

Polystyrene/nano-SiO₂ composite microspheres fabricated by Pickering emulsion polymerization: Preparation, mechanisms and thermal properties

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Abstract. We report the preparation, mechanisms and thermal properties of core-shell structured polymer/inorganic nanoparticle composite microspheres prepared by Pickering emulsion polymerization. Stable Pickering emulsion was firstly fabricated by using surface-modified nano-SiO₂ particles as stabilizer. And then, two kinds of polystyrene/nano-SiO₂ (PS/SiO₂) composite microspheres with different sizes and morphologies were synthesized using hydrophobic azobisisobutyronitrile (AIBN) and hydrophilic ammonium persulfate (APS) as initiator, respectively. The possible mechanisms of Pickering emulsion polymerization initiated by different initiators were proposed according to the results of transmission electron microscope (TEM) and scanning electron microscope (SEM). The chemical structure and molecular weight of the composite microspheres were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD) and gel permeation chromatography coupled with a multi-angle laser light scattering photometer (GPC-MALLS). Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were used to comparatively analyze the thermal properties of nanocomposites and corresponding pure polymer. The results indicated that the decomposition temperature and glass transition temperature (T_g) of nanocomposites were elevated to a certain degree due to the existence of nano-SiO₂.

Keywords: nanocomposites, Pickering emulsion polymerization, mechanism, thermal properties

1. Introduction

Organic/inorganic nanocomposite microspheres have attracted increasing attention because of their unique properties emerging from the combination of the advantageous properties of inorganic nanoparticles and polymers. In comparison with the pure polymers or their traditional composites, the resultant nanocomposites exhibit many markedly improved properties such as increased modulus and strength, enhanced barrier properties, improved heat resistance and decreased flammability [1, 2]. Therefore, the nanocomposite microspheres have been widely used in the various fields such as safety, protective

garments, aerospace, electronics and optical devices [3, 4].

Generally, organic/inorganic nanocomposite microspheres can be prepared by many methods such as miniemulsion polymerization [5], soap-free emulsion polymerization [6], seeded emulsion polymerization [7] and dispersion polymerization [8], etc. The composite microspheres with inorganic core and polymer shell are mostly fabricated by these conventional methods. In recent years, self-assembly of ultrafine solid particles at the oil/water interface to stabilize so-called Pickering emulsion has been well documented and offers a straightforward

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pathway for the production of organic/inorganic nanocomposite microspheres [9–12]. In Pickering emulsions, solid nanoparticles possessing intermediate wettability are added as both a component and a stabilizer during the polymerization process. There is no need to use conventional low-molecular-weight surfactants. There are also no by-products produced in the process, and no unwanted contaminants are left in the polymer [13]. In contrast to the often reported core-shell structure in which inorganic particles serve as the core and polymer serves as the shell, the nanocomposite microspheres fabricated by Pickering emulsion polymerization has a polymer core and the nanoparticles shell. Such materials provide a new class of supramolecular building blocks and are likely to exhibit unusual, possibly unique properties [14].

So far, the preparation and forming principle of Pickering emulsion have been well documented by Binks and coworkers [15–17], Midmore [18], and Bon and coworkers [19, 20]. Moreover, a series of nanocomposite microspheres have been prepared. Bon and Colver [21] reported the fabrication of a variety of armored latex by Pickering miniemulsion polymerizations using Laponite clay discs as stabilizer. Zaragoza-Contreras *et al.* [22] described the synthesis of carbon black/polystyrene conductive nanocomposite by Pickering suspension polymerization technique. Zhang *et al.* [23] have prepared Poly(N-isopropylacrylamide)/poly(methyl methacrylate)/silica hybrid capsules via inverse Pickering emulsion polymerization. However, the suggested mechanisms of Pickering emulsion polymerization in these papers are preliminary. And, most of the mechanisms research only focused on the case in which monomer and initiator were in the same phase. Additionally, the thermal properties of the resultant composites have seldom been systematic studied. However, the evaluation of the thermal stability and degradation behaviors of composites is an effective method to verify synergistic effects between polymer and inorganic particles, and useful to modify the composites for further application. Herein, two kinds of polystyrene/nano-SiO₂ composite microspheres with core-shell structure were prepared by Pickering emulsion polymerization. The possible mechanisms of Pickering emulsion polymerization initiated by hydrophobic azobisisobutyronitrile (AIBN) and hydrophilic ammo-

nium persulfate (APS) were discussed, respectively. The chemical structure and molecular weight of the product were characterized by FTIR, XRD and GPC-MALLS. At last, the influences of nanoparticles on the decomposition temperature and on the glass transition temperature (T_g) of the resultant nanocomposite microspheres were systematically studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Materials

Dodecyltrimethoxysilane (WD-10) was obtained from Wuhan University Silicone New Material Co. Ltd (China). Styrene, azobisisobutyronitrile (AIBN) and ammonium persulfate (APS) were purchased from Tianjin Chemical Reagent Corporation (China). Tetraethylorthosilicate (TEOS), methanol, ammonium hydroxide (NH₃ 25%) were all analytical reactant grade and were supplied by Xi'an Chemical Reagent Co. Ltd (China). Styrene was distilled under reduced pressure before use and the other reagents were used as received. Deionized water was used throughout the experiments.

