Mechanism of the formation and growth of fine particles clustered polymer microspheres by simple one-step polymerization in aqueous alcohol system

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A B S T R A C T

By using the one-step copolymerization of styrene (St) and 1-vinyl-3-ethylimidazolium bromide (VEIB), fine particles clustered (FPC) poly(St-co-VEIB) microspheres have been successfully prepared in the present of sodium dodecylsulfonate (SDS) in aqueous alcohol system. The FPC poly(St-co-VEIB) microspheres are composed of small poly(St-co-VEIB) nanospheres with the average diameter of 40 nm. The formation mechanism of FPC poly(St-co-VEIB) microspheres is proposed by investigating the influence of reaction conditions on their morphologies and observing their growth process. It can be well convinced that VEIB not only acted as a kind of monomers, which participated in the polymerization and provided electropositivity for FPC poly(St-co-VEIB) microspheres, but also acted as emulsifier and reactive stabilizer. The FPC poly(St-co-VEI[SO_3CF_3]) microspheres, which were obtained by anion-exchange between $^-SO_3CF_3$ of HSO_3CF_3 and Br^- in FPC poly(St-co-VEIB) microspheres due to the existence of imidazolium groups with electropositivity, showed higher catalytic efficiency for hydration of 1,2-epoxypropane with H_2O and esterification between acetic acid and ethanol than that of H_2SO_4.

1. Introduction

In the past decade, many attentions have been attracted to polymer microspheres materials, along with the rapid development of their researches and applications. Due to the adjustable sizes and special morphologies as well as functionalized surfaces, polymer microspheres materials with different functions have played a special and crucial role in many important fields, such as microstorages, microreactors, microseparators, elementary microstructures, which can be applied to encapsulation of products (cosmetics, inks, and dyes), drug delivery, protein and enzyme transplantation, design and assembly of three-dimensional structures for imitating hybridized atomic orbitals [1–4].

Up to now, many methods have been developed for the preparations of polymer microspheres materials with various morphologies, for instance, solid polymer microspheres can be easily synthesized by conventional emulsion polymerization [5] and precipitation polymerization [6]; hollow polymer microspheres can be obtained by self-assembly method [7] and SPG (Shirasu porous glass) emulsification technique [8], which can be also used for the preparation of porous polymer microspheres followed by swelling process of droplets [9]. In addition, some novel polymer microspheres with special morphologies have been also successfully fabricated, such as monodisperse dumbbell-shaped polymer microspheres obtained by seeded suspension polymerization [10], onion-like poly(ionic liquid) nanoparticles with the highly ordered and tunable inner structures formed spontaneously by precipitation polymerization from water [11], two-dimensional patterned conducting polymer-nanobowl sheet prepared by template method [12], golf-ball-like polymer microspheres obtained through membrane emulsification technique and subsequent suspension polymerization [13,14], speckled colloids facilely prepared via one-step seeded polymerization [15], and so on.

Recently, a kind of novel polymer microspheres, which were composed of the aggregations of smaller fine particles and called as fine particles clustered (FPC) microspheres, have been unexpectedly obtained when the polymerization reactions were carried

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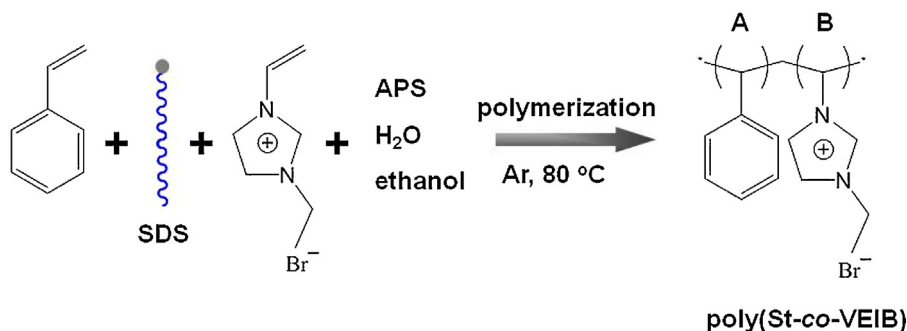
Scheme 1. Polymerization of St and VEIB.

out in the presence of some particular block copolymers [16,17] which were employed as a reactive emulsifier and synthesized by reversible addition–fragmentation chain transfer (RAFT) method. These block copolymers usually show different solubility in organic solvent [16] or amphiphilic property with carboxyl (—COOH) as the hydrophilic group [17]. Herein, a kind of novel FPC microspheres, fine particles clustered poly(St-*co*-VEIB) microspheres (FPC poly(St-*co*-VEIB) microspheres), have been successfully prepared in the present of sodium dodecylsulfonate (SDS) in aqueous alcohol system by using an one-step copolymerization of styrene (St) and 1-vinyl-3-ethylimidazolium bromide (VEIB). Unlike controlled/living free-radical polymerization (LFRP) [18–20], such as RAFT method [20], which is usually carried out under certain complicated reaction conditions or multi-step synthesis, it is a very simple self-assembly method of common free radical initiated emulsion polymerization by one step. It has been observed that the FPC poly(St-*co*-VEIB) microspheres are indeed composed of poly(St-*co*-VEIB) nanospheres with the average diameter of 40 nm. The formation mechanism of FPC poly(St-*co*-VEIB) microspheres is proposed by detailedly investigating the influence of reaction conditions on their morphologies and observing their growth process. It can be well convinced that VEIB not only acted as a kind of monomers, which participated in the polymerization and provided electropositivity for FPC poly(St-*co*-VEIB) microspheres, but also acted as emulsifier and reactive stabilizer. Due to the existence of imidazolium groups with electropositivity, a kind of FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres can be obtained by the ion-exchange between $^-SO_3CF_3$ of HSO_3CF_3 and Br^- in FPC poly(St-*co*-VEIB) microspheres, which show higher catalytic efficiency for hydration of 1,2-epoxypropane with H_2O and esterification between acetic acid and ethanol than that of H_2SO_4.

