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SHORT COMMUNICATION

Synthesis of poly(styrene-co-3-trimethoxysilyl propyl methacrylate) microspheres coated with polysiloxane layer

Xin Lu · Zhong Xin

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Abstract A procedure has been developed to coat micron-sized poly(styrene-co-3-trimethoxysilyl propyl methacrylate) microspheres with a smooth layer of polysiloxane by the hydrolysis and condensation of methyl trimethoxylsilane (MTMS). Firstly, polystyrene microspheres containing silanol groups were prepared by conventional dispersion polymerization using 3-(trimethoxysilyl) propyl methacrylate (MPS) as a functional comonomer in an ethanol/water medium. Secondly, the synthesis of the polysiloxane shell was carried out using a sol–gel process of MTMS. The thickness of the shells can be easily varied with different copolymer seeds and MTMS feed ratio. When we used copolymer particles with 2.00 μm diameter as seeds, the thickness of the polysiloxane shells can be varied from 0.10 to 0.18 μm. The core/shell structure of the composite microspheres was characterized by transmission electron microscope (TEM).

Keywords Dispersion polymerization · Polystyrene · Polysiloxane · Core/shell microspheres · Synthesis · Characterization

Introduction

In recent years, the synthesis of core/shell polymer particles has raised great interests in material science as the magnetic, electrical, and optical properties of core particles can be easily altered by building a shell layer on a core. Such materials may have potential application in various fields such as optics, catalysis, biology, medicine [1–3]. In addition, the development of the heterophase polymerization and colloidal chemistry make it possible to control the synthesis of core/shell particles with designed morphologies. Several polymerization techniques have been developed to obtain micron-size core/shell composite particles. Dynamic swelling method was used to prepare micron-size polystyrene (PS)/poly(ethyl methacrylate) [4], PS/poly(butyl methacrylate) [5] composite particles. Seeded dispersion polymerization has been employed to produce micron-size PS /PMMA [6], PMMA /PS [7], and PS/poly(*n*-butyl acrylate) (PBA) [8] composite particles.

Most of the works have focused on the micron-sized core/shell composite particles prepared from styrene and acrylic monomer. Nevertheless, little research has been focused in the micro-sized core/shell composites of vinyl monomers and siloxane. In applications, polysiloxane has many specific properties such as good water repellency, weather resistance, lubricity, and excellent thermal stability. Therefore, the combination of vinyl polymer with polysiloxane can exhibit unusual, even unique properties. Some studies investigated the composite latex particles with polysiloxane shell using seeded emulsion polymerization [9–12]. However, most of the composite latex particles are obtained in the form of a latex. A few studies have been made on the preparation of composites of vinyl monomers and siloxane in the particulate form, even more so in the form of spherical particles with uniform sizes.

In our previous work, micron-sized polystyrene/polysiloxane composite particles consisted of PS core, and polysiloxane shells were successfully prepared without using silane coupling agent [13]. Polystyrene seed particles were prepared by conventional dispersion polymerization, and the synthesis of the polysiloxane shell was carried out using a sol–gel

X. Lu · Z. Xin (✉)
State Key Laboratory of Chemical Engineering,
UNILAB of Chemical Reaction Engineering,
College of Chemical Engineering,
East China University of Science and Technology,
P.O. Box 545, Meilong Road 130,
Shanghai 200237, People's Republic of China
e-mail: xzh@ecust.edu.cn

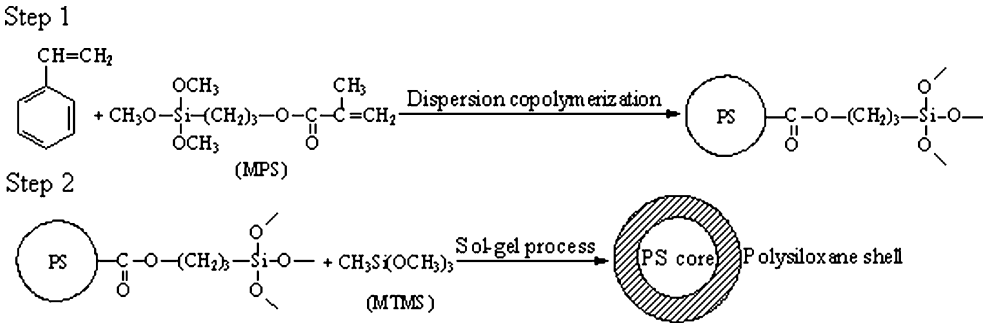


Fig. 1 Schematic representation of the preparation of micron-sized poly(St-co-MPS)/polysiloxane microspheres