2.2. Characterization

Laser particle size analyzer (Malvern Zetasizer Nano ZS3600) was used to obtain the average particle size and particle size distribution of the nano-SiO₂ before and after modification. The morphology and size of the composite microspheres were observed by TEM (JEM-3010, Japan) and SEM (JSM6380, Japan). FTIR spectra were obtained by a FTIR spectrometer (Nicolet is10, USA) in range of 4000–400 cm⁻¹. The samples were prepared into KBr pellets. X-ray diffraction (XRD) analysis was carried out with a Rigaku D/max-IIIc X-ray diffractometer with graphite monochromatized Cu-K α radiation ($\lambda = 0.1548$ nm), the scan rate of 4°/min allowed to record the patterns in the 2θ range of 10–60°. The molecular weight and molecular weight distribution of the resultant polystyrene (PS) after eliminating SiO₂ nanoparticles was measured by gel permeation chromatography coupled with a multi angle laser light scattering photometer (GPC-MALLS) with a Wyatt GPC instrument. The column temperature was 40°C and the chromatographic grade dimethylformamide (DMF) was used as solvent. TGA was performed with a thermal

analysis instrument (TA Q50, USA) under nitrogen gas. The flow rate was 40 cm³/min and heating rate was 20°C/min. DSC (TA 2910, USA) was used to obtain the glass transition temperature (T_g) of the products. The sample was first heated from 20 to 140°C with the scan rate of 20°C/min to remove thermal history. T_g is obtained by the second scanning from 20 to 140°C with the scan rate of 10°C/min.

2.3. Preparation and modification of silica nanoparticles

Silica nanoparticles were prepared via an improved Stöber method as follows [24]. To a round-bottom flask of 500 mL capacity were added 10 mL TEOS and 100 mL methanol under sonication. After 5 min, 20 mL of 25% ammonium hydroxide and 200 mL of methanol were added into the reaction mixture synchronously. Sonication was continued for a further 3 h to get a bluish translucent nano-SiO₂ colloidal solution. Circulating water was used to maintain the temperature of the sonication bath below 30°C.

The hydrophilic nano-SiO₂ was hydrophobically modified with dodecyltrimethoxysilane (WD-10) to attach long chain alkyl on the surface and reduce the surface density of silanol groups. WD-10 (0.1 mL) was added to 100 mL of silica dispersion and the solution was refluxed at 80°C for 3 h. Before adding WD-10, the pH of the colloidal solution was adjusted to pH 7 with acetic acid under stirring conditions. After reaction, the reaction mixture was centrifuged (15 000 rpm, 15 min) and washed by repeating redispersion in anhydrous ethanol at least three times. The modified silica particles were collected and dried under vacuum at 40°C for 8 h.

2.4. Preparation of PS/nano-SiO₂ composite microspheres by Pickering emulsion polymerization

A representative preparation procedure was as follows. A given mass of modified nano-SiO₂ particles were ultrasonically dispersed into water for 15 min. For AIBN used as initiator, AIBN was dissolved in

styrene to form oil phase, and subsequently the oil phase was mixed with the nano-SiO₂ dispersions. A stable Pickering emulsion was generated using KUSON 500 W digital sonifier for 2 min at 80% amplitude. The resulted Pickering emulsion was poured into a 100 mL three-neck flask equipped with a nitrogen inlet and a reflux condenser. The emulsion was agitated mildly (200 rpm) and polymerized under nitrogen atmosphere at 75°C for 12 h. The precipitates after filtration were washed with water and ethanol for three times, respectively. The collected product was dried at 30°C under vacuum for 4 h and referred to as composite microspheres I. As for APS system, APS was dissolved in modified nano-SiO₂ dispersions to form water phase. Then styrene monomer was added into water phase and Pickering emulsion was generated by ultrasonic emulsification. The subsequent procedures were the same as AIBN system. The product was referred to as composite microspheres II. The compositions of recipe to prepare two kinds of polystyrene/nano-SiO₂ composite microspheres were listed in Table 1.

3. Results and discussion

3.1. Formation of Pickering emulsions stabilized by surface-modified nano-SiO₂

The sizes of nano-SiO₂ before and after modification using the laser particle size analyzer are shown in Figure 1. Obviously, the particle size and poly-

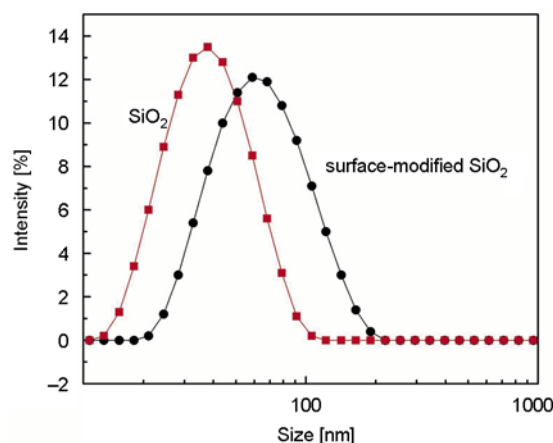


Figure 1. Results of particle size and particle size distribution of nano-SiO₂ and surface-modified nano-SiO₂

Table 1. Recipe to prepare polystyrene/nano-SiO₂ composite microspheres

Sample	Styrene monomer [mL]	Initiator	Initiator dosage [mg]	Surface-modified SiO ₂ [g]	Pure water [mL]
I	2	AIBN	12	0.2	20
II	2	APS	12	0.2	20

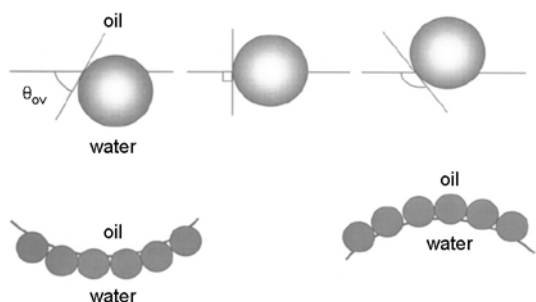


Figure 2. Schematic diagram of the relationship between three-phase contact angle and emulsion types [26]

dispersity index of modified nano-SiO₂ (z-average: 57.7 nm, PDI: 0.153) are larger than that of original nano-SiO₂ (z-average: 34.9 nm, PDI: 0.128). It may be ascribed to the agglomeration of nano-SiO₂ caused by some operating procedures such as pH adjusting, heating reflux reaction and high speed centrifugation in the entire process of surface modification [25].

The research results of Binks and Lumsdon [15] and Aveyard *et al.* [26] indicated that the type and stability of Pickering emulsion were determined mostly by the wettability (often expressed as a contact angle θ at the three-phase boundary) of ultra-fine particles. As is shown in Figure 2, for

hydrophilic particles, θ measured into the aqueous phase is normally smaller than 90° and a larger fraction of the particle surface resides in water than in oil. For hydrophobic particles, θ is generally greater than 90° and the particle resides more in oil than in water. Thus, the monolayers of hydrophilic particles will curve and tend to form oil-in-water (O/W) emulsions whereas hydrophobic particles form water-in-oil (W/O) emulsions. For $\theta = 90^\circ$, it means that a particle is amphiphilic and the ability of stabilizing emulsions is the most powerful.

In general, it is difficult to measure the contact angle of individual particles when their primary particle sizes are below 100 nm. The three-phase contact angle of the nanoparticles could be measured using the compressed disk method reported by Yan *et al.* [27] and Kostakis *et al.* [28]. As shown in Figure 3a, the three-phase contact angle of pure SiO₂ is about 35°, meaning that the surfaces of them are more hydrophilic. While the θ of modified nano-SiO₂ particles is nearly 90° (Figure 3b), implying that the surface of modified SiO₂ should be amphiphilic. In order to confirm the surface wettability, the behavior of modified nano-SiO₂ suspended in a toluene/ water dual-phase mixture was observed. As shown in Figure 4a, modified nano-

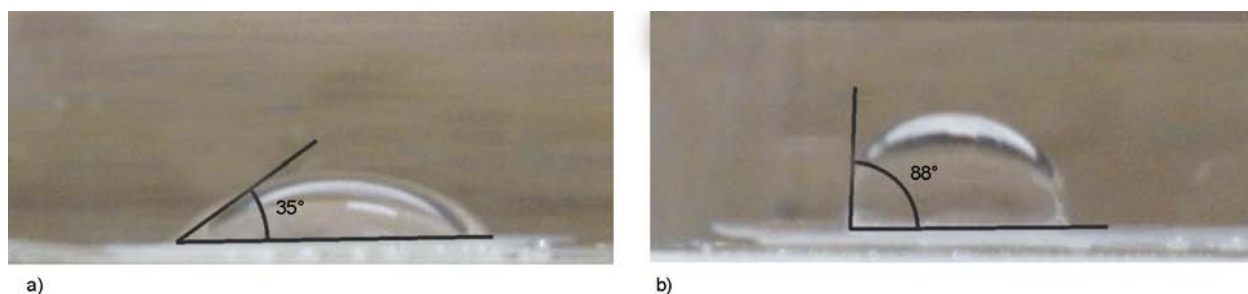


Figure 3. Three-phase contact angle determination photographs of pure SiO₂ (a) and modified SiO₂ (b)