2. Experimental

2.1. Materials

Styrene (St) and N-vinyl imidazole were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and Yancheng Medical Chemical Factory (China), respectively, which were distilled under vacuum before use. Bromoethane (Sinopharm Chemical Reagent Co. Ltd., ≥98.0%) and sodium dodecylsulfonate (SDS) (Sinopharm Chemical Reagent Co. Ltd., ≥97.0%) are chemical grade. All the other reagents were analytical grade, and used without further purification, including ammonium peroxydisulfate (APS) (Tianjin Benchmark Chemical Reagent Co. Ltd., ≥98.0%), trifluoromethanesulfonic acid (HSO_3CF_3) (Alfa Aesar, ≥98.0%), 1,2-epoxypropane (Sinopharm Chemical Reagent Co. Ltd., ≥99.5%), propane-1,2-diol (Sinopharm Chemical Reagent Co. Ltd., ≥99.0%), toluene (Sinopharm Chemical Reagent Co. Ltd., ≥99.5%), acetonitrile (Tianjin Bodi Chemical Holding Co. Ltd., ≥99.5%), acetic acid

(Sinopharm Chemical Reagent Co. Ltd., ≥99.5%), ethylacetate (Tianjin Bodi Chemical Holding Co. Ltd., ≥99.5%) and ethanol (Tianjin Damao Chemical Factory, ≥99.7%).
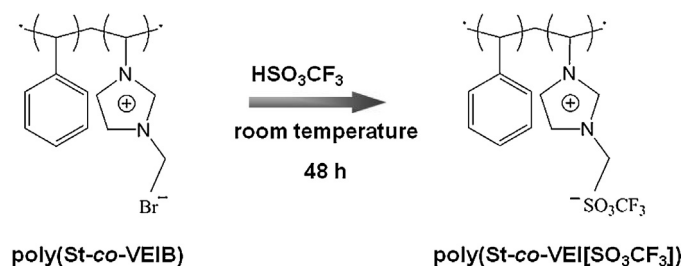
2.2. Preparation of FPC poly(St-co-VEIB) microspheres

Firstly, 1-vinyl-3-ethylimidazolium bromide (VEIB) was synthesized according the literature [21]. The preparation process is described in the Supporting Information (Scheme S1) and ^{1}H NMR [300-MHz, CDCl$_3$, tetramethylsilane (TMS)] spectrum of VEIB is shown in Fig. S1.

FPC poly(St-*co*-VEIB) microspheres was prepared by a copolymerization of styrene (St) and VEIB. In a typical procedure (Scheme 1), 0.4 mmol SDS and 0.37 mmol APS were dissolved in a mixture of 13 mL of de-ionized water and 37 mL of ethanol (EtOH) with stirring uniformly, and then 3.21 M VEIB aqueous solution (22.5 mmol VEIB dissolved in 7 mL of de-ionized water) and 5 mL of St were added into it. After magnetically stirring for 30 min under Ar, the reaction was carried out in a three-necked flask with a reflux condenser under Ar at 80 °C for 12 h. Then, the products were collected by centrifugation and washed with de-ionized water and ethanol for several times, respectively. Finally, the obtained white powders were dried in vacuum at 45 °C for 24 h. Otherwise, polystyrene (PS) microspheres were prepared correspondingly by the above method without VEIB in the reaction system and polyVEIB was synthesized by the polymerization of VEIB, which is consistent with the literature [21].

2.3. Synthesis of FPC poly(St-co-VEI[SO$_3$CF$_3$]) microspheres as catalyst

FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres were obtained by anion-exchange process using the above FPC poly(St-*co*-VEIB) microspheres with HSO_3CF_3. In a typical procedure (Scheme 2), 50 mg FPC poly(St-*co*-VEIB) microspheres were firstly dispersed in 2 mL toluene under magnetic stirring. Then, 300 μL HSO_3CF_3 was added into the above dispersion liquid with constant stirring

Scheme 2. Anion-exchange process of FPC poly(St-*co*-VEIB) microspheres with HSO_3CF_3.

for 48 h at room temperature. Finally, the products were collected by centrifugation and washed with ethanol for several times and the obtained yellowish powders were dried in vacuum at 45 °C for 24 h.

2.4. Characterizations and apparatus

The images of FPC poly(St-co-VEIB) microspheres were obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements, respectively. SEM measurements were performed on a Hitachi SU-8010 electron microscope with primary electron energy of 1 kV. TEM experiments were performed on a Hitachi H-7650 electron microscope with an acceleration voltage of 80 kV. ^{1}H NMR spectra were recorded with a Mercury Vx-300 MHz spectrometer (Varian Inc., USA) using CDCl$_3$ as solvent and TMS as the internal standard. Fourier transform infrared spectroscopy (FTIR) Spectra of KBr powder-pressed pellets were recorded on a Perkin Elmer Spectrum one FTIR spectrometer (Perkin-Elmer Corp., USA). The zeta-potential data of FPC poly(St-co-VEIB) microspheres and PS microspheres were obtained by using a Zeta-Plus4 instrument (Brookhaven Corp., USA). Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB 250 using Al as the exciting source. Element analysis was performed on a CHNS-O Analyzer (FlashEA 1112 Series). An SDT Q600 Simultaneous DSC-TGA Instrument (TA Corp., USA) was used to investigate the thermal stability of FPC poly(St-co-VEIB) microspheres powder in the temperature range from 100 °C to 700 °C under condensed N$_2$ at a rate of 10.0 °C/min.

2.5. Catalyst tests

Hydration of 1,2-epoxypropane with H$_2$O was chosen as a model reaction. In a typical reaction, 45 mg FPC poly(St-co-VEI[SO$_3$CF$_3$]) microspheres were firstly dispersed in 3.6 g (200 mmol) of H$_2$O under magnetic stirring. Then, 1.16 g (20 mmol) of 1,2-epoxypropane were added into the above dispersion liquid with constant stirring for 6 h at 27 °C.

Esterification between acetic acid and ethanol was chosen as another model reaction. In a typical reaction, 1.2 g (20 mmol) of acetic acid and 1.38 g (30 mmol) of ethanol were firstly mixed, and then 45 mg FPC poly(St-co-VEI[SO$_3$CF$_3$]) microspheres were added to the above mixture under magnetic stirring. The reaction was carried out for 6 h at 70 °C with constant stirring.

Otherwise, in order to compare the catalytic activity of FPC poly(St-co-VEI[SO$_3$CF$_3$]) microspheres and H$_2$SO$_4$, this reaction was also carried out under the same conditions using H$_2$SO$_4$ as catalyst.

The products obtained through above reactions were analyzed by gas chromatography of VARIAN CP-3800 with a flame ionization detector (FID). The column was VARIAN CP-8762 capillary column (CP SIL 19CB 30 m); the initial temperature was 50 °C, temperature rate was 20 °C/min, and final temperature was 250 °C; the temperature of FID detector was 300 °C; the temperature of injection port was 250 °C. The split ratio was 100 and the flow rate of N$_2$ was 1 mL/min. In these reactions, toluene was used as an internal standard.