process of methyl trimethoxylsilane (MTMS). However, we found there were some clear voids between the PS core and the polysiloxane shell that indicated that there is little chemical affinity between the core and the shell.

In this paper, to improve the compatibility of the PS core and the polysiloxane shell, polystyrene seed particles were prepared by conventional dispersion polymerization of styrene (St) using 3-trimethoxysilylpropyl methacrylate (MPS) as a functional comonomer in an ethanol/water medium.

The synthesis of the polysiloxane shell was carried out using a sol–gel process of methyl trimethoxylsilane (MTMS). The sol–gel process provided a convenient route with mild operating conditions: many previous studies have investigated the sol–gel chemistry of MTMS [14–20]. Schematic representation of the two steps involved in the preparation of micron-sized poly(St-co-MPS)/polysiloxane microspheres is shown in Fig. 1. The morphology and particle size of the seed particles and the core/shell particles were then characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), and size analyzer, respectively.

Experimental

Materials

Styrene (St, Shanghai Lingfeng Chemical, China), methyl trimethoxysilane (MTMS, Hangzhou Guibao Chemical, China), 3-(trimethoxysilyl)propyl methacrylate (MPS, Dow Corning, USA), polyvinylpyrrolidone (PVP K30, M_w=40000, Fluka Chemical), ethanol (Shanghai Lingfeng Chemical, China), hydrochloric acid (HCl, Shanghai Lingfeng Chemical, China), and ammonium hydroxide (NH_4OH, Yixin Sunan Chemical Material Plant, China) were all reagent grades and used as received.

Synthesis of seed microspheres

The seed microspheres were prepared by dispersion copolymerization of St and MPS. St, MPS, AIBN, PVP, ethanol, and deionized water were all weighed into a 250-ml four-neck glass reactor equipped with a mechanical stirrer, a refluxing condenser, and a nitrogen inlet system. In the initial stage, all ingredients were homogeneously dissolved in the ethanol/H_2O mixture. After sealing in a nitrogen atmosphere, the reactor was submerged into a preheated thermostated water bath at 70 °C and the polymerization was carried out for 24 h. The resulting latex was filtrated with a buchner funnel and the filter cake was washed by ethanol, followed by drying. The conversions of the seed particles were determined by conventional gravimetric method. All the ingredients used are summarized in Table 1.

Preparation of core/shell microspheres

Poly(St-co-MPS)/polysiloxane core/shell microspheres were prepared by a sol–gel process. MTMS (1 g) was hydrolyzed in water (5 g), with HCl as catalyst to control the pH value of the solution to 5.0, and the aqueous silanol mixed with copolymer seeds (2 g) by 10-min sonication, and then an ammonia solution was added into the mixture

Table 1 The ingredient in dispersion copolymerization of St and MPS

Sample	Ethanol (g)	Water (g)	St (g)	MPS (g)	PVP K30 (g)	AIBN (g)
PS1	36	4	10	0	2.5	0.1
MPS1	36	4	9.5	0.5	2.5	0.1
MPS2	36	4	9	1	2.5	0.1

Table 2 Particle size of the seed microspheres

Sample	[MPS] in the feed (%)	d_n (μm)	CV (%)	Conversion (%)
PS1	0	1.76	24	88
MPS1	5	2.00	28	90
MPS2	10	2.95	31	89

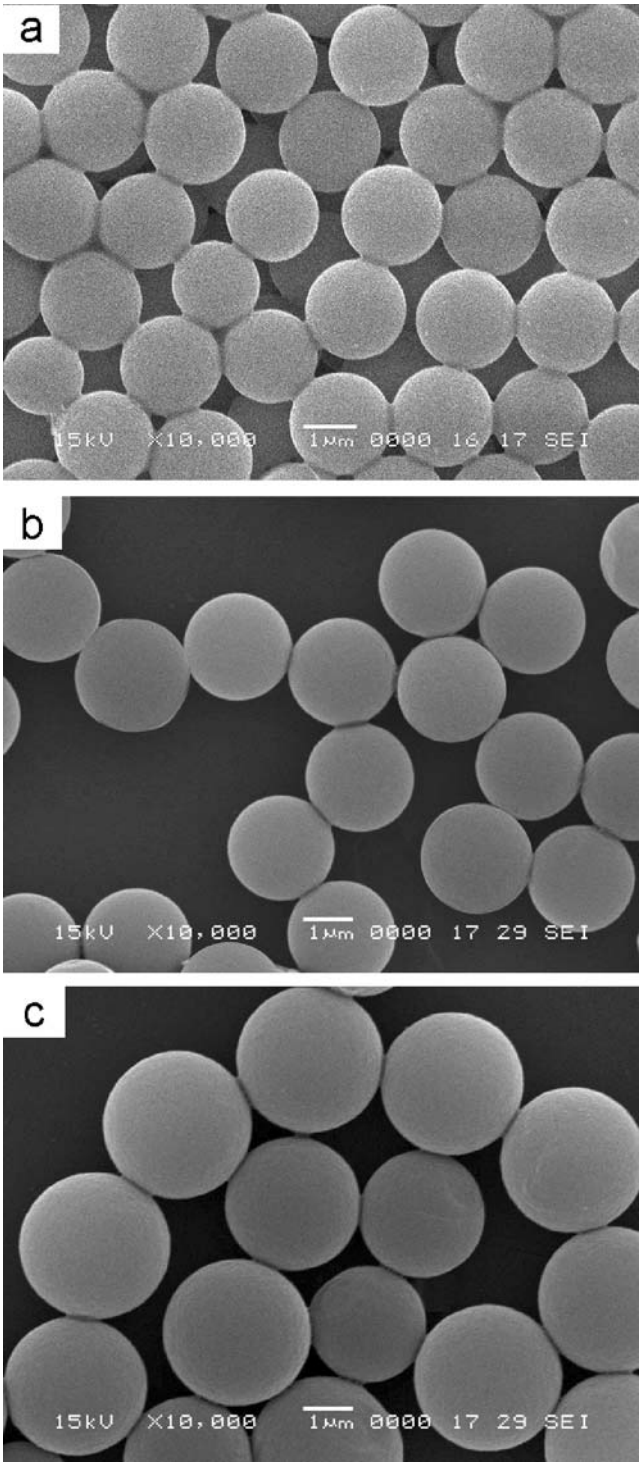


Fig. 2 SEM photographs of PS and poly(St-co-MPS) seed microspheres. **a** PS1, **b** MPS1, **c** MPS2

to control the pH value of the solution to 8.0 to catalyze the condensation reactions of silanol. The reaction was continued for 5 h, and polysiloxane shells were generated on the seed microspheres. The microspheres with different core/shell weight ratio can easily be prepared through adjusting the feed ratio of the seed microspheres and silanol. The

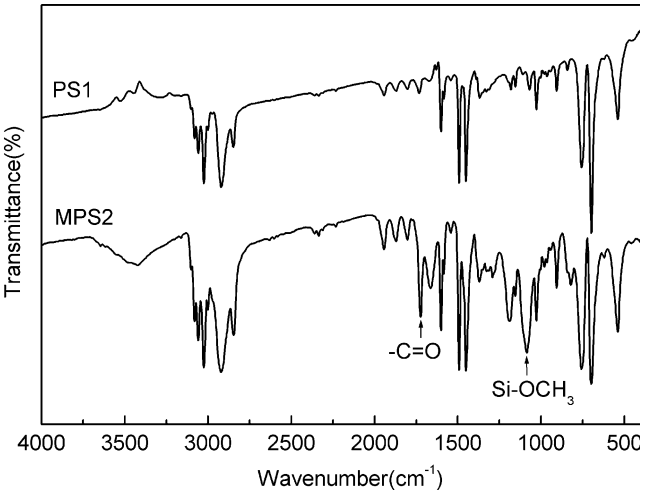


Fig. 3 FT-IR spectra of PS and poly(St-co-MPS) seed microspheres

resulting latex was filtrated with a buchner funnel and the filter was washed, followed by drying, and the composite microspheres were attained.

Characterization

The number average diameter (d_n) and size distribution coefficient (CV) of the particles were measured by a size analyzer (Mastersizer 2000, Malvern). The chemical structures were identified by FT-IR (EQUINOX-55, Bruker). The samples for FT-IR analyses were mixed with KBr powder and pressed into pellets. To determine the glass transition temperature (T_g) of the seed particles, a thermal analysis was carried out by using a differential scanning calorimeter (DSC; Diamond, Perkin Elmer) operating at a heating rate of 10 °C/min in the range 50–200 °C. The morphology of the particles was observed with scanning electron microscopy (JSM-6360LV, JEOL). Dried core/shell

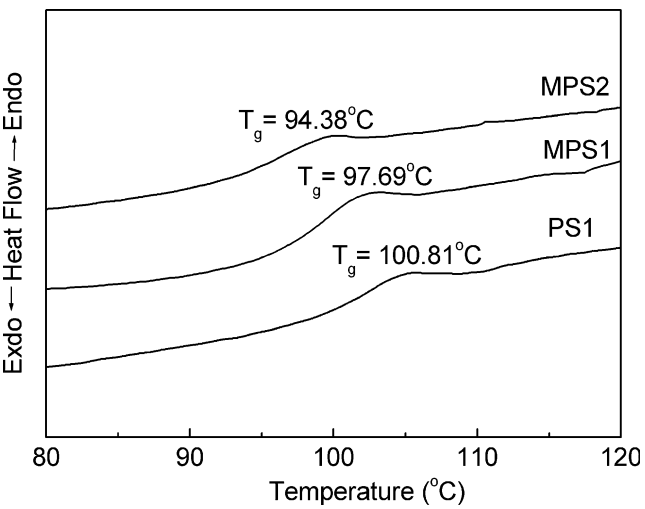


Fig. 4 DSC thermograms of PS and poly(St-co-MPS) seed microspheres

Table 3 The particle size and size distribution of the seeds and the core/shell microspheres

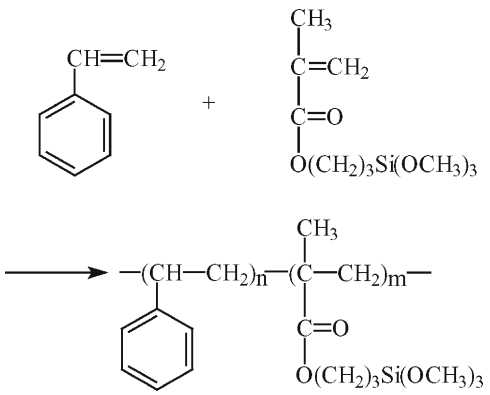
Seed particles	Core/shell particles	m_{shell}/m_{core}	d_n (μm)	CV (%)
MPS1			2.00	28
	SMPS1-1	18/82	2.20	34
	SMPS1-2	26/74	2.22	35
	SMPS1-3	35/65	2.30	31
	SMPS1-4	43/57	2.35	33
MPS2			2.95	31
	SMPS2-1	18/82	3.12	34

particles were dispersed in epoxy resin matrix, cured at room temperature for 24 h, and at 40 °C for 1 h, and microtomed. The ultrathin cross-sections were observed using the TEM (JEOL-100CX III, JEOL).

Results and discussion

Synthesis and characterization of seed microspheres

The copolymer seed microspheres were prepared by dispersion copolymerization of St and MPS. The copolymerization reaction is described by the following formula:



Tissot and Bourgeat-Lami [12, 21–23] synthesized SiOH-functionalized polymer latexes by emulsion copolymerization of styrene and 3-trimethoxysilylpropyl methacrylate (MPS). However, few studies on dispersion copolymerization of St and MPS have been reported. Dispersion polymerization is highly sensitive to small changes in the numerous reaction parameters involved in the process. The polymerization system may be affected evidently in the presence of another monomer; even different comonomer ratios should be treated as new polymerization systems. In the present paper, we studied the effects of the amount of MPS on the properties of poly(St-co-MPS) seed particles.

The influence of the MPS concentration on the size of the seed microspheres was examined and the results are given in Table 2. The particle size of the microspheres increased and the size distribution became broader with increasing MPS concentration. The increase of particle size may be because the acrylic structure of MPS increased the solvency of the homogeneous reaction mixture. So the copolymer is more soluble in the reaction medium than PS, resulting in larger particle sizes. Figure 2 shows SEM photographs of seed microspheres with different MPS concentrations.

The chemical structures of PS homopolymer PS1 and copolymer seed MPS2 were characterized by FT-IR (Fig. 3). The characteristic bands of MPS units appeared at 1,730 cm^{-1} for the C=O bond and at 1,083 cm^{-1} for the Si–OCH_3 bond. The characteristic bands of the aromatic ring contributing from St are observed at 1,604, 1,492, and 1,450 cm^{-1}.

To investigate the copolymer microstructure, we measured the glass transition temperature (T_g) of copolymer seed microspheres with different MPS feed ratio (Fig. 4). The results showed that T_g of the seed microspheres decreased from 100.81 to 94.38 °C as the MPS concentration in feed increased from 0 to 10%. This indicates that the pending alkoxysilyl group provides a plasticizing effect to the copolymer particles. A previous work on the synthesis of poly(styrene-*co*-MPS) also reported the similar result that incorporation of pendant alkoxysilyl groups in the copolymer gave rise to a significant decrease of T_g [24].

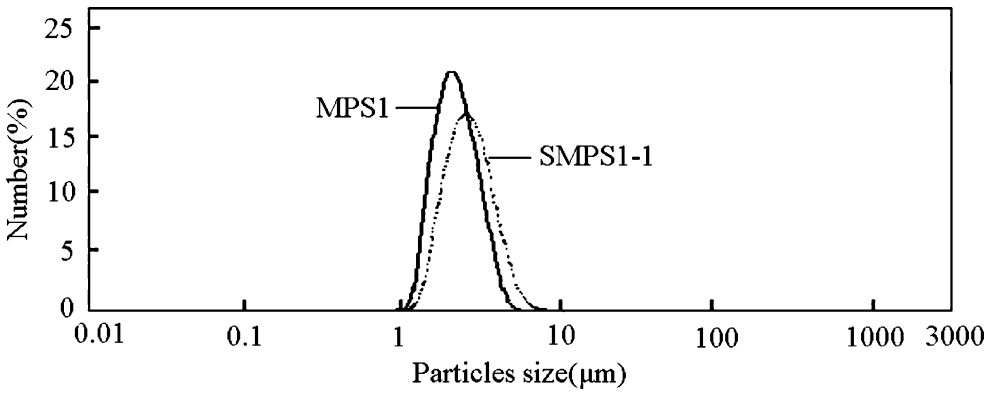


Fig. 5 The particle size and size distribution of microspheres MPS1 and SMPS1-1

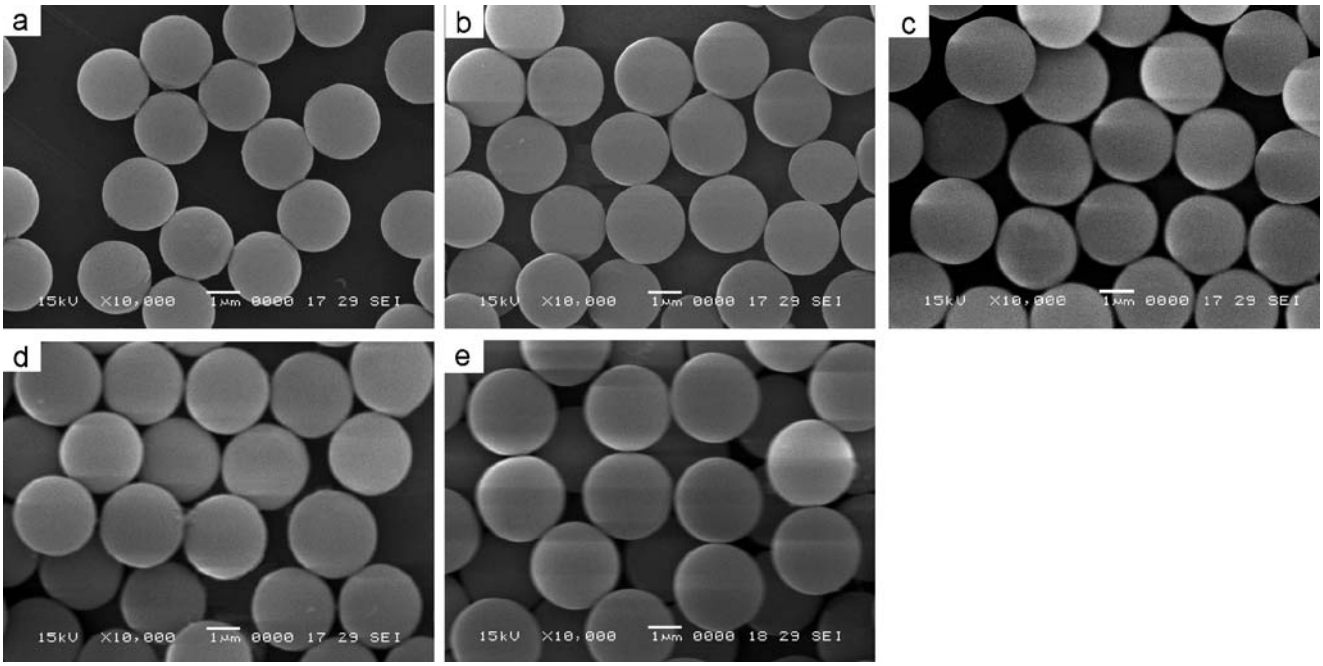


Fig. 6 SEM of seed particles and core/shell particles. **a** MPS1, **b** SMPS1-1, **c** SMPS1-2, **d** SMPS1-3, **e** SMPS1-4

Synthesis and characterization of core/shell microspheres

As mentioned above, to improve the compatibility between the PS core and the polysiloxane shell, we select a coupling agent to covalently attach alkoxysilane groups in PS seed microspheres. The seed microspheres then mixed with aqueous silanol catalyzed with an ammonia solution to prepare core/shell microspheres. The particle size and size distribution of the core/shell particles with different core/shell mass ratio are shown in Table 3. In this table, SMPS1-1,

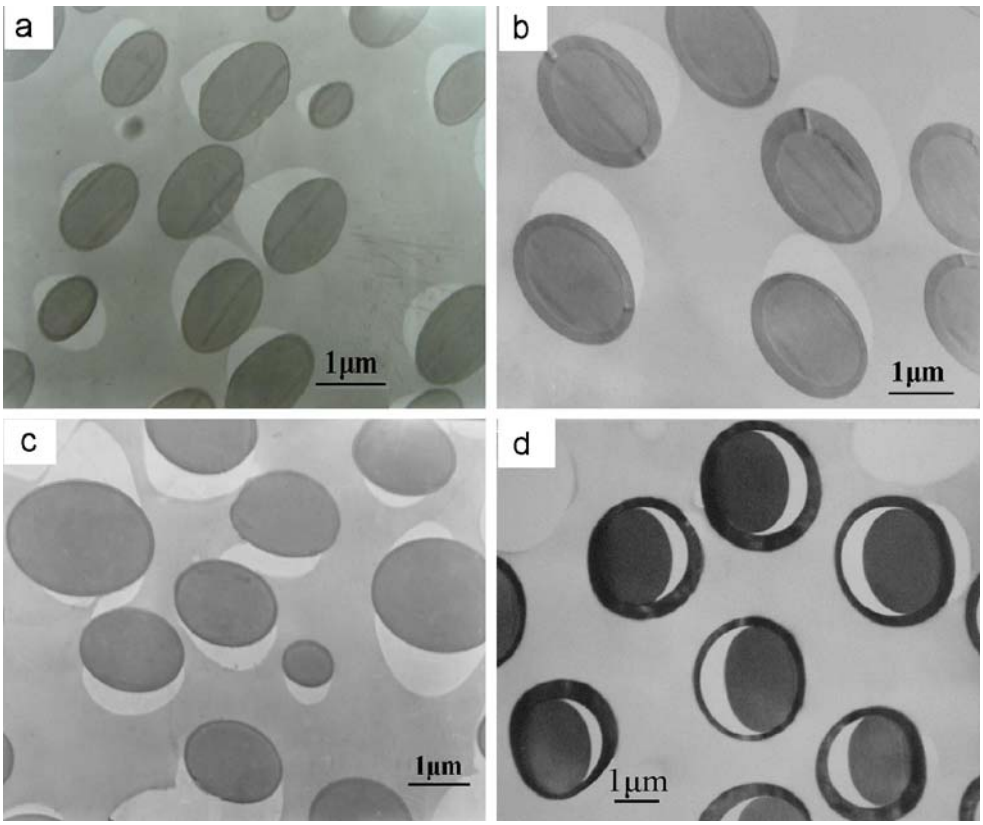


Fig. 7 TEM photographs of ultrathin cross-sections of core/shell microspheres. **a** SMPS1-1, **b** SMPS1-4, **c** SMPS2-1, **d** SS3-4

SMPS1-2, SMPS1-3, and SMPS1-4 are the core/shell particles with MPS1 as the seed particles, and SMPS2-1 are the core/shell particles with MPS2 as the seed particles. The results reported in Table 3 show that the particle size of the core/shell microspheres increased with the increase of the MTMS feed ratio. This indicates that the sol–gel process of MTMS proceeded in the corresponding seed microspheres.

The particle size distribution curves of MPS1 and SMPS1-1 particles are shown in Fig. 5. After the sol–gel process, the particle size increased and the size distribution still appeared as a single peak. Again, the result indicated that the polysiloxane was incorporated into the seed particles.

SEM photographs of seed particles and core/shell particles are shown in Fig. 6. All the particles were spherical in shape even at a high MTMS concentration and the particle size increased with the increase of the MTMS feed ratio. It is evident that the polysiloxane shell on the MPS1 seed particles is very smooth and uniform. As expected, the attached alkoxysilane functions played the role of anchored groups that promote the formation of a polysiloxane layer on the seed surface.

Figure 7 shows TEM photographs of the ultrathin cross-section of the core/shell particles. As a comparison sample, SS3-4 is the core/shell particles using PS monopolymer microspheres as seed and with the core/shell mass ratio of 58/42 [13]. In Fig. 7, all the composite microspheres have heterogeneous contrasts and the boundaries of the core and polysiloxane shell can be clearly observed. However, we can see some clear voids between the core and the shell of SS3-4 that was prepared without using silane couple agent. The formation of the void may be caused by the different shrinkage of the PS core and the cross-linked polysiloxane shell during the dryness process. We also can see that the core and the shell are connected tightly to the composite microspheres SMPS1-1, SMPS1-4 and SMPS2-1. The results indicate that the existence of alkoxysilane groups in seeds improve the compatibility between the core and the polysiloxane shell effectively.

Conclusion

In the current work, polystyrene microspheres carrying alkoxysilane groups were synthesized in dispersion polymerization using MPS as a functional comonomer. We found that T_g of the seed microspheres decreased and the particle size increased as the MPS concentration increased.

Stable core/shell particles consisting of a poly(St-co-MPS) core and a polysiloxane shell were prepared in this study by the condensation of silanol in the presence of poly (St-co-MPS) seed microspheres. The shell is very smooth and uniform and can be varied in thickness with different feed ratio of the seed particles and methyl trimethoxysilane. When we used copolymer particles with diameter 2.00 μm as seeds, the thickness of the polysiloxane shells can be varied from 0.10 to 0.18 μm. The core/shell particles have nearly the same size distribution as the copolymer seed particles. The addition of silane couple agent MPS as a comonomer in the preparation of seeds improves the compatibility between the core and the polysiloxane shell effectively, and TEM characterization confirms that the core and the shell are connected tightly to the composite microspheres.

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