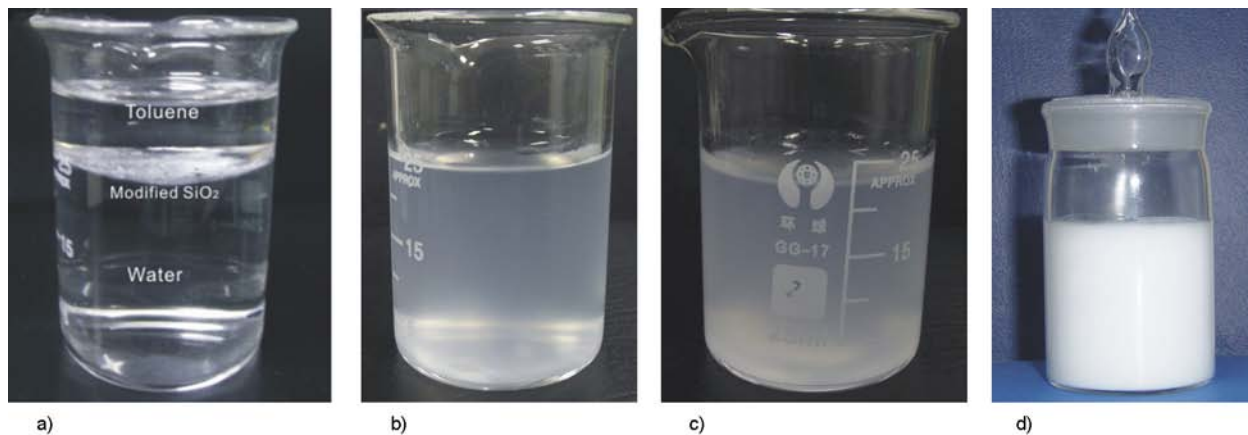


Figure 4. Digital photographs of distribution in toluene-water interface of modified nano-SiO₂ (a), aqueous modified nano-SiO₂ dispersions (b), dispersions of modified nano-SiO₂ in toluene (c) and O/W Pickering emulsion (d)

SiO₂ spread out and assemble spontaneously at the toluene-water interface. The subsequent dispersibility results demonstrate that the modified SiO₂ can easily disperse in both water and oily solvent such as benzene, toluene or liquid paraffin at nano-scale under ultrasonic conditions (Figure 4b and 4c). Based on the obvious amphipathic character, a stable O/W Pickering emulsion should be certainly obtained using this modified nano-SiO₂ as stabilizer (Figure 4d).

3.2. Mechanism analysis of PS/SiO₂ composite microspheres prepared by Pickering emulsion polymerization initiated by different initiators

The mechanism of conventional emulsion polymerization stabilized by surfactants has been discussed for several decades and some consensus has been reached [29–31]. That is, depending on the recipes and reaction conditions, one or more particle nucleation mechanisms, such as micelle nucleation, homo-

geneous nucleation and monomer droplet nucleation, are operative in emulsion polymerization [32]. Based on the fundamental understandings in conventional emulsion polymerization and taking into account the differences between modified nanoparticles and surfactant molecules, the possible Pickering emulsion polymerization mechanisms were studied by using oil-soluble AIBN and water-soluble APS as initiator respectively. Since the nanoparticles do not form micelles like surfactant molecules, micelle nucleation is excluded. Thus, there are two possible nucleation mechanisms involved. On the one hand, AIBN was used as the initiator in the initial stage of Pickering emulsion polymerization. Figure 5 shows the TEM (Figure 5a) and SEM (Figure 5b) images of composite microspheres I. It is clearly visible that the surfaces of polystyrene particles are covered with a dense layer of nano-SiO₂. The microspheres are between 0.5~2.0 μm in diameter and the surfaces of them are rough. These observations suggest that the Pickering emulsion

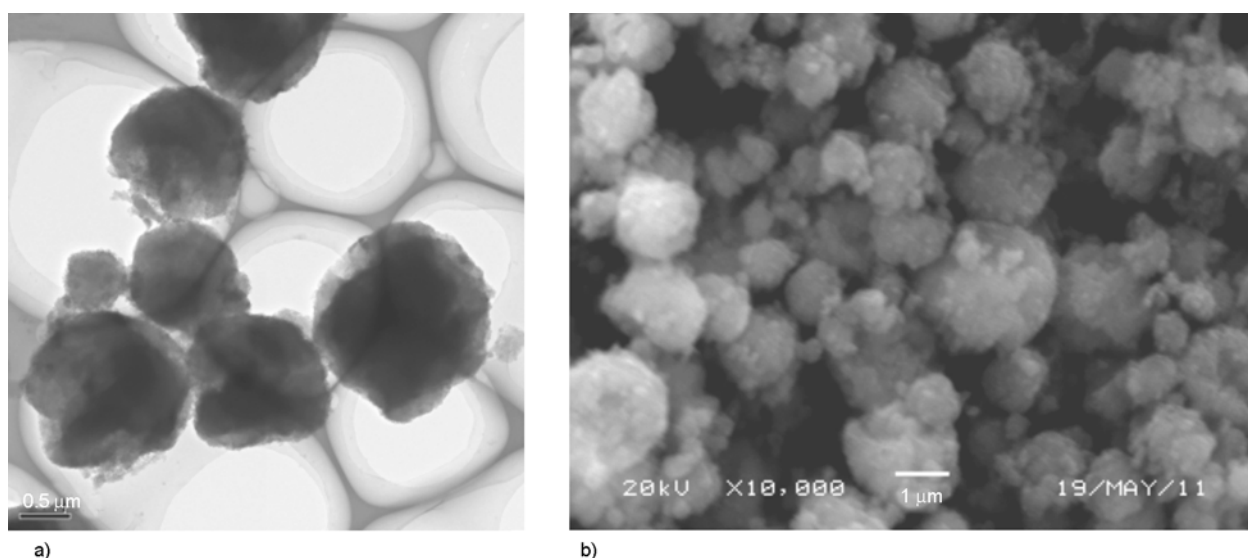


Figure 5. TEM image (a) and SEM image (b) of PS/SiO₂ composite microspheres I

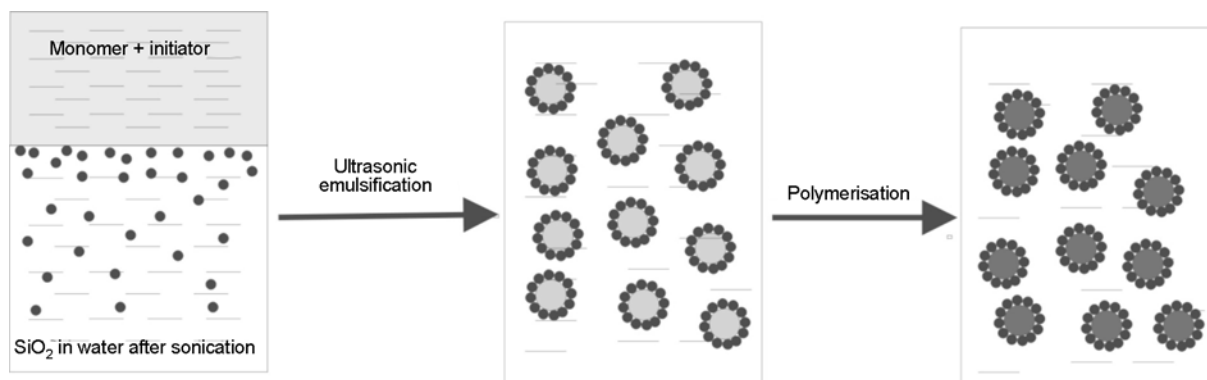


Figure 6. Schematic of the fabrication of composite microspheres I

polymerization using AIBN as the initiator mainly obeys the monomer droplet nucleation mechanism [33, 34]. Figure 6 shows the suggested formation mechanism of composite microspheres I. After being treated by ultrasound, nano-SiO₂ particles self-assemble at the O/W interface and act as effective stabilizers to generate O/W type Pickering emulsion droplets. Based on the hydrophobicity of AIBN, the polymerization reaction occurs mainly in inner oil phase composed of styrene monomer and AIBN. The silica nanoparticles initially adsorbed at droplet interfaces still remain at the interface during the polymerization as the droplets solidify, which could lead to high silica coverage of these composite microspheres, resulting in the compact core-shell morphology.

On the other hand, when the initiator was changed into hydrophilic APS, totally different results were observed. The TEM and SEM images of the composite microspheres II are shown in Figure 7a and Figure 7b, respectively. The diameters of the microspheres are sub-micron-sized (0.1~0.5 μm) and

smaller than those of composite microspheres I. It can be seen that a small amount of nano-SiO₂ are loosely located at the outside surfaces of polystyrene microspheres. For APS initiation Pickering emulsion system, initiator and monomer exist separately in water and oil phase, the homogeneous coagulative nucleation is likely to be the dominating mechanism. Figure 8 shows the possible formation mechanism of composite microspheres II. Upon APS decomposition, free radicals form in the aqueous phase, a small quantity of styrene monomers which dissolve in the water react with the decomposed initiator and form primary polymer chain, i. e. oligomers. After the growing oligomers reach a critical length, they are no longer dissolved in water, but coagulate to form nuclei and further grow into monomer swollen primary particles. With the continuous supply of styrene molecules from the monomer droplets through diffusion, the particles could grow either via swelling of particles by monomers or deposition of oligomers onto their surfaces. After the exhaustion of monomers in the

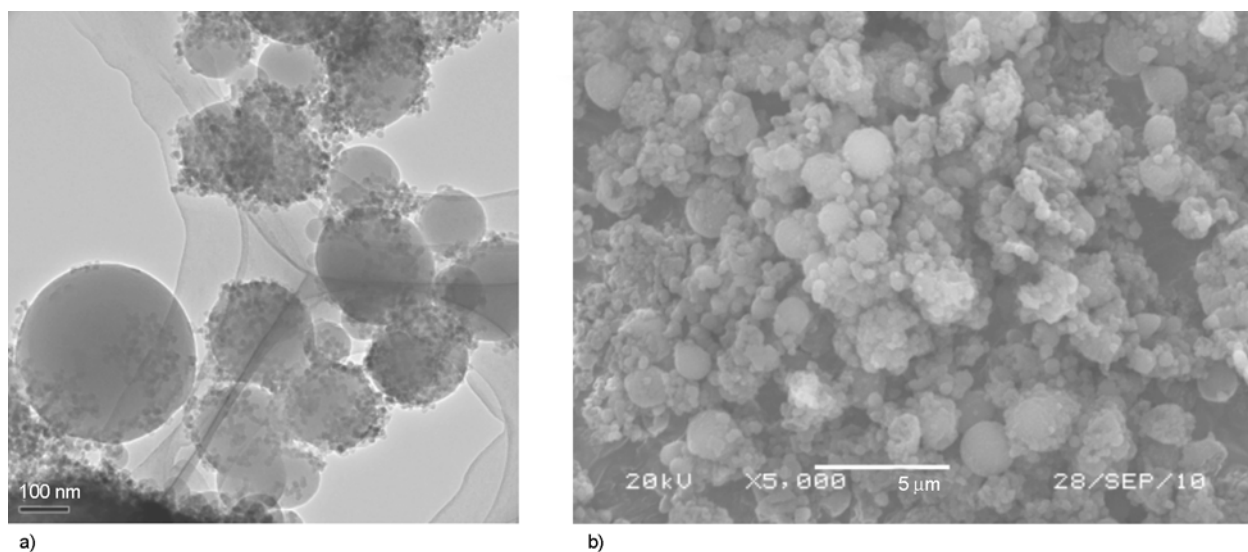


Figure 7. TEM image (a) and SEM image (b) of PS/SiO₂ composite microspheres II

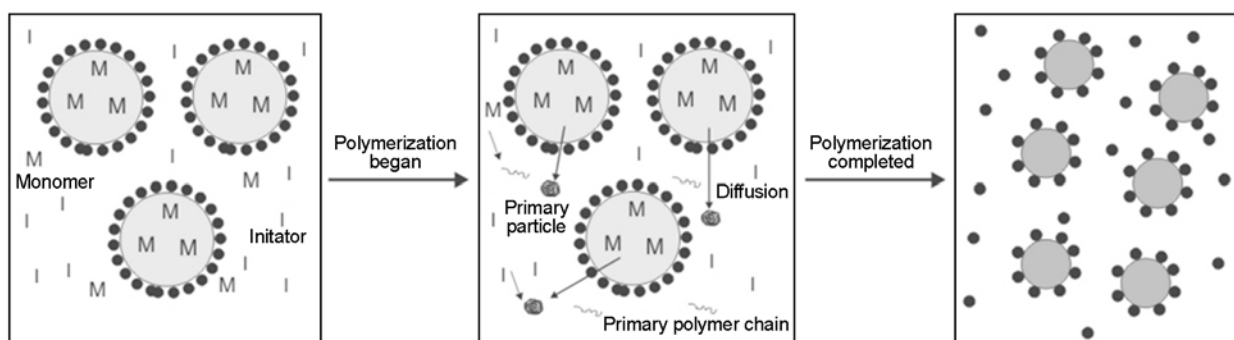


Figure 8. Illustration of the fabrication of composite microspheres II

droplets, the nano-SiO₂ initially adsorbed at droplets interfaces might re-disperse in the aqueous phase gradually, and some of them would self-assemble at the surfaces of the newly created polystyrene microspheres. However, it is likely due to the steric hindrance of nanoparticles or the repulsive interaction between the anionic initiator residues and the negatively charged nano-SiO₂ [35], the polystyrene microspheres are barely covered with silica nanoparticles and show loose core-shell morphology.

3.3. Characterization on the structure of PS/SiO₂ composite microspheres

The FTIR spectra of pure PS, modified SiO₂ and two kinds of PS/nano-SiO₂ composite microspheres are shown in Figure 9. In FTIR spectrum of pure PS (Figure 9a), the peak at 699 and 756 cm⁻¹ are attributed to flexural vibrations (δ C–H) of the benzene ring and those at 1453, 1493, and 1602 cm⁻¹ correspond to benzene ring vibrations (ν C–C) of polystyrene. The FTIR spectrum of modified SiO₂ (Figure 9b) shows the typical IR adsorption signal from silica at wave numbers of 472, 803 and 1100 cm⁻¹, which are assigned to the bending vibration, symmetrical and asymmetrical stretching vibrations of Si–O–Si bonds. The absorption peaks at 2927 and 2855 cm⁻¹ correspond to the –CH₂ groups of dodecyltrimethoxysilane, showing that the long chain alkyl has bonded to the surface of nano-SiO₂ particles. In FTIR spectrum of two kinds of PS/nano-SiO₂ composite microspheres (Figure 9c and 9d), all the major characteristic spectral bands of composite are not significantly different from the FTIR spec-

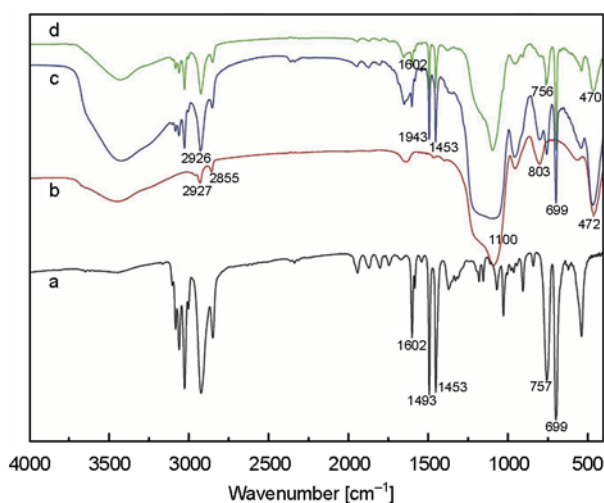


Figure 9. FTIR spectra of pure PS (a), modified SiO₂ (b) and two kinds of PS/nano-SiO₂ composite microspheres (c, d)

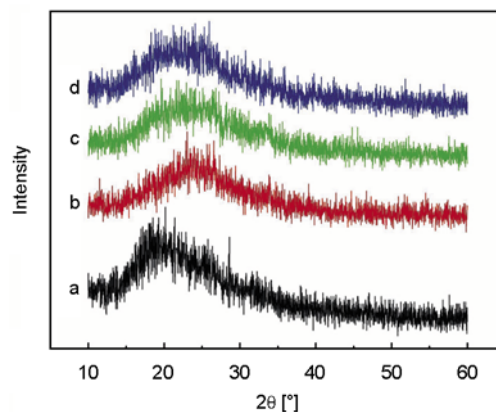


Figure 10. XRD patterns of: (a) PS; (b) nano-SiO₂; (c) PS/SiO₂ composite microspheres I; (d) PS/SiO₂ composite microspheres II

trum of pure PS and modified SiO₂. It indicates that PS/SiO₂ composite was successfully synthesized in this work.

The XRD patterns of the PS, nano-SiO₂ and as-prepared two kinds of composite microspheres are given in Figure 10. The broad non-crystalline diffraction peak at 2θ of about 19° (Figure 10a) corresponds to the amorphous polymer PS [36] and the wide peak at 22–26° (Figure 10b) is assigned to amorphous SiO₂ [37]. In Figure 10c and 10d, it is clearly observed that XRD patterns of two kinds of composite microspheres are more consistent with that of SiO₂ nanoparticles. This means that the main component in the surface of the composite microspheres is SiO₂. The result again confirms the fact that SiO₂ particles are covered on the surface of PS cores and the core-shell structure is successfully formed.

After eliminating nano-SiO₂ located at the surfaces of composite microspheres by hydrofluoric acid

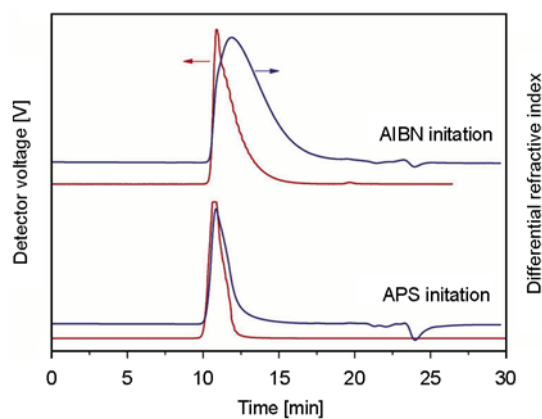


Figure 11. GPC curves of polystyrene prepared by Pickering emulsion polymerization initiated by different initiator

Table 2. Results of molecular weight and polydispersity of PS prepared by Pickering emulsion polymerization initiated by different initiator

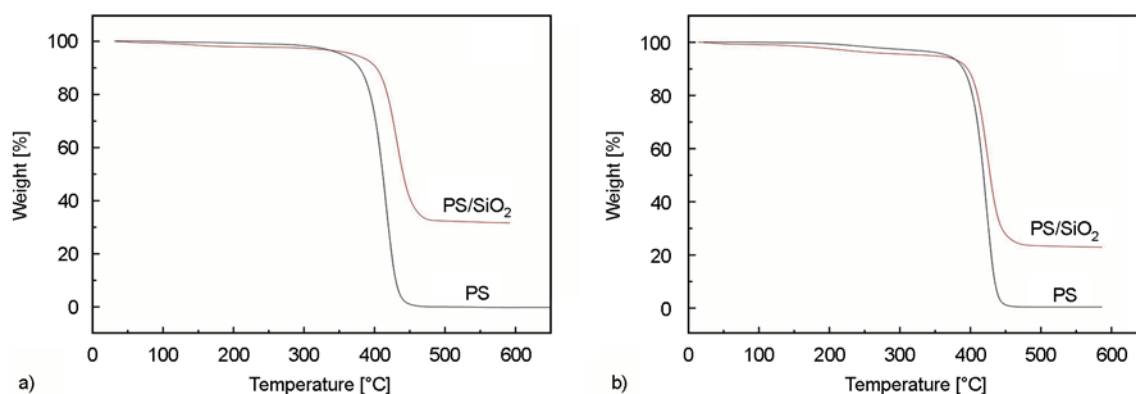
Sample name	Molar mass moments [g/mol]		Polydispersity index
	M_n	M_w	M_w/M_n
AIBN initiation	$2.300 \cdot 10^4$	$4.780 \cdot 10^4$	2.078
APS initiation	$2.215 \cdot 10^5$	$3.411 \cdot 10^5$	1.540

etching, the molecular weight and molecular weight distribution of the resultant PS were characterized by GPC-MALLS. The GPC curves are presented in Figure 11, and the according molecular weight and molecular weight distribution are summarized in Table 2. The results indicate that the molecular weight and molecular-weight distribution of PS using APS as initiator are higher and narrower than that of PS using AIBN as initiator. It can be explained according to the different nucleation mechanism analyzed above. For AIBN initiation system, hydrophobic AIBN and styrene monomer are both in the oil droplets during polymerization process, active chains are easier to terminate with free radicals generated by AIBN, so polystyrene with low molecular weight and broader molecular-weight distribution is obtained. When hydrophilic initiator APS is used, on the contrary, the free radicals generated by APS are captured by the nuclei in the aqueous phase. And they would remain active over a much longer time for the effect of isolation and embedding. In this case, polystyrene of higher molecular weight and narrower molecular weight distribution is synthesized.

3.4. Thermal properties analysis of PS/SiO₂ composite microspheres

The thermal decomposition behaviors of composite microspheres I and II were analyzed by TGA, as

shown in Figure 12a and 12b, respectively. Two samples including the composite microspheres and the corresponding pure PS after removal of the silica component were measured in each group. The results show that both of thermo decomposition temperatures of two composite microspheres are obviously higher than those of corresponding pure PS. This improvement on the thermal stability of composite microspheres is certainly attributed to the protective effect of nano-SiO₂ shell, which restricts the thermal motion of PS chains and shields the degradation of PS in the composite microspheres. Furthermore, there is an evident positive correlation between the content of silica in the composite and thermo decomposing temperatures. As indicated by the Figure 12a, the silica weight content is about 31.6% and the corresponding temperature of the fastest decomposing rate is about 424°C. However, the silica weight content is about 20.1% and the corresponding temperature of the fastest decomposing rate is about 417°C (Figure 12b). DSC curves of the composite microspheres I and II and their corresponding pure PS are shown in Figure 13a and 13b, respectively. Similarly, T_g of two kinds of composite microspheres are higher than those of corresponding pure PS. It is an further evidence that the existence of inorganic shells can contribute to improve the thermal performance of composite microspheres.

**Figure 12.** TGA curves of PS/SiO₂ composite and corresponding pure PS prepared by Pickering emulsion polymerization initiated by AIBN (a) and APS (b)

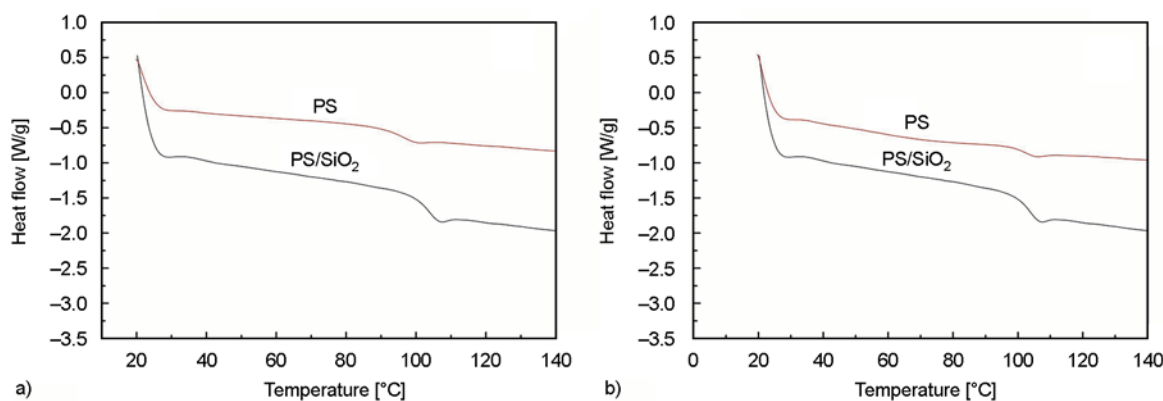


Figure 13. DSC curves of pure PS and PS/SiO₂ composite prepared by Pickering emulsion polymerization initiated by AIBN (a) and APS (b)

4. Conclusions

In conclusion, two kinds of PS/SiO₂ composite microspheres with core-shell structure have been successfully synthesized via Pickering emulsion polymerization using amphiphilic silica nanoparticles as the stabilizers. When hydrophobic AIBN was used as the initiator, the composite microspheres could be micron-sized and high silica coverage. While the sub-micron-sized and barely covered composite microspheres could be obtained by using hydrophilic APS as the initiator. The monomer droplet nucleation was considered as the dominating mechanism in Pickering emulsion polymerization when using AIBN as the initiator, whereas homogeneous coagulative nucleation could be proposed as the polymerization mechanism in the system with APS. TG and DSC analysis suggests that the thermal stability of the composite microspheres is higher than that of the corresponding pure polystyrene.

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