3. Results and discussion

3.1. Morphology and formation mechanism of FPC poly(St-co-VEIB) microspheres

Fig. 1 gives SEM and TEM images of FPC poly(St-co-VEIB) microspheres synthesized by the copolymerization of St and VEIB. Their diameters were visibly inhomogeneous, which were about in the range of 0.5–2 μm. But it is very clearly observed that the surfaces of all the poly(St-co-VEIB) microspheres appear rough (Fig. 1(a) and (b)), which is significantly different from the ordinary PS microspheres with smooth surfaces. Fig. 1(a') and (b') presents the amplified SEM and TEM images of one FPC poly(St-co-VEIB) microspheres, respectively. Many small nanospheres with the diameter
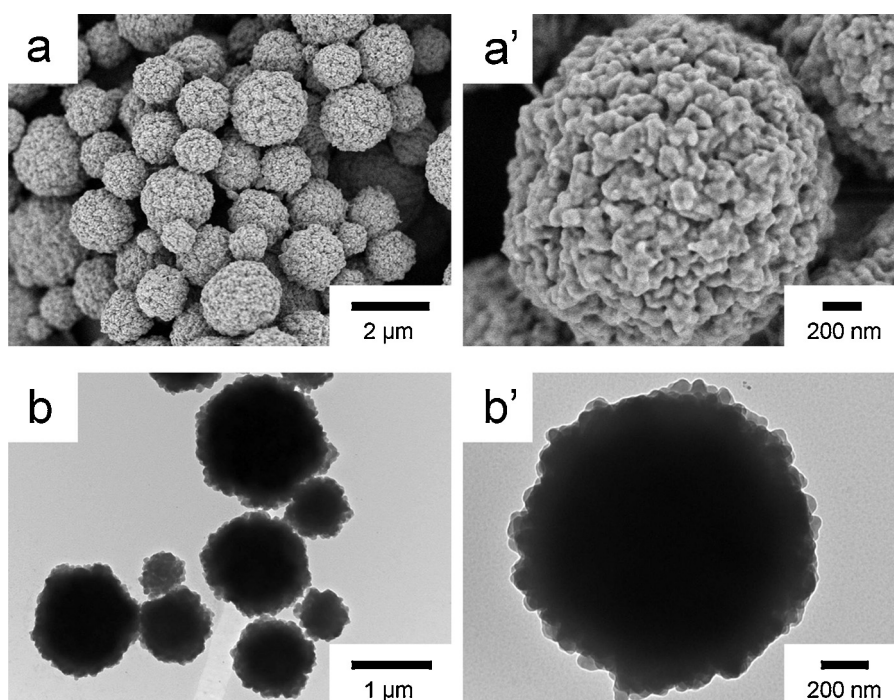
Fig. 1. (a, a') SEM and (b, b') TEM images of FPC poly(St-co-VEIB) microspheres, (a') and (b') are the amplified images of (a) and (b), respectively. Preparation conditions: [St]/[VEIB] = 1:0.5, [SDS] = 0.02 M (in H$_2$O), V_{St} = 5 mL, EtOH/H$_2$O (v/v) = 37/20.
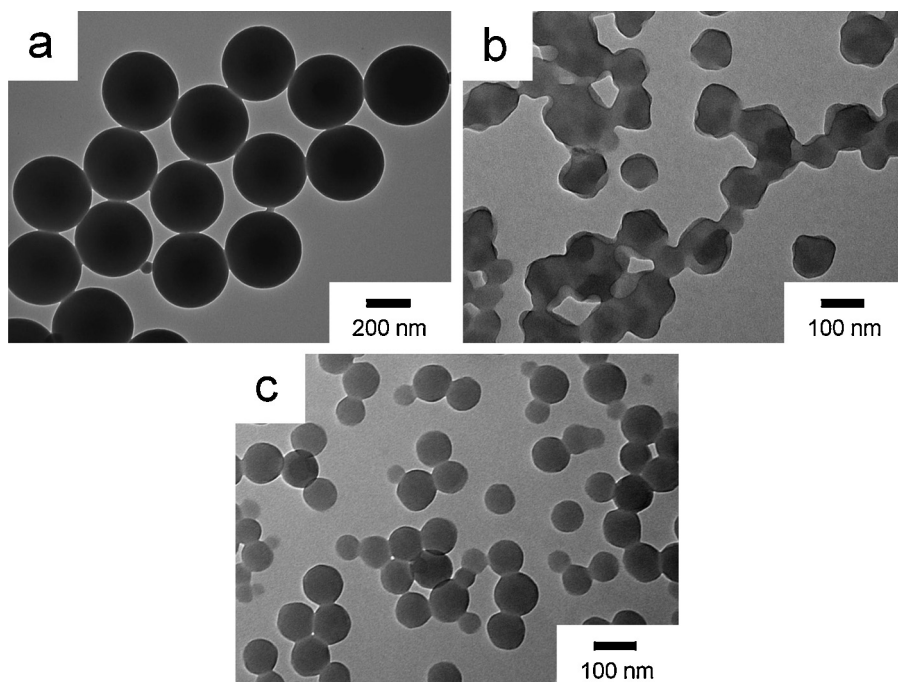
Fig. 2. TEM images of (a) PS microspheres and (b, c) poly(St-*co*-VEIB) nanospheres obtained under different [St]/[VEIB]: (a) [St]/[VEIB] = 1:0; (b) [St]/[VEIB] = 1:0.25 and (c) [St]/[VEIB] = 1:1. Other conditions: [SDS] = 0.02 M (in H_2O), V_{St} = 5 mL, EtOH/H_2O (v/v) = 37/20.

of about 40 nm are clustered together and exist on the surface of the FPC poly(St-*co*-VEIB) microspheres, which looks most like a fried meatball. However, its inner appears solid and do not have any gap and some small gaps appear on its surface, which may be due to the clusters of small nanospheres.

In order to investigate the formation mechanism of FPC poly(St-*co*-VEIB) microspheres, it must be firstly confirmed that what factors in the reaction conditions will have a significant impact

