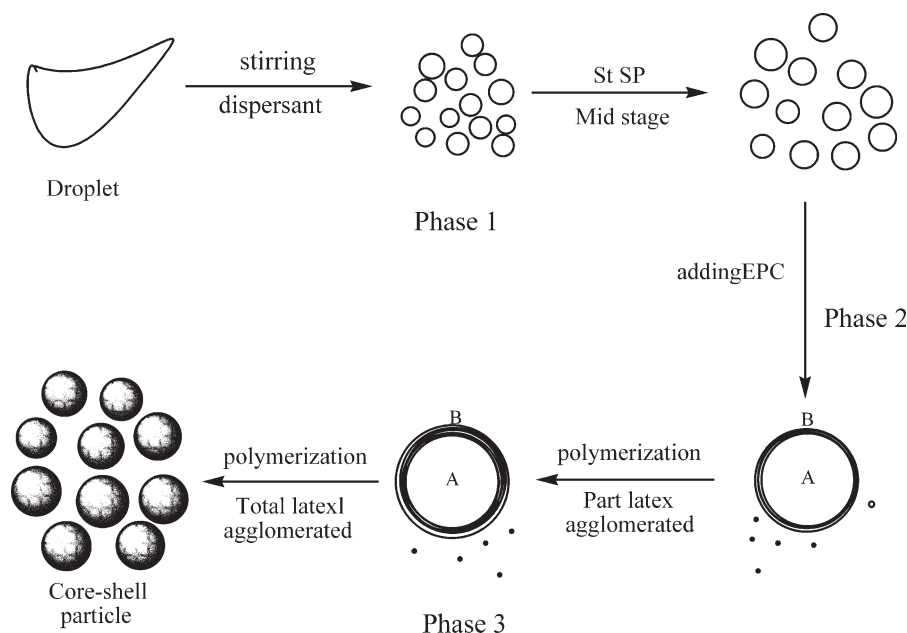


Figure 16 Model of SECP feeding EPC at the mid stage of St SP. A: Core particle prepared by St SP; B: Shell formed by PMMA latex particles agglomerated on the surface of core particle; C: PMMA latex particles.

particles and polymerize at the outer layer of PS particles, owing to the greater hydrophilicity of MMA than that of St. PMMA latex particles would also be formed in the aqueous phase through emulsion polymerization mechanism. When the feeding rate of EPC and the emulsion rate are suitable, St suspension polymerization would still stay at the viscous energy dominated stage as MMA emulsion polymerization finished. In this case, the formed PMMA latex particle would be coagulated with suspension particles when the colloid protection to latex particles is not very stronger. As more and more PMMA formed at the surface of PS particles or coagulated with PS particles, the shell mainly composed of PMMA would be formed, and PS/PMMA composite particles with a perfect core-shell structure and a great size would be obtained.

Figure 16 illustrates the three stages of the formation of the core-shell composite particles: (1) PS-St particles formation through St suspension polymerization; (2) PMMA latex formation and the coagulation with PS particles following the feeding of MMA EPC into the reactor; (3) The formation of perfect core-shell polymer particles through the complete coagulation of PMMA latex particles suspension particles.

CONCLUSIONS

SECP was a feasible method to prepare core-shell composite polymer particles with a great size *in situ* during one-stage polymerization. The feeding condition and the composition of EPC had great influen-

ces on the structure of polymer particles. When the EPC was added at the interfacial energy or viscoelastic energy dominated particle formation stage of St suspension polymerization, the formed PS/PMMA would not exhibit a perfect core-shell structure. While, the feeding of the EPC with a suitable composition at the viscous energy dominated particle formation stage of St suspension would result in the formation of PS/PMMA composite particles with a perfect core-shell structure and a great size. The emulsion polymerization rate of MMA and the colloidal protection to PMMA latex particles were also important factors influencing the formation of core-shell composite particles with a narrow particle size distribution and a great size. The latex particles or their aggregates would be existed in the final product when the feeding time of EPC was not in due time, or the concentrations of MMA, SDS, or KPS were unsuitable. The formation of PS/PMMA composite particles with a core-shell structure can be divided into three stages.

References

1. Guo, T. Y.; Tang, G. L.; Hao, G. J.; Song, M. D.; Zhang, B. H. *J Appl Polym Sci* 2003, 90, 1290.
2. Guo, T. Y.; Tang, G. L.; Hao, G. J.; Wang, S. F.; Song, M. D.; Zhang, B. H. *Polym Adv Technol* 2003, 14, 232.
3. Tuncel, A.; Kahraman, R.; Piskin, E. *J Appl Polym Sci* 1994, 51, 1485.
4. Sharon, L.; Alfred, R. *J Polym Sci: Polym Chem* 1992, 30, 865.
5. Dobler, F.; Pith, T.; Holl, Y.; Lambla, M. *J Appl Polym Sci* 1992, 44, 1075.

6. Chen, S. A.; Chang, H. S. *J Polym Sci: Poly Chem* 1990, 28, 2547.
7. Lee, C. F. *Polymer* 2000, 41, 1337.
8. Lee, C. F. *J Appl Polym Sci* 2003, 88, 312.
9. Okubo, M.; Izumi, J.; Hosotani, T.; Yamashita, T. *Colloid Polym Sci* 1997, 275, 797.
10. Russell, G. T.; Gilbert, R. G. *Polymer* 2002, 43, 4557.
11. Zhao, K.; Sun, P. Q.; Liu, D. Z.; Dai, G. C. *Eur Polym J* 2004, 40, 89.
12. Kiatkamjornwong, S.; Akkarakittimongkol, P.; Omi, S. *J Appl Polym Sci* 2002, 85, 670.
13. Sivakumar, M.; Rao, K. P. *J Appl Polym Sci* 2002, 83, 3045.
14. Lenzi, M. K.; Silva, F. M.; Lima, E. L.; Pinto, J. C. *J Appl Polym Sci* 2003, 89, 3021.
15. Brian, C. S. *Fundamentals of Fourier Transform Infrared Spectroscopy*; CRC Press: Boca Raton, FL, 1996.
16. Kunio, A.; Mikio, K.; Yuichi, M.; Shozaburo, S. *J Chem Eng Jpn* 1977, 10, 325.
17. Mikio, K.; Kunio, A.; Shozaburo, S. *J Chem Eng Jpn* 1982, 15, 131.
18. Yuan, H. G.; Kalfas, G.; Ray, W. H. J. *Macromol Sci Rev Macromol Chem Phys* 1991, C31, 215.