

DESIGN AND CONTROL OF SOAP-FREE HYDROPHILIC-HYDROPHOBIC CORE-SHELL LATEX PARTICLES WITH HIGH CARBOXYL CONTENT IN THE CORE OF THE PARTICLES

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Abstract Soap-free hydrophilic-hydrophobic core-shell latex particles with high carboxyl content in the core of the particles were synthesized *via* the seeded emulsion polymerization using methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), styrene (St) and ethylene glycol dimethacrylate (EGDMA) as monomers, and the influences of MMA content used in the core preparation on polymerization, particle size and morphology were investigated by transmission electron microscopy, dynamic light scattering and conductometric titration. The results showed that the seeded emulsion polymerization could be carried out smoothly using “starved monomer feeding process” when MAA content in the core preparation was equal to or less than 24 wt%, and the encapsulating efficiency of the hydrophilic P(MMA-BA-MAA-EGDMA) core with the hydrophobic PSt shell decreased with the increase in MAA content. When an interlayer of P(MMA-MAA-St) with moderate polarity was inserted between the P(MMA-BA-MAA-EGDMA) core and the PSt shell, well designed soap-free hydrophilic-hydrophobic core-shell latex particles with 24 wt% MAA content in the core preparation were obtained.

Keywords: Soap-free emulsion polymerization; Hydrophilic-hydrophobic core-shell particles; Morphology; TEM; Carboxyl distribution.

INTRODUCTION

Preparation of the core-shell particles with defined morphology has been a topic of great interest in the past few decades as they have a spectrum of application properties broader than that of the particles with uniform composition, and the core-shell latex particles have been widely used in many industrial applications such as impact modifiers, adhesives, coatings, biomedical and optical sensors^[1–5]. However, it is not easy to achieve well-designed core-shell latex since any change in thermodynamic and kinetic conditions would affect the particle morphology^[6–9], and various alternative morphologies such as sandwich-like, raspberry-like, and even invert core-shell structure might be generated as intermediates of the phase separation in previous literature^[10–18]. In fact, most of investigations on the core-shell latex particles with a defined morphology were primarily limited to the particles with a hydrophobic core and hydrophilic shell^[10–15, 19], and only a few reports were focused on the hydrophilic core-hydrophobic shell particles because such particle morphology is thermodynamically instable^[20, 21], leading to form undesired particle morphology.

The final morphology of the latex particles was determined by the thermodynamic and kinetic factors^[22], and effective methods to achieve desirable particle morphology were only through developing the emulsion polymerization techniques and controlling process conditions so far^[17, 23, 24]. The seeded emulsion

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Received December 30, 2011; Revised February 6, 2012; Accepted February 8, 2012

doi: 10.1007/s10118-012-1160-0

polymerization has been considered as the best process to prepare the core-shell latex particles, and the core-shell latex particles with controllable carboxyl content and its distribution were of great importance both in theory and practice. In our previous work, carboxyl distribution in the latexes has been investigated by conductometric titration^[25, 26]. Recently, we have been engaged in the preparation of porous latex particles using post-treatment process in the presence of surfactant, and found that the final morphology of the porous particles was mainly determined by two factors, one is the content of unsaturated acid monomer used in the latex preparation, and the other is the morphology of the untreated latex particles^[27, 28]. In this study, in order to obtain the core-shell particles with a high carboxyl content in hydrophilic core encapsulated by a hydrophobic shell, the latex particles were designed and synthesized *via* soap-free seeded emulsion polymerization, and the influences of methacrylic acid used in the core preparation on the particle size, the particle morphology and the carboxyl distribution were investigated by TEM, DLS analysis and conductometric titration.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA) and styrene (St), all were of AP grade from First Chemical Reagent Factory, Tianjin, China and purified by distillation under reduced pressure. Ammonium persulfate (APS, AP grade) was purified by recrystallization in deionized water twice before use. Ethylene glycol dimethacrylate (EGDMA) (98.0% purity), NaOH and H₂SO₄ (all AP grade) were used as received. Deionized water was distilled before use.

Preparation of Core Latex

The hydrophilic P(MMA-BA-MAA-EGDMA) core latex was prepared *via* soap-free semi-continuous emulsion polymerization, and the recipe is given in Table 1. At first, 70 mL of water, 5 wt% of the monomer mixture of MMA, MAA, BA and EGDMA and 0.10 g of APS dissolved in 10 mL of water were charged into the reactor, and the polymerization was carried out at 80°C for 40 min with stirring at 300 r/min. Then, 0.15 g of APS dissolved in 10 mL of water was added into the reactor, and the residual monomer mixture was simultaneously drop-wise added into the reactor at 80°C for 3 h. During the feeding, 0.15 g of APS dissolved in 10 mL of water was added into the reactor in two steps at different polymerization time: 5 mL at 1.5 h and 5 mL at 2.5 h. After then, the polymerization was continued for an additional 30 min.

Table 1. Recipe for the preparation of P(MMA-BA-MAA-EGDMA) core latex (Unit: gram)

MMA	MAA	BA	EGDMA	APS	H ₂ O
16.50	Variable	14.60	0.25	0.40	100

Preparation of Two-layer Core-shell Latex

The two layer P(MMA-BA-MAA-EGDMA)/PSt core-shell latex was prepared using soap-free seeded emulsion polymerization at 90°C with stirring at 300 r/min. At first, 10 g of the core latex diluted with 25 mL of water was charged into the reactor, and 11.84 g of St was drop-wise added into the reactor in 3 h. The APS aqueous solution (0.10 g of APS dissolved in 10 mL of water) was introduced into the reactor in two steps at different polymerization time: 7 mL at the beginning and 3 mL at 1.5 h. After the monomer feeding, the polymerization was continued for an additional 30 min.

Preparation of Three-layer Core-shell Latex

The interlayer and the outer shell of the three-layer P(MMA-BA-MAA-EGDMA)/P(MMA-MAA-St)/PSt core-shell latex were formed separately during the second and third stages of soap-free seeded emulsion polymerization with stirring at 300 r/min.

In the P(MMA-MAA-St) interlayer preparation, 15 g of the core latex diluted with 37 mL of water and 0.15 g of APS dissolved in 15 mL of water were first charged into the reactor, and then the monomer mixture of 11.00 g of MMA, 1.26 g of MAA and 3.05 g of St was drop-wise added into the reactor at 80°C in 1 h. After the monomer feeding, the polymerization was continued for an additional 30 min.

The PSt outer shell was prepared by feeding St into the above emulsion system. The recipe and the procedure were the same as in the preparation of the two-layer core-shell latex.

Characterization

Monomer conversion was determined gravimetrically. The dried diameter (D_p) and the morphology of the latex particles were characterized by transmission electron microscopy (TEM, JEOL JEM-1200EX, Japan) using phosphotungstic acid as staining agent. The hydrodynamic diameter (D_h) and zeta potential of the latex particles were determined by Zetasizer 3000HS (Malvern, UK). The theoretical diameter (D_{theo}) of the core-shell latex particles was calculated assuming that all monomers were polymerized and uniformly covered onto the seed particles in the soap-free seeded emulsion polymerization.

The distribution of $-\text{COOH}$ in the latex was determined by conductometric titration at 25°C as follows: 1.00 g of original latex was diluted with 100 g of water, and pH value of the diluted latex was first adjusted to 3.00 ± 0.05 using a H_2SO_4 solution of 0.051 mol/L concentration, and then the latex was titrated with a NaOH solution of 0.077 mol/L concentration under the monitor of a DDS-307 conductometer (Leici, Shanghai, China). The total amount of $-\text{COOH}$ on the surface of the particles and those free in aqueous phase (SF_a) expressed as per gram polymer were calculated directly based on conductometric titration curve, and the amount of buried $-\text{COOH}$ (E_a) inside the particles was obtained from the difference between the initial charge of MAA and SF_a , and the value of SF_p and E_p expressed as the percentages of SF_a and E_a to the total carboxyl groups in the core-shell latex, respectively.

RESULTS AND DISCUSSION

Influence of MAA Content on the Core Latex

It is well known that using appropriate amount of unsaturated acid monomer is beneficial to stabilize emulsion polymerization process and the resultant latex due to the hydrophilicity and electrostatic repulsion of the carboxyl groups on the particle surface^[29]. Nevertheless, excessive carboxyl groups would induce the latex coagulation and the undesired particle morphology especially under the soap-free condition. In order to obtain the core latex with more carboxyl groups, different amount of MAA was used in the preparation of P(MMA-BA-MAA-EGDMA) core latex, and the results are given in Table 2. Experiments showed that the emulsion polymerization could be carried out smoothly, and the monomer conversion was higher than 91% when the MAA content was equal to or less than 24 wt%, and the further increase in MAA content would make the polymerization system unstable and lead to some coagulation.

Table 2. Influence of MAA content on the polymerization and the properties of core latex

Sample	MAA ^a (wt%)	Conversion ^b (%)	D_p (nm)	D_h (nm)	Zeta (mV)
C1	8	93.93	470	545	-41.7
C2	16	91.26	530	675	-40.0
C3	24	93.11	620	1087	-36.1

^a Amount relative to the total amount of monomers used in the core preparation;

^b Percentage relative to the all of the monomers

According to the soap-free emulsion polymerization principle, the homogenous nucleation is dominant. The monomers dissolved in water are first initiated and polymerized, and when the growing oligomers reach a certain length (critical chain length), they are no longer water-soluble and precipitate out from aqueous phase to form primary particles. These primary particles act as polymerization loci in the following process of particle growth. In this study, due to the water-solubility of MAA, the number of precipitated primary particles increased with the increase in MAA content, giving rise to a large number of primary particles in the system, then several small particles would be gathered in the early stage of the polymerization to form a relatively large one so as to decrease the potential energy by decreasing the interfacial area. On the other hand, excessive amount of MAA would produce much more water-soluble polymers, which bring about "bridge" flocculation of several growing

particles. Thus, the dried diameter of the latex particles (D_p) increased from 470 nm to 620 nm with the content of MAA increased from 8 wt% to 24 wt%. It is worth pointing out that, with the increase in MAA content, more carboxyl-enriched polymer segments and chains would be located on the surface of particles to form “the hairy layer” through the carboxyl hydration, hence, the value of D_h was larger than that of D_p , particularly for the sample C3 with 24 wt% MAA content.

The morphology of the core latex particles was also influenced by MAA content (Fig. 1), and TEM observation agreed with the principle of soap-free emulsion polymerization as discussed above. When MAA content was 8 wt%, the core particles were perfect spheres and their surface was smooth, meanwhile the spherical degree of the core particles decreased and the particle surface became rough gradually with the increase in MAA content. When MAA content reached 24 wt%, the particles exhibited rough spherical morphology as shown in Fig. 1(c), and this was due to the coagulation of small particles during soap-free emulsion polymerization and the entanglement of carboxyl-enriched hydrophilic polymer chains.

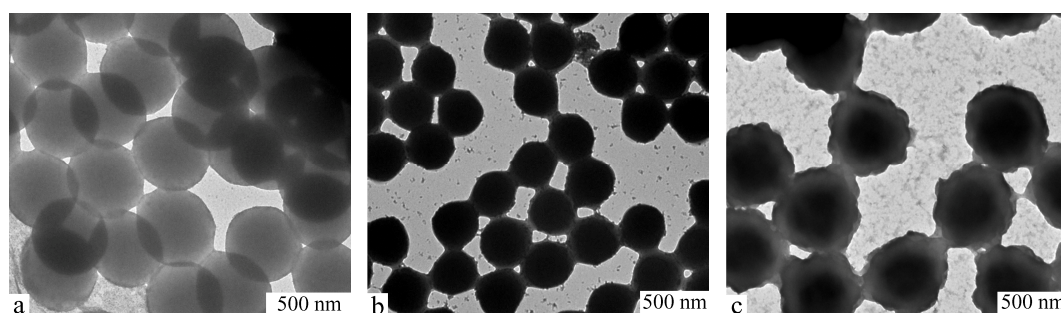


Fig. 1 TEM micrographs of P(MMA-MAA-BA-EGDMA) core latexes prepared with different contents of MAA: (a) 8 wt%, (b) 16 wt% and (c) 24 wt%

Influence of MAA Content in the Core Preparation on the Two-layer Core-shell Latex

In order to encapsulate the hydrophilic P(MMA-BA-MAA-EGDMA) core with the hydrophobic PSt shell, different monomer feeding processes have been used in the seeded emulsion polymerization, and the experiments showed that batch or quick feeding would induce coagulation of the polymerization system due to the great polarity difference between the core polymer and styrene. When “starved monomer feeding process” was utilized in the seeded emulsion polymerization, stable P(MMA-BA-MAA-EGDMA)/PSt core-shell latexes with the monomer conversion over 90% were obtained. From Table 3 one can see that, the D_p value of the core-shell particles was approximately equal to its theoretical value of D_{theo} except the sample C3/S, implying that the seeded emulsion polymerization was successful and few new latex particles were generated for the sample C1/S and C2/S. As for the sample C3/S with a high level of carboxyl content in the core, since the hydrophilicity of the core was too strong to be encapsulated by the hydrophobic shell, the homogeneous nucleation of St would be unavoidable in the soap-free seeded emulsion polymerization, namely that some monomers would first polymerize and precipitate out from water phase to generate secondary particles, thereafter these small secondary particles would either grow and aggregate to form the new latex particles, or absorbed on the particle surface to form core-shell latex particles. For the above reason, the value of D_p was less than that of D_{theo} for the sample C3/S.

Table 3. Influence of MAA content in the core preparation on the two-layer P(MMA-BA-MAA-EGDMA)/PSt core-shell latex

Sample	MAA ^a (wt%)	St conversion (%)	D_p (nm)	D_{theo} (nm)	D_h (nm)	Zeta (mV)
C1/S	8	91.93	862	840	1093	-37.5
C2/S	16	91.26	960	949	1099	-34.8
C3/S	24	93.11	875	1103	1100	-32.0

^a Amount relative to the total amount of the monomers used in the core preparation

The morphology of the core-shell latex particles was also affected by the MAA content used in the core preparation, and TEM micrographs of P(MMA-MAA-BA-EGDMA)/PSt core-shell latex are shown in Fig. 2. From the viewpoint of thermodynamics, during the soap-free seeded emulsion polymerization, the hydrophilic core polymer chains tended to migrate towards aqueous phase, while the hydrophobic monomer and its polymer chains preferred to move towards the inside of particles, which probably lead to the generation of the latex particles with undesired morphology. However, under the starved monomer feeding condition, highly instantaneous monomer conversion would promote the viscosity of polymerizing loci, so as to decrease the possibilities of phase migration and generation of undesired particle morphology, which is identified in Fig. 2(a). Nevertheless, with the increase in MAA content in the core preparation, the homogeneous nucleation of St would produce secondary particles in the seeded emulsion polymerization and as a result, the particles with low spherical degree and rough surface generated as shown in Figs. 2(b) and 2(c). This phenomenon was in accordance with the difference between D_p and D_{theo} for the sample C3/S, demonstrating that the generation of secondary particles and undesired hydrophilic-hydrophobic core-shell particles could not be prevented in the two-step soap-free seeded emulsion polymerization process, especially for the sample with large amount of MAA used in the core latex preparation.

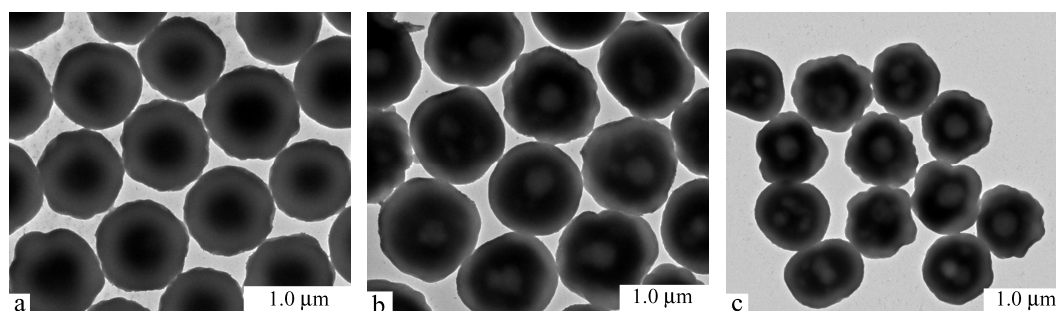


Fig. 2 TEM micrographs of P(MMA-MAA-BA-EGDMA)/PSt core-shell latex particles with different content of MAA in the core preparation: (a) 8 wt%, (b) 16 wt% and (c) 24 wt%

Influence of MAA Content in the Core Preparation on the Three-layer Core-shell Latex

As mentioned above, it is difficult to prepare the core-shell latex particles with high carboxyl content in the core just by using two-step soap-free seeded emulsion polymerization, owing to the fact that the polarity difference between the core and the shell polymers was too high, that is, the hydrophilicity of the core was too strong to be encapsulated by hydrophobic shell. For the purpose of achieving well-defined hydrophilic-hydrophobic core-shell latex, an intermediate layer was designed and inserted between the hydrophilic core and the hydrophobic shell to balance their polar difference, and the three-layer P(MMA-BA-MAA-EGDMA)/P(MMA-MAA-St)/PSt core-shell latex was prepared *via* three-step soap-free seeded emulsion polymerization under the starved monomer feeding condition.

Results in Table 4 show that the monomer conversion was higher than 99%, and the values of D_p were very close to those of D_{theo} for all runs regardless of the MAA content in the core preparation, indicating that few secondary particles were generated in the preparation processes of interlayer and outer shell, in other words, a majority of monomers were polymerized onto the seed particles in the soap-free seeded emulsion polymerization.

Table 4. Influence of MAA content in the core preparation on the three-layer P(MMA-BA-MAA-EGDMA)/P(MMA-MAA-St)/PSt core-shell latex

Sample	MAA ^a (wt%)	Conversion ^b (%)	D_p (nm)	D_{theo} (nm)	D_h (nm)	Zeta (mV)
C1/I/S	8	99.99	895	884	925	-38.9
C2/I/S	16	99.71	992	997	1275	-39.3
C3/I/S	24	99.99	1185	1165	1324	-32.9

^a Amount relative to the total amount of the monomers used in the core preparation;

^b Percentage relative to all of the monomers used in the interlayer and out shell preparation

TEM microphotos of the latexes are shown in Fig. 3. Because the interlayer with moderate polarity inserted between the hydrophilic P(MMA-BA-MAA-EGDMA) core and the hydrophobic PSt outer shell, the homogenous nucleation was prevented and the thermodynamic motivate force of phase migration was restrained in the soap-free three-step seeded emulsion polymerization, therefore the well-designed core-shell particles were synthesized. In comparison with the two-layer core-shell latex particles in Fig. 2, it was obvious that the three-layer core-shell latex particles were more spherical and their surfaces were much more glabrous, suggesting that the MAA content in the core preparation has little influence on the three-layer core-shell particle morphology.

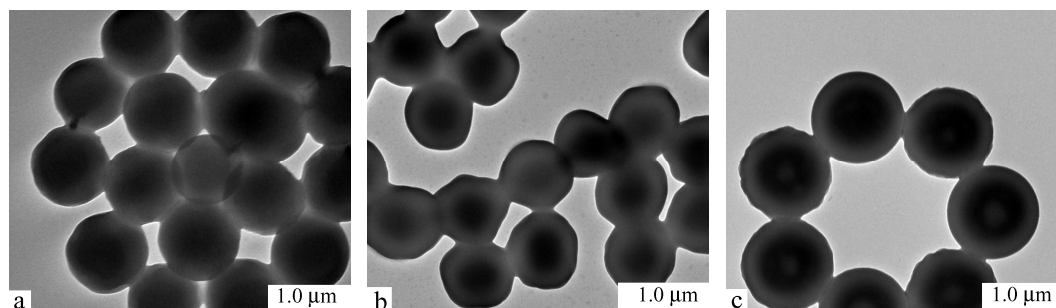


Fig. 3 TEM micrographs of P(MMA-MAA-BA-EGDMA)/P(MMA-MAA-St)/PSt core-interlayer-shell latex particles with different contents of MAA in the core preparation: (a) 8 wt%, (b) 16 wt% and (c) 24 wt%

Carboxyl Distribution in the Hydrophilic-hydrophobic Core-shell Latexes

For the purpose of further confirming the encapsulation of the hydrophilic core with the hydrophobic shell and comparing the structural difference between the two-layer and three-layer soap-free hydrophilic-hydrophobic core-shell latex particles, the conductometric titration was used to characterize the carboxyl distribution, and the conductometric titration curves of different core-shell latexes are shown in Fig. 4.

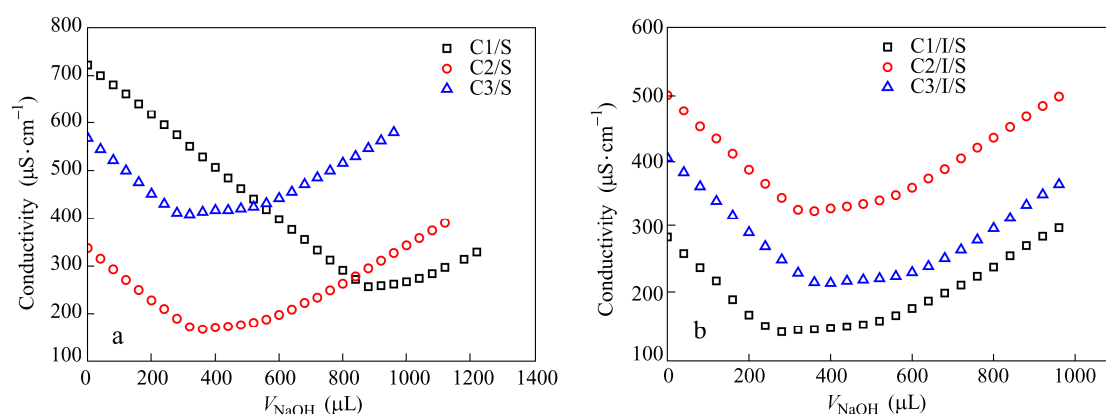


Fig. 4 Conductometric titration curves of (a) P(MMA-MAA-BA-EGDMA)/PSt core-shell latex and (b) P(MMA-MAA-BA-EGDMA)/P(MMA-MAA-St)/PSt core-interlayer-shell latex with different contents of MAA in the core preparation: 8 wt% (square), 16 wt% (circle) and 24 wt% (triangle)

Based on the conductometric titration curves in Fig. 4, the total amount of carboxyl groups bounded on the particle surface and free in aqueous phase (SF_a) and that of buried inside the particles (E_a) were calculated and listed in Table 5. Obviously, regardless of the MAA content used in the core preparation, the values of SF_a were greater than those of E_a in the two-layer core-shell latex, however, in the three-layer core-shell latex the formers were less than the latters, indicating that much more carboxyl groups were buried inside the three-layer core-shell latex particles.

Table 5. Carboxyl distribution in the soap-free core-shell latex

Sample		$SF_a \times 10^4$ (mol/g)	$E_a \times 10^4$ (mol/g)
Two-layer core-shell latex	C1/S	1.55	0.04
	C2/S	2.48	0.77
	C3/S	3.43	1.94
Three-layer core-shell latex	C1/I/S	1.54	3.35
	C2/I/S	2.00	3.99
	C3/I/S	2.49	4.62

The relationship between the MAA content in the core preparation and the percentage of carboxyl distribution in the core-shell latexes is shown in Fig. 5. In the two-layer core-shell latex (Fig. 5a), although the percentage of buried carboxyl groups (E_p) to the total carboxyl groups increased with the increase in MAA content in the core preparation, most of carboxyl groups buried inside particles were titrated during the conductometric titration process on account of a large number of $-OH$ entering into the inside of the particles. Thus, the calculated values of the total amount of $-COOH$ (SF_a) based on the titration curves were greater than the real ones, that is, the obtained values of SF_a contained a portion of $-COOH$ inside the particles. This indicated that the encapsulation of hydrophilic P(MMA-BA-MAA-EGDMA) core with the PSt shell was not sufficient and effective, and the interpenetration of the core and the shell polymer chains and even the phase migration might occur during the seeded emulsion polymerization process, and the resultant defects on the shell would allow NaOH to come into the core to neutralize the inside carboxyl groups. However, the carboxyl distribution in the three-layer core-shell latex was little affected by the MAA content in the core preparation, and 65%–68% of carboxyl groups were buried inside the particles. Since the encapsulation of the hydrophilic P(MMA-BA-MAA-EGDMA) core with the PSt out shell was effective and uniform under this circumstance, the buried carboxyl groups could not be titrated during the conductometric titration process (Fig. 5b). These results were also consistent with the TEM observation as showed in Fig. 2 and Fig. 3.

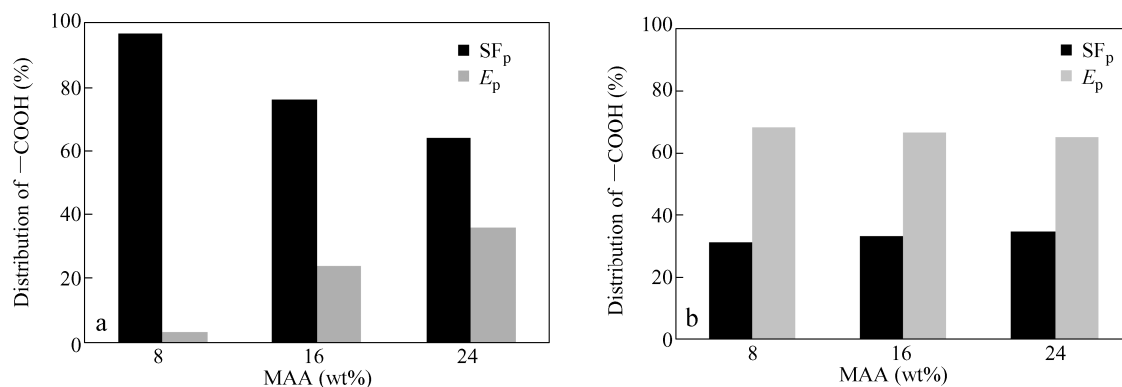


Fig. 5 Carboxyl distribution in (a) P(MMA-MAA-BA-EGDMA)/PSt core-shell latex and (b) P(MMA-MAA-BA-EGDMA)/P(MMA-MAA-St)/PSt core-interlayer-shell latex

E_p (grey bar) and SF_p (black bar) represent, respectively, the percentage of the carboxyl groups buried inside particles and the total amount of carboxyl groups on the particle surface and free in aqueous phase.

CONCLUSIONS

In this work, the soap-free hydrophilic-hydrophobic core-shell latex particles with high carboxyl content in the core were synthesized *via* the seeded emulsion polymerization using “starved monomer feeding process”. The encapsulating efficiency of the hydrophilic core with the hydrophobic shell was investigated by TEM observation along with the carboxyl distribution for the two-layer and three layer core-shell latexes. The morphology and thermodynamic stability of soap-free hydrophilic-hydrophobic core-shell latex particles were significantly improved by inserting an intermediate polarity interlayer between the hydrophilic core and the hydrophobic shell.

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