to the formation of them. Therefore, the molar ratio of St and VEIB ([St]/[VEIB]), the volume of St (V_{St}) and the concentrations of SDS ([SDS]) (in H_2O) were adjusted, respectively. Fig. 2 shows TEM images of the products with different morphologies obtained under different [St]/[VEIB]. When VEIB was not added into the reaction system, the homogeneous PS microspheres with smooth surfaces were obtained and their average diameters were about 350 nm (Fig. 2(a)). When [St]/[VEIB] was 1:0.25, poly(St-*co*-VEIB)
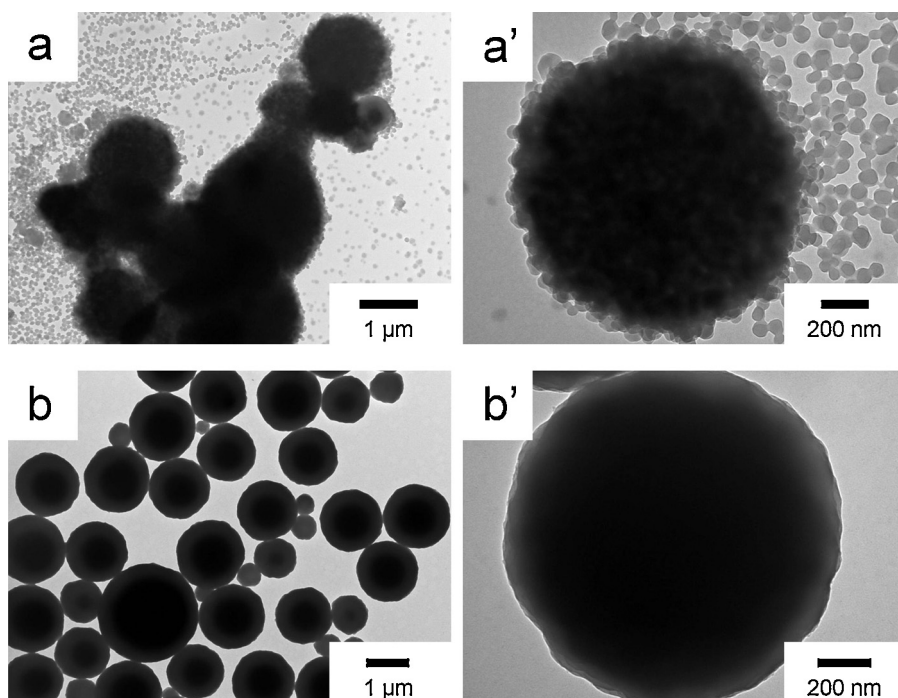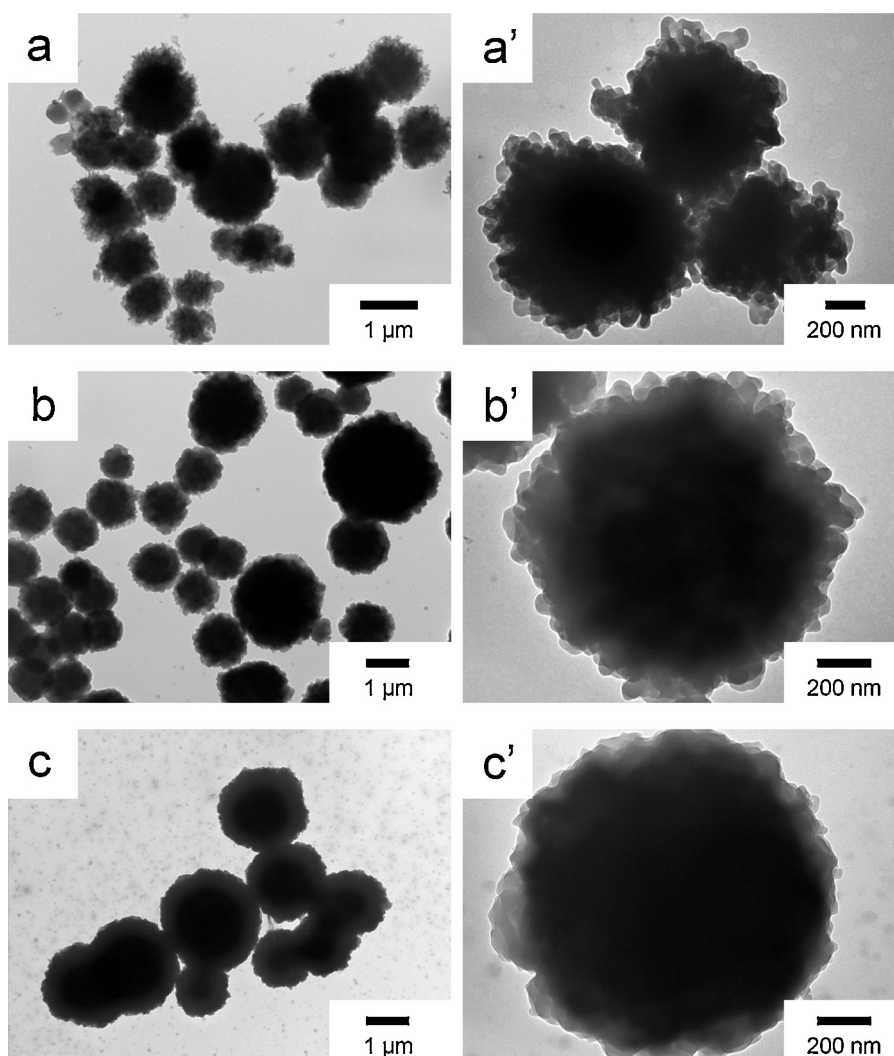

Fig. 3. TEM images of FPC poly(St-*co*-VEIB) microspheres obtained under different V_{St}: (a) V_{St} = 2.5 mL and (b) V_{St} = 10 mL. (a') and (b') are the amplified images of (a) and (b), respectively. Other conditions: [St]/[VEIB] = 1:0.5, [SDS] = 0.02 M (in H_2O), EtOH/H_2O (v/v) = 37/20.

nanospheres with irregular morphologies were obtained, and most of them were conglutinated together with each other, whose sizes were less than 100 nm (Fig. 2(b)). However, when [St]/[VEIB] was changed to 1:1, poly(St-co-VEIB) nanospheres with smooth surfaces were prepared and their diameters were in the range of 30–90 nm, which is shown in Fig. 2(c). It is indicated that the amount of VEIB in the reaction system played an important role in the formation of FPC poly(St-co-VEIB) microspheres in the case of other reaction conditions fixed. In the conditions of either too much the amount of VEIB or too little, FPC poly(St-co-VEIB) microspheres could not form.

Then, the influence of V_{St} in the reaction system on the morphology of FPC poly(St-co-VEIB) microspheres was investigated by adjusting V_{St} in the case of [St]/[VEIB] = 1:0.5, while other conditions were kept constant. In other words, the concentrations of both two monomers ([St] and [VEIB]) in the reaction system were simultaneously changed. Compared with the reaction conditions in which FPC poly(St-co-VEIB) microspheres could be prepared, when V_{St} and corresponding [VEIB] were both reduced to the half, most poly(St-co-VEIB) nanospheres with the diameter of 50 nm and a few of large microspheres could be observed in Fig. 3(a). As shown in Fig. 3(a'), these large microspheres were constructed by the clusters of the small poly(St-co-VEIB)

nanospheres. When V_{St} increased to 10 mL accompanied with the corresponding increase of [VEIB], many solid microspheres with inhomogeneous sizes were obtained and their surfaces appear a little rough (Fig. 3(b')). Therefore, the concentrations of monomers could also significantly affect the morphology of FPC poly(St-co-VEIB) microspheres.

During the growth process of micro/nano-structures, the kinds and amount of surfactants often affect their morphologies and sizes [22]. Herein, the influence of [SDS] (in H_2O) on the morphology of FPC poly(St-co-VEIB) microspheres was also investigated. If there was no surfactant added into the reaction system, FPC poly(St-co-VEIB) microspheres with inhomogeneous sizes could be obtained and the poly(St-co-VEIB) nanospheres on their surfaces appear a little incompact, simultaneously, few of small microspheres with smooth surface are also observed (Fig. 4(a) and (a')). When [SDS] (in H_2O) was 0.01 M, some large FPC poly(St-co-VEIB) microspheres with the diameter over 2 μm were obtained, as shown in Fig. 4(b). However, when [SDS] (in H_2O) increased to 0.04 M, the poly(St-co-VEIB) nanospheres which constructed the FPC microspheres became very compact to each other (Fig. 4(c) and (c')). Therefore, SDS as the surfactant only affected the compactness of poly(St-co-VEIB) nanospheres clusters. Both introduction of VEIB and the amount of two monomers (St and VEIB) are

Fig. 4. TEM images of FPC poly(St-co-VEIB) microspheres obtained under different [SDS] (in H_2O): (a) [SDS] = 0 M; (b) [SDS] = 0.01 M; (a) [SDS] = 0.04 M. (a'), (b') and (c') are the amplified images of (a), (b) and (c), respectively. Other conditions: [St]/[VEIB] = 1:0.5, V_{St} = 5 mL, EtOH/H_2O (v/v) = 37/20.
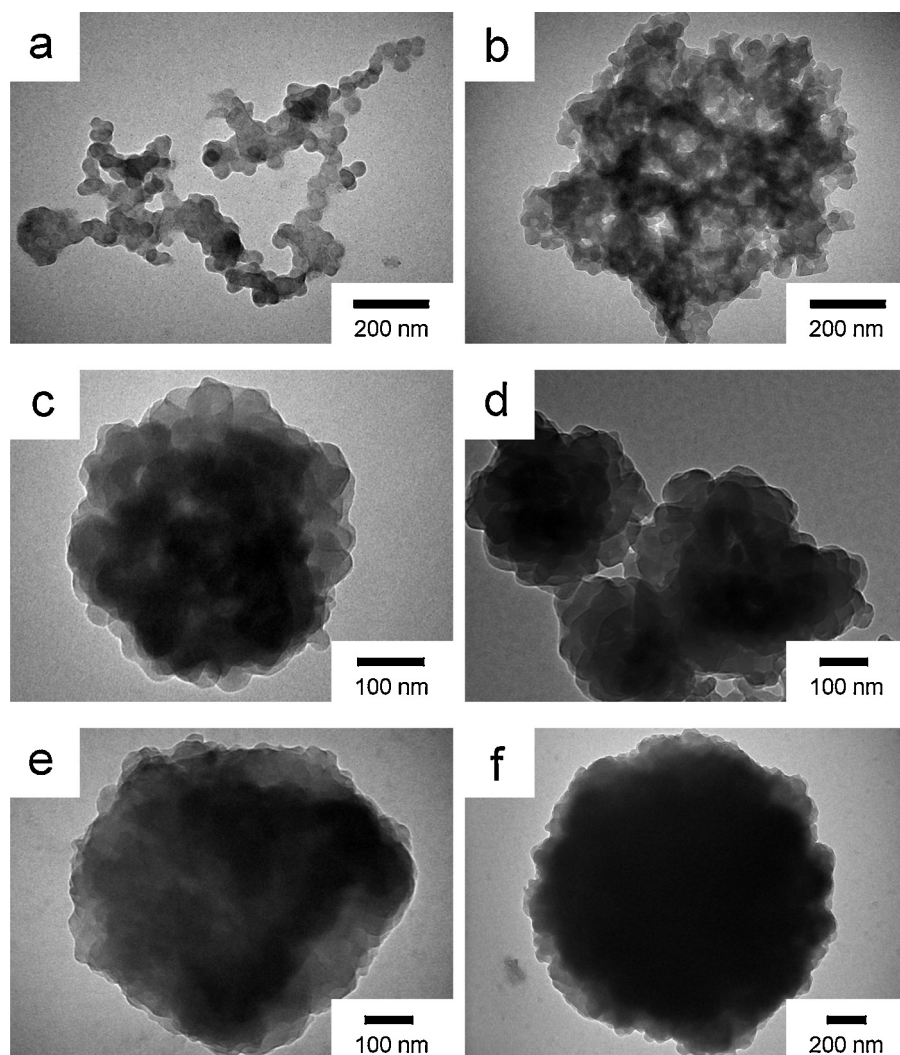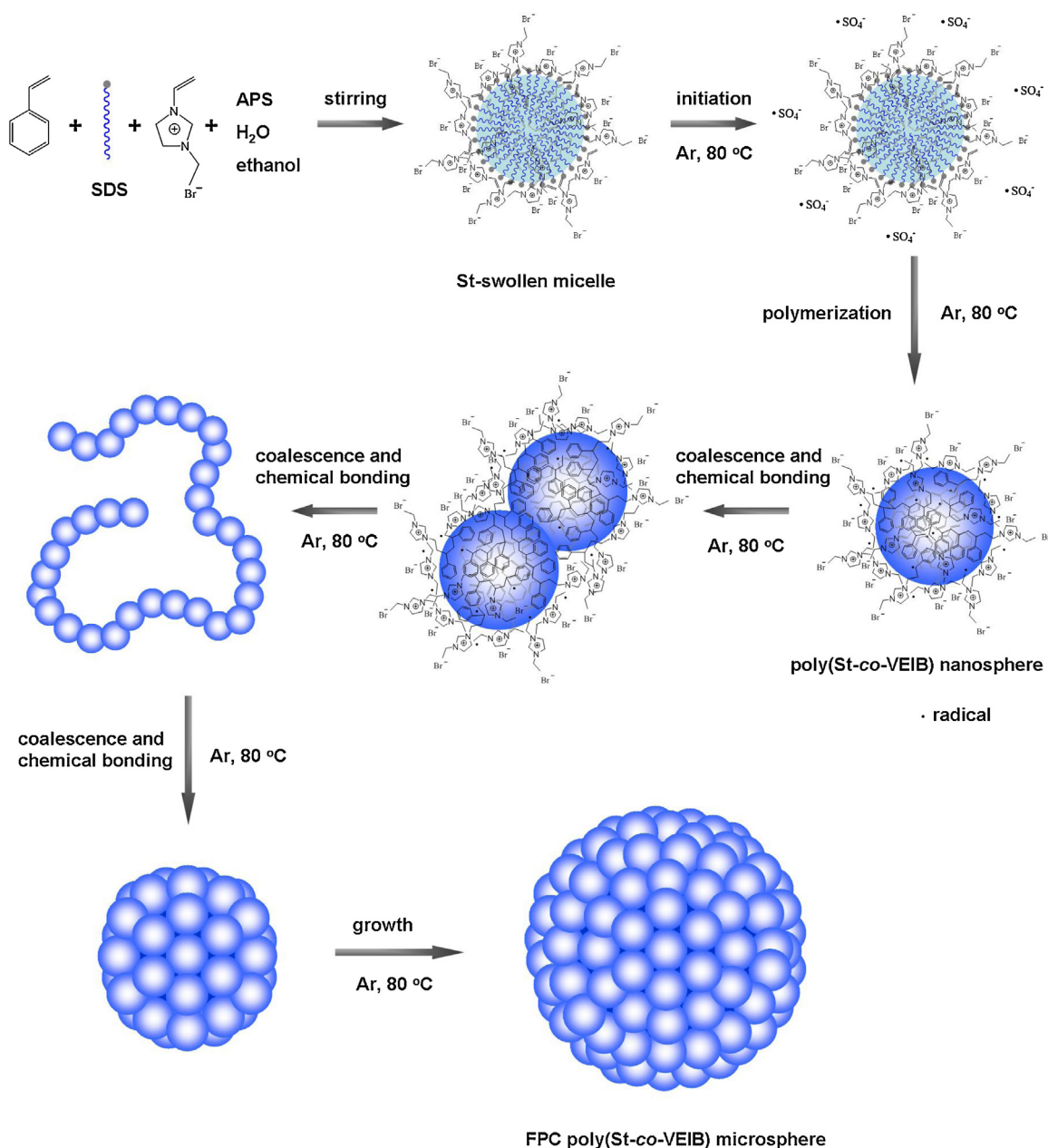
Fig. 5. TEM images of FPC poly(St-*co*-VEIB) microspheres synthesized under different reaction time: (a) 0.5 h; (b) 1 h; (c) 3 h; (d) 6 h; (e) 9 h and (f) 12 h.

the key factors for the formation of FPC poly(St-*co*-VEIB) microspheres.

In order to further investigate the formation mechanism of FPC poly(St-*co*-VEIB) microspheres, Fig. 5 shows TEM images of the FPC poly(St-*co*-VEIB) microspheres synthesized under different reaction time, such as 0.5, 1, 3, 6, 9 and 12 h. According to Fig. 5, the growth process of FPC poly(St-*co*-VEIB) microspheres can be further visually described in Scheme 3. In fact, the preparation of FPC poly(St-*co*-VEIB) microspheres is a typical reaction of free radical initiated emulsion polymerization, in which St acts as oil phase and EtOH/H_2O act as aqueous phase or disperse phase, respectively. At first, St, SDS and VEIB can form the enhanced micelles in the emulsion system under magnetically stirring. SDS is a kind of conventional anionic surfactant and the surface of micelles formed by SDS behaves electronegative in the emulsion system. VEIB is a kind of water-soluble and polymerizable ionic liquid salt with a positive charge of the imidazolium and Br^- of corresponding negative ion. Therefore, when the enhanced micelles form, VEIB can be adsorbed on the surface of the enhanced micelles due to the electrostatic interactions of the positive and negative charges. At the beginning of polymerization reaction, $S_2O_8^{2-}$ releases the free-radical $^\bullet SO_4^-$, which can initiate the copolymerization of St and VEIB. According to our previous report [23], poly(St-*co*-VEIB) microspheres

behave electropositive due to the introduction of imidazolium-groups during the copolymerization of St and VEIB. Therefore, the small poly(St-*co*-VEIB) nanospheres with electropositivity can be obtained and they also own free-radicals, and so each poly(St-*co*-VEIB) nanosphere can act as an initiator unit, which can further initiate the copolymerization of monomers. When the poly(St-*co*-VEIB) nanospheres start to coalesce with each other, due to the electrostatic repulsion between poly(St-*co*-VEIB) nanospheres with electropositivity, they cannot completely coalesce together and become a large one, but merely a part of them coalesce and grow together by chemical bonding during the process of polymerization. Therefore, along with the increase of polymerization time, many of the poly(St-*co*-VEIB) nanospheres can connect together by the coalescing to form a chain which looks most like a pearl necklace. The chain composed of poly(St-*co*-VEIB) nanospheres with the average diameter of 40 nm could be obviously observed at the copolymerization time of 0.5 h in Fig. 5(a). Then, many chains were twined together by the coalescence and chemical bonding between some poly(St-*co*-VEIB) nanospheres in each chain and became compact, which showed a fine particles clustered morphology (Fig. 5(b) and (c)). Along with the increase of reaction time, the microsphere gradually grew up and became more and more large (Fig. 5(d) and (e)). Finally, the FPC poly(St-*co*-VEIB) microspheres were obtained

Scheme 3. The growth process of FPC poly(St-*co*-VEIB) microspheres. Conditions: [St]/[VEIB] = 1:0.5, [SDS] = 0.02 M (in H_2O), V_{St} = 5 mL, EtOH/H_2O (v/v) = 37/20.

after polymerization for 12 h (Fig. 5(f)). It is found that during the growth process of FPC poly(St-*co*-VEIB) microspheres, poly(St-*co*-VEIB) nanospheres which constructed the FPC microspheres did not became large and their dimensions remained constant, still keeping about 40 nm, the same sizes as that at the time they formed the chains of nanospheres.

Otherwise, Fig. 6(a) and (b) shows the zeta-potential data of FPC poly(St-*co*-VEIB) microspheres with a strongly positive charge of nearly 53 mV and PS microspheres with a strongly negative charge of nearly −19 mV in aqueous solution, respectively, which is similar to our previous report [23]. The FPC poly(St-*co*-VEIB) microspheres were prepared by using a very simple self-assembly method of common free radical initiated emulsion polymerization. Besides SDS, any other emulsifier and reactive stabilizer, such as some block copolymers with complex chemical structure and polymerizable activity [16], were not added into the polymerization system. Therefore, VEIB not only acted as a kind of monomers

which participated in the polymerization and provided electropositivity for FPC poly(St-*co*-VEIB) microspheres, but also acted as emulsifier and reactive stabilizer. The introduction of VEIB to the polymerization system is the most important factor and plays an irreplaceable role during the formation of FPC poly(St-*co*-VEIB) microspheres.

3.2. Characterizations of FPC poly(St-co-VEIB) microspheres

The chemical structure of FPC poly(St-*co*-VEIB) microspheres was also characterized by FTIR spectra, XPS spectra, elemental analysis and TGA thermograms. Fig. 7 gives a typical FTIR spectrum of the FPC poly(St-*co*-VEIB) microspheres, which is consistent with previous reports [24–26]. The peaks at 3026, 2923 and 2850 cm^{-1} are due to C—H stretching vibration of aromatic ring, C—H asymmetric and symmetric stretching vibrations of methylene, respectively.
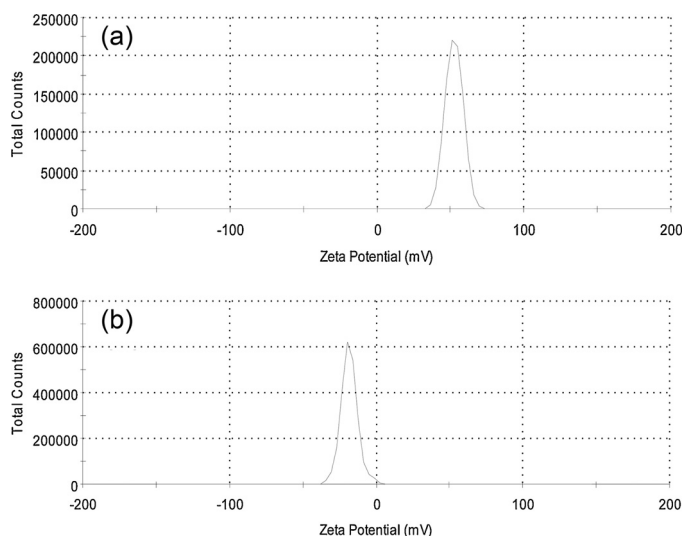
Fig. 6. Zeta-potential data of (a) FPC poly(St-*co*-VEIB) microspheres and (b) PS microspheres in aqueous solution.

The peaks at 1600, 1492 and 1452 cm^{-1} are associated to skeleton vibration of the benzene ring. The absorption at 1180 cm^{-1} is assigned to C—H in-plane deformation vibration of the imidazolium ring. The peaks at 757 and 698 cm^{-1} are associated to C—H vibration of long-chain —CH$_2$— and characteristic mono-substituted absorption in a benzene ring, respectively.

XPS data have also been used to characterize the chemical structure of FPC poly(St-*co*-VEIB) microspheres, which is shown in Fig. 8. Although the elements of C, N, O, S and Br were hoped to be all detected, but only C, N and O are obviously observed in the survey spectrum (Fig. 8(i)) because the content of S and Br is very little in the FPC poly(St-*co*-VEIB) microspheres. In the C 1s core-line spectrum of the FPC poly(St-*co*-VEIB) microspheres, the main peak is fitted with three peaks at 284.8, 286.5 and 291.3 eV, which are associated with C—C/C—H [27], C$_{hetero}$[28] and π–π* [27], respectively (Fig. 8(ii)). For the N 1s core-line spectrum as shown in Fig. 8(iii), the two types of nitrogen atoms have been found at the peaks of 398.7 and 401.7 eV, respectively, which are similar to the previous report [29]. According to the precious report [30,31], the two nitrogen atoms in a free imidazolium ion

of conventional ionic liquid often have the same binding energy mostly over 401 eV. Herein, the two observed types of nitrogen atoms may consequently result from the interactions between the imidazolium of VEIB and benzene ring of St, such as π–π*, π-cationic, hydrophobic, or electrostatic interactions, which is similar to the interactions between the imidazolium ion and the single-walled carbon nanotubes [32–34]. The results well demonstrate that the imidazolium-groups existed in the surface of FPC poly(St-*co*-VEIB) microspheres and the copolymerization of VEIB and St really occurred. The main peak of O 1s at 532.2 eV in Fig. 8(iv) is associated with —SO$_n$ ($n > 1$) [35]. In addition, the peak at 168.5 eV in the S 2p spectrum and the peak at 68.0 eV in the Br 3d spectrum have been also observed (Fig. 8(v) and (vi)), which are due to S^{6+} [36] and Br 3d$_{5/2}$ [37], respectively. According to the results of XPS data, the atomic percentages of C and N on the surface of FPC poly(St-*co*-VEIB) microspheres are 95.85% and 1.19%, respectively. Therefore, it is calculated that on the surface of FPC poly(St-*co*-VEIB) microspheres, the molar ratio of both constitutional units (St segments (A in Scheme 1) and VEIB segments (B in Scheme 1)) in the copolymer is about 20:1. Besides the XPS measurement, the elemental analysis data shows that the weight content of N element in the FPC poly(St-*co*-VEIB) microspheres is in average of 0.96%, and thus it can be also calculated that the molar ratio of both constitutional units (St segments and VEIB segments) in the copolymer is about 25:1, which is close to the result of XPS data. The result also indicates that imidazolium-groups not only existed on the surface of FPC poly(St-*co*-VEIB) microspheres, all of the microspheres are the copolymer synthesized by the copolymerization of St and VEIB.

Thermogravimetric analysis (TGA) data can further prove that the FPC poly(St-*co*-VEIB) microspheres are prepared by the copolymerization of St and VEIB. Fig. 9 exhibits TGA thermograms of the FPC poly(St-*co*-VEIB) microspheres, PS microspheres, polyVEIB and the mixtures of polyVEIB and PS microspheres (the molar ratio of their monomer segments is 1:20) in the temperature range from 100 °C to 700 °C under condensed N$_2$ at a rate of 10 °C/min, respectively. It is clearly observed that the thermal stability of FPC poly(St-*co*-VEIB) microspheres is slightly better than that of PS microspheres after 323 °C by comparing curve a and b. In view of the much higher thermal stability of PVEIB than PSt above 407 °C, the difference between the existing states of PVEIB in PVEIB and poly(St-*co*-VEIB) should be the main reason for the higher decomposition temperature of poly(St-*co*-VEIB) than that of PVEIB and PSt. Otherwise, the —SO$_4^-$ groups as the initiator residues exist at the end of the copolymer chains and some ionic bonds can form by the electrostatic interaction between —SO$_4^-$ groups with negative charges and imidazolium groups with positive charges, which may also increase the decomposition temperature of FPC poly(St-*co*-VEIB) microspheres. Therefore, the introduction of imidazolium groups improve the thermal stability of conventional PS microspheres. Fig. 9(c) presents a typical TGA characteristic curve of polyVEIB, which is consistent with the previous report [38]. When the temperature was higher than 421 °C, the FPC poly(St-*co*-VEIB) microspheres exhibited the similar characteristic to polyVEIB, which demonstrates that imidazolium groups indeed existed in FPC poly(St-*co*-VEIB) microspheres. As shown in Fig. 9(d), when polyVEIB and PS microspheres were physically blended by the molar ratio of their monomer segments of 1:20, due to the different thermal stability of polyVEIB and PS microspheres, a bend appeared in the range from 300 to 340 °C, which did not appear in the TGA curve of FPC poly(St-*co*-VEIB) microspheres (Fig. 9(a)), which well demonstrates that the two monomers of St and VEIB are bonded together by covalent bonding in the copolymerization reaction and the chemical composition of FPC poly(St-*co*-VEIB) microspheres are indeed the copolymer of St and VEIB.
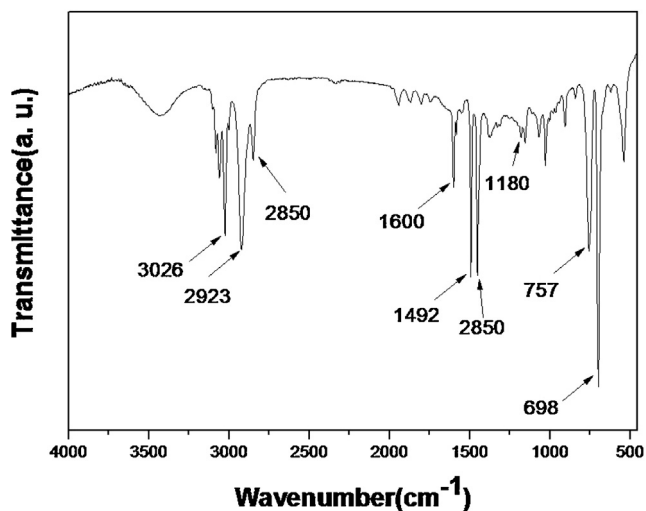

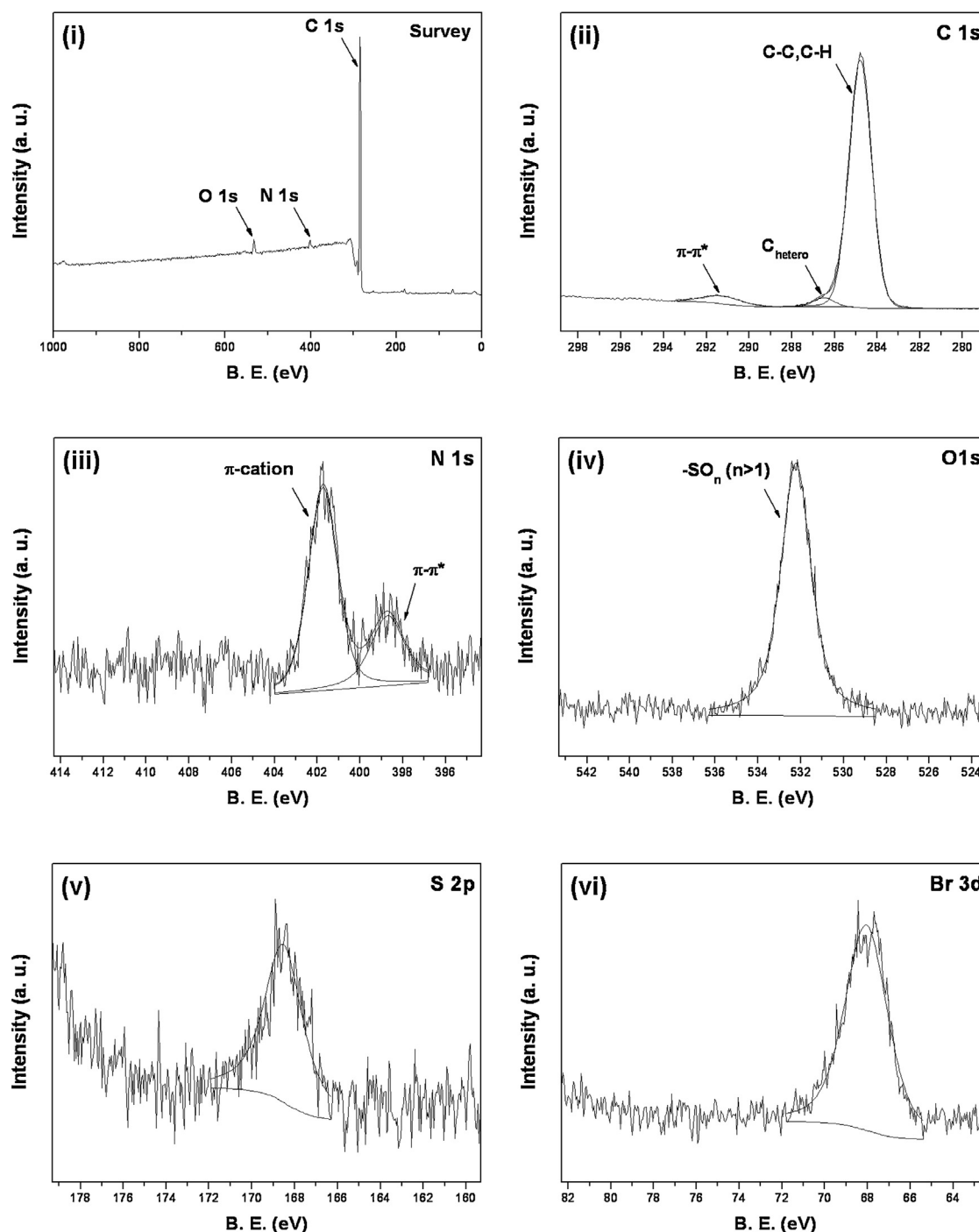**Fig. 7.** FTIR spectrum of FPC poly(St-*co*-VEIB) microspheres.

Fig. 8. XPS spectra of FPC poly(St-*co*-VEIB) microspheres: (i) survey spectra; (ii) C 1s; (iii) N 1s; (iv) O 1s; (v) S 2p and (vi) Br 3d.

Otherwise, after an anion-exchange treatment by HSO_3CF_3, the obtained imidazolium-groups functionalized superhydrophobic mesoporous polydivinylbenzene exhibited significantly enhanced catalytic activities for some organic reactions [29]. Herein, an anion-exchange process was carried out between the FPC poly(St-*co*-VEIB) microspheres and HSO_3CF_3. In this process, At least Br^- on the surface of FPC poly(St-*co*-VEIB) microspheres were replaced by $^-SO_3CF_3$, obtaining a kind of FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres. In order to test their catalytic activities, in the same reaction conditions, the FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres and H_2SO_4 were selected as catalysts for hydration of 1,2-epoxypropane with H_2O and esterification between acetic acid and ethanol, respectively. Table 1 gives the catalytic efficiency of the FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres and H_2SO_4 for the hydration reaction and the esterification reaction. The catalytic efficiency of the FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres for the hydration reaction and the esterification reaction could reach to 88.9% and 88.4%, respectively, but that of H_2SO_4 was only 53.9% and 48.6%, respectively. The results indicate that the catalytic activity of the FPC poly(St-*co*-VEI[SO_3CF_3]) microspheres is much higher than that of H_2SO_4.
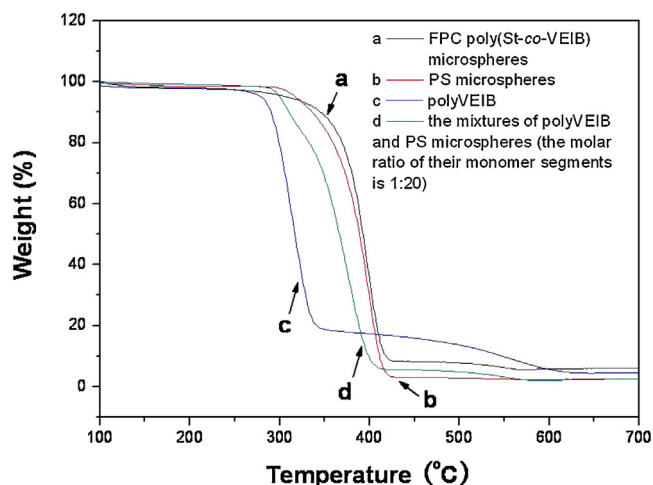
Fig. 9. TGA thermograms of (a) FPC poly(St-*co*-VEIB) microspheres, (b) PS microspheres, (c) polyVEIB as well as (d) the mixtures of polyVEIB and PS microspheres (the molar ratio of their monomer segments is 1:20).

Table 1
The catalytic efficiency of the FPC poly(St-*co*-VEI[SO$_3$CF$_3$]) microspheres and H$_2$SO$_4$ for the hydration reaction and the esterification reaction.

Entry	Catalyst	Hydration of propylene oxide yield (%)	Esterification of ethylacetate yield (%)
1	FPC poly(St-*co*-VEI[SO$_3$CF$_3$]) microspheres	88.9	88.4
2	H$_2$SO$_4$	53.9	48.6

4. Conclusions

In summary, FPC poly(St-*co*-VEIB) microspheres have been successfully prepared in the present of SDS in aqueous alcohol system by using the one-step copolymerization of St and VEIB. In general, polymer microspheres with hierarchical nanostructures are prepