

Preparation of Core–Shell Poly(acrylic acid)/Polystyrene/SiO₂ Hybrid Microspheres

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ABSTRACT: Core–shell poly(acrylic acid)/polystyrene/SiO₂ (PAA/PS/SiO₂) hybrid microspheres were prepared by dispersion polymerization with three stages in ethanol and ethyl acetate mixture medium. Using vinyltriethoxysilane (VTEOS) as silane agent, functional silica particles structured vinyl groups on surfaces were prepared by hydrolysis and polycondensation of tetraethoxysilane and VTEOS in core stage. Then, the silica particles were used as seeds to copolymerize with styrene and acrylic acid sequentially in shell stage I and stage II to form PAA/PS/SiO₂ hybrid microspheres. Transmission electron microscope results show that most PAA/PS/SiO₂ hybrid microspheres are about 40 nm in diameter, and the silica cores are about 15 nm in diameter, which covered with a layer of PS about 7.5-nm thick and a layer of PAA about

5-nm thick. This core–shell structure is also conformed by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and differential scanning calorimetry. FTIR results show that silica core, PS shell, and PAA outermost shell are bonded by covalents. In the core–shell PAA/PS/SiO₂ hybrid microsphere, the silica core is rigidity, and the PAA outermost shell is polarity, while the PS layer may work as lubricant owing to its superior processing rheological property in polymer blending. These core–shell PAA/PS/SiO₂ hybrid microspheres have potential as new materials for polar polymer modification. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1729–1733, 2006

Key words: core–shell; poly(acrylic acid)/polystyrene/SiO₂; hybrid microsphere; preparation; dispersion polymerization

INTRODUCTION

Core–shell synthesis particles with a silica shell and a core of different materials was patented by Iler in 1959.¹ Recently, micro- and nanocomposites with core–shell structure have been drawing much interest because they always exhibit improved physical and chemical properties over their single-component counterparts.^{2–6}

Core–shell composites have in general been prepared by emulsion, and dispersion polymerization techniques. Ding et al.⁷ reported the synthesis of monodisperse polystyrene/SiO₂ composite particles (PSCPs) with core–shell structure by *in situ* emulsion polymerization of styrene on the surface of grafted silica nanoparticles. Zhang et al.⁸ succeeded in preparing core–shell PSCPs by emulsion polymerization using silica nanoparticles grafted by methacryloxypropyltrimethoxysilane (MPTMS) as seeds. Gu et al.⁹ proposed a method for producing core–shell MPTMS in water–ethanol media with an anionic monomer, sodium *p*-styrenesulfonate, using the MPTMS to introduce vinyl groups onto silica nanoparticles. Bourgeat-

Lami and Lang^{10,11} had prepared core–shell PSCPs by the nonaqueous dispersion polymerization in alcoholic media using the 3-(trimethoxysilyl) propylmethacrylate as coupling agent. Moreover, Fleming et al.⁵ had prepared core–shell PSCPs by colloidal assembling PS nanospheres onto silica microspheres. Cho et al.¹² reported the synthesis of a core–shell type resins with a highly crosslinked PS core and a poly(ethylene glycol) shell by suspension polymerization for use in solid-phase synthesis.

Described in this work is the preparation of core–shell poly(acrylic acid)/polystyrene/SiO₂ (PAA/PS/SiO₂) hybrid microspheres in three stages by dispersion polymerization. A common silane agent, vinyltriethoxysilane (VTEOS), was used to synthesize functional silica particles structured vinyl groups on surfaces in core stage. Then, the functional silica particles were used as seeds to copolymerize with styrene and acrylic acid sequentially in shell stage I and stage II to form PAA/PS/SiO₂ hybrid microspheres. In the core–shell structure, the silica core is rigidity, and the PAA outermost shell is polarity, while the PS layer may work as lubricant owing to its superior processing rheological property in polymer blending, which can improve the flowability of blend. These core–shell PAA/PS/SiO₂ hybrid microspheres have potential as new materials for polar polymer modification.

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TABLE I
Ingredients and Conditions for the Synthesis of Functional Silica Particles (Core Stage)

Tetraethoxysilane (g)	20.8
Vinyltriethoxysilano (g)	19
Deionized water (g)	5.4
Ethanol (mL)	40
Catalyst (HCl, 37%)	0.1
Temperature (°C)	50
Stirring rate (rpm)	300
Reaction method	Water batch

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTEOS) JS-A151 is obtained from Shanghai Jinshan Chemical Co., Ltd. Styrene (Shanghai Lingfeng Chemical Reagent Co., Ltd.) and acrylic acid (Shanghai Reagent Co., Ltd.) are distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Benzoyl peroxide (BPO) used as initiator is purchased from Shandong Laiwu Meixing Chemical Co., Ltd., Shandong province, China.

Sample preparation

Functional silica particles (core stage)

As seen in Table I, the functional silica particles used as seeds were synthesized. With HCl as catalyst, the hydrolysis and polycondensation of TEOS and VTEOS were conducted in ethanol at 50°C in a 250-mL four-necked round-bottomed flask for 4 h. The stirring rate was controlled and kept at 300 rpm. The reaction system was heated in a water bath at the temperature of reaction.

Active core-shell ps/SiO₂ hybrid microspheres (shell stage I)

As shown in Table II, the functional silica particles were used as seeds to copolymerize with styrene to form active PS/SiO₂ hybrid microspheres. While ethyl acetate and BPO were added in the above reactor, nitrogen was bubbled through the reaction mixture and the temperature was raised and kept at 80°C. Under the protection of nitrogen, styrene was dropped in. Two hours later, active core-shell PS/SiO₂ hybrid microspheres were obtained.

TABLE II
Ingredients and Conditions for the Synthesis of Active Core-Shell PS/SiO₂ Hybrid Microspheres (Shell Stage I)

Functional silica particles dispersion solution (g)	73.3
Styrene (g)	20.8
Ethyl acetate (mL)	40
Initiator (BPO, g)	1.0
Temperature (°C)	80
Stirring rate (rpm)	300
Reaction method	Water batch

TABLE III
Ingredients and Conditions for the Synthesis of Core-Shell PAA/PS/SiO₂ Hybrid Microspheres (Shell Stage II)

Active core-shell PS/SiO ₂ hybrid microspheres dispersion solution (g)	131.1
Acrylic acid	14.4
Temperature (°C)	80
Initiator (BPO, g)	0.5
Stirring rate (rpm)	300
Reaction method	Water batch

Core-shell PAA/PS/SiO₂ hybrid microspheres (shell stage II)

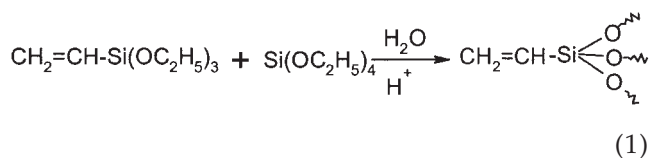
As shown in Table III, the active PS/SiO₂ hybrid microspheres were copolymerized with acrylic acid to synthesize core-shell PAA/PS/SiO₂ hybrid microspheres. After another BPO was added in the above reactor, acrylic acid was added in and polymerized for 4 h. Then the organic solvents were removed by evaporation under vacuum. When the organic solvents evaporated completely, the core-shell PAA/PS/SiO₂ hybrid microspheres were obtained.

Transmission electron microscope (TEM) photographs were taken on a JEM-100SX transmission electron microscope. Fourier transform infrared spectroscopy (FTIR) spectra were measured with Nicolet Nexus-870 spectrometer, using KBr pellets. X-ray photoelectron spectroscopy (XPS) was performed using MgK α radiation from a VG ESCALAB MKII X-ray photoelectron spectrometer. Differential scanning calorimetry (DSC) was conducted with a Mettler Toledo DSC-821E at a scanning rate of 10°C/min, under nitrogen atmosphere at a flow of 80 mL/min.

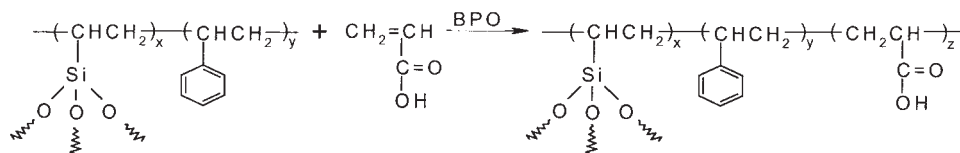
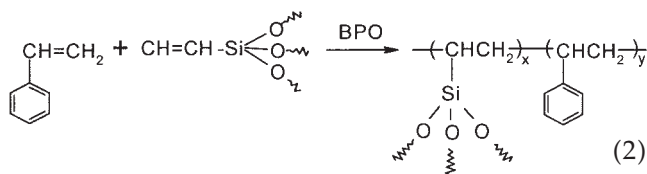
RESULTS AND DISCUSSION

Formation mechanism of core-shell PAA/PS/SiO₂ hybrid microspheres

In core stage, with HCl as catalyst, the functional silica particles were prepared by the hydrolysis and polycondensation of TEOS and VTEOS in ethanol as follows:



In shell stage I, in the presence of BPO initiator, the functional silica particles structured with vinyl groups were used as seeds to copolymerize with styrene to form active PS/SiO₂ hybrid microspheres in ethanol and ethyl acetate mixture medium, and the main reaction equation was as given below



Morphology of microspheres

Figure 1(a,b) show TEM photographs of active PS/SiO₂ hybrid microspheres and PAA/PS/SiO₂ hybrid microspheres respectively. It can be seen from Figure 1(a) that most of the active PS/SiO₂ hybrid microspheres sized 30 nm in diameter have been formed in shell stage I, and the silica cores are about 15 nm in diameter, which covered with a layer of PS shell about 7.5-nm thick. In Figure 1(b), we found when the active PS/SiO₂ hybrid microspheres were copolymerized with acrylic in shell stage II, most PS/SiO₂ hybrid microspheres were covered with a layer of PAA about 5-nm thick, and the size of most PAA/PS/SiO₂ hybrid microspheres increased to about 40 nm in diameter. It could be PAA that may be formed as homopolymer *in situ* that could act as stabilizer for the dispersion polymerization.

FTIR analysis

Figure 2(a–c) are the FTIR spectra of functional silica particles, active PS/SiO₂ hybrid microspheres, and PAA/PS/SiO₂ hybrid microspheres respectively. In Figure 2(a), the characteristic peaks for formation of Si—O—Si bands: $\nu_{\text{Si—O—Si}}$ at 1145 and 1078 cm⁻¹(broad), and $\delta_{\text{Si—O—Si}}$ at 606 cm⁻¹ respectively, are found. Besides these characteristic peaks for the inorganic silica particles, the presence of vinyl groups connected to silicon atoms are found by identification of absorption bands: ν_{asCH_2} at 3060 cm⁻¹, ν_{aCH_2} at 2982 cm⁻¹, ν_{CH} at 2958 cm⁻¹, $\nu_{\text{C=C}}$ at 1600 cm⁻¹, ω_{CH_2} or CH at 968 cm⁻¹, and δ_{CH} at 547 cm⁻¹ respectively. This fact confirmed that the functional silica particles structured vinyl groups on surfaces shown as eq. 1 had been formed in core stage.

In the case of the FTIR spectrum of active PS/SiO₂ hybrid microspheres presented in Figure 3(b), besides the absorption bands characteristic for Si—O—Si, the presence of benzene identified for the following characteristic vibrations are presented: $\nu_{\text{C=C}}$ at 1600, 1500, and 1447 cm⁻¹. Moreover, comparing with Figure 2(a), the intensities of characteristic peaks for vinyl

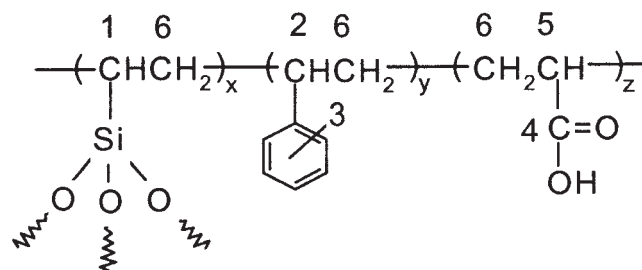
In shell stage II, in the presence of BPO initiator, the active PS/SiO₂ hybrid microspheres were copolymerized with acrylic acid, shown as eq. 3, to form core-shell PAA/PS/SiO₂ hybrid microspheres.

groups have decreased. This can be explained that styrene has been copolymerized with the vinyl groups structured on the functional silica particles and polymerized partially in shell stage I. It was confirmed that the silica core and PS shell are bonded by covalent bonds, and the PS/SiO₂ hybrid microspheres are still active because of the active free radicals shown as eq. 2.

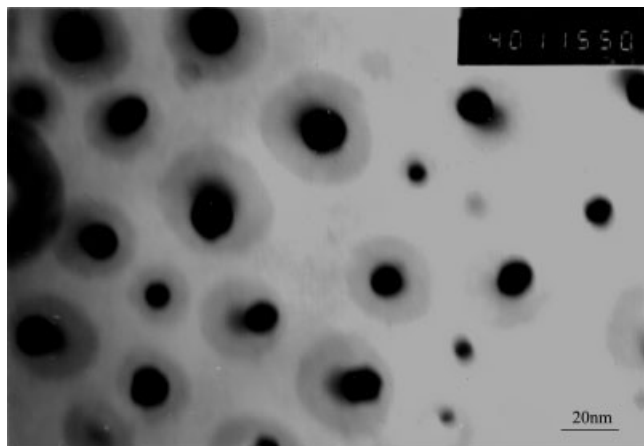
In the case of the FTIR spectrum of PAA/PS/SiO₂ hybrid microspheres presented in Figure 2(c), besides the absorption bands characteristic for Si—O—Si and benzene, the presence of carbonyl identified for $\nu_{\text{C=O}}$ at 1736 cm⁻¹ is presented. Comparing with Figure 2(b), the intensity of $\nu_{\text{C=C}}$ at 1600 cm⁻¹ is nearly unchanged. This fact confirmed that the active PS/SiO₂ hybrid microspheres were copolymerized with acrylic in shell stage II and formed PAA outermost shell. Based on FTIR analysis results, we deduce that the silica core, PS shell, and PAA outermost shell are bonded by covalents shown as eq. 3.

XPS analysis

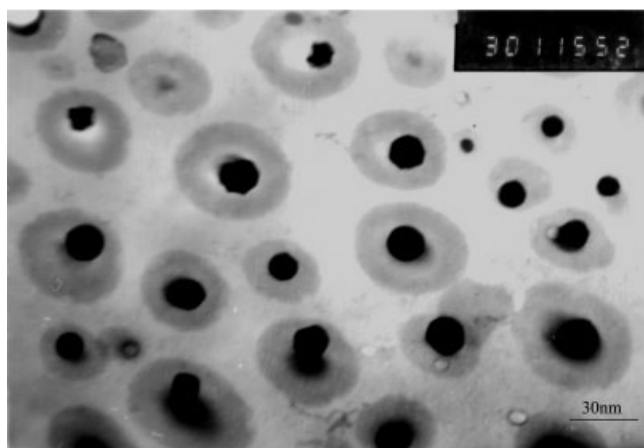
Figure 3 is XPS full-scan spectrum of PAA/PS/SiO₂ hybrid microspheres. In Figure 3, the peaks Si2p, C1s, and O1s are at 102.80, 285.15, and 532.60 eV respectively. When the peak C1s was fitted, six peaks at 284.33, 284.60, 284.67, 288.85, 285.95, and 287.15 eV were obtained as shown in Figure 4, corresponding to six different carbons (C1~C6) in PASHs molecular structure as shown below:



Peak C1 conforms the formation of silica core. Peaks C2, C3, and C6 signify the synthesis of active PS/SiO₂



(a)



(b)

Figure 1 TEM photographs of samples (a, active PS/SiO₂ hybrid microspheres; b, PAA/PS/SiO₂ hybrid microspheres).

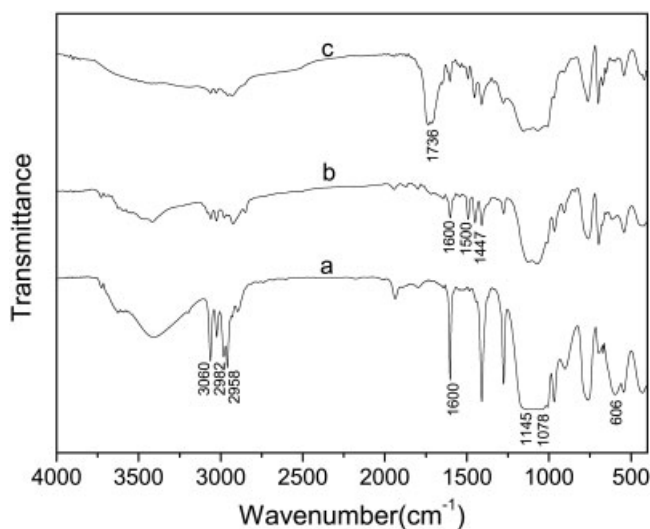


Figure 2 FTIR spectra of samples (a, functional silica particles; b, active PS/SiO₂ hybrid microspheres; c, PAA/PS/SiO₂ hybrid microspheres).

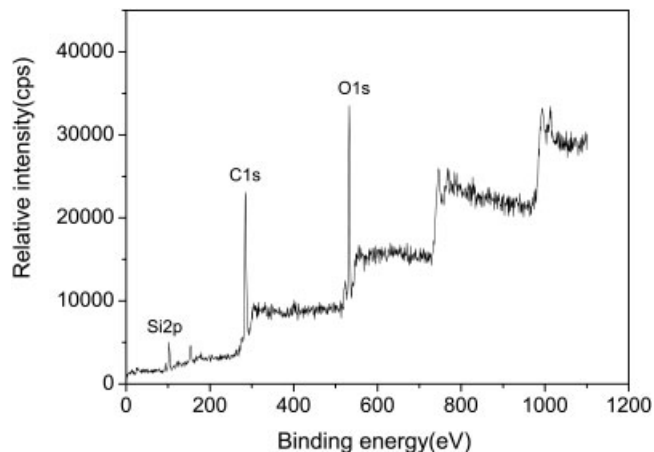


Figure 3 XPS full-scan spectrum of PAA/PS/SiO₂ hybrid microspheres.

hybrid microspheres in shell stage I that styrene has been copolymerized with the vinyl groups structured on the surface of functional silica particles. While Peaks C4, C5, and C6 imply that the active PS/SiO₂ hybrid microspheres has been copolymerized with acrylic and formed PAA outermost shell in shell stage II. As shown in Table IV, the composition of PAA/PS/SiO₂ hybrid microspheres in at. % is C61.34, O29.99, and Si8.67; moreover, C/Si and C/O ratios are of 7.08 and 3.46 respectively.

DSC analysis

Figure 5(a,b) is the DSC heating scans of PS/SiO₂ and PAA/PS/SiO₂ hybrid microspheres respectively. An endothermic peak at about 420°C, corresponding to the melting of PS/SiO₂ hybrid microspheres, was observed in Figure 5(a). While in Figure 5(b), two endothermic peaks were found. Comparing with Figure 5(a), we de-

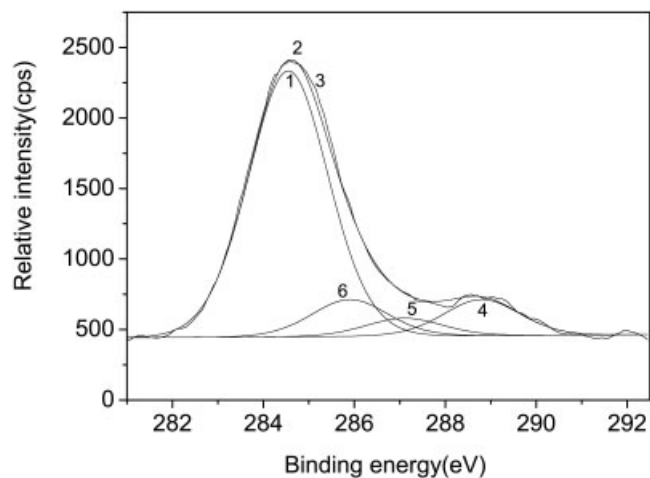


Figure 4 Curve-fitted XPS C1s spectrum of PAA/PS/SiO₂ hybrid microspheres.

duce that the peak about 406°C corresponds to the melting of the copolymer resulted from the styrene copolymerized with the vinyl groups on the functional silica surfaces, another broad peak at about 258°C may correspond to the melting process of PAA, PS, and the acrylic acid and styrene copolymer. These facts agree well with the conclusions drawn from TEM, FTIR, and XPS analysis. Besides these information, when the temperature is above 420°C, the PAA/PS/SiO₂ hybrid microspheres begin to decompose.

CONCLUSIONS

Core-shell PAA/PS/SiO₂ hybrid microspheres were prepared by dispersion polymerization in ethanol and ethyl acetate mixture medium in three stages. The functional silica cores, active PS/SiO₂ hybrid microspheres, and PAA/PS/SiO₂ hybrid microspheres were prepared in core stage, shell stage I, and shell stage II respectively. Most PAA/PS/SiO₂ hybrid microspheres are composed of silica cores about 15 nm in diameter, a layer of PS shell about 7.5-nm thick, and a layer of PAA outermost shell about 5-nm thick. Moreover, the silica core, PS shell, and PAA outermost shell are bonded by covalents.

TABLE IV
Composition of PAA/PS/SiO₂ Hybrid Microsphere as Determined by XPS

Sample	Concentration (at %)			Atomic ratio	
	C	O	Si	C/Si	O/Si
PAA/PS/SiO ₂ hybrid microsphere	61.34	29.99	8.67	7.08	3.46

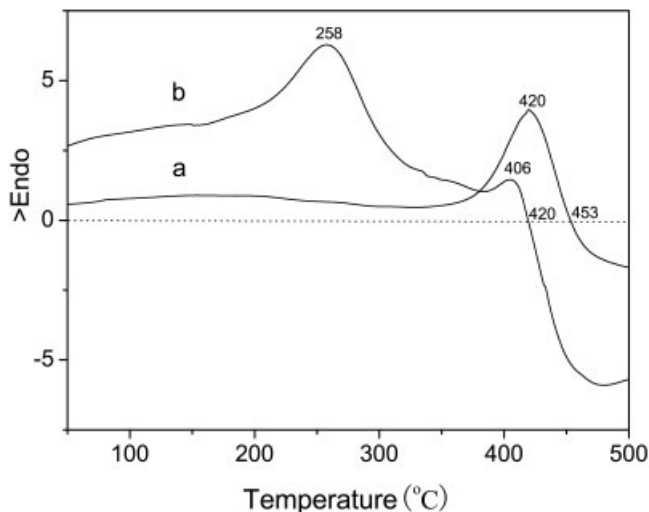


Figure 5 DSC heating scan of samples (a, PS/SiO₂ hybrid microspheres; b, PAA/PS/SiO₂ hybrid microspheres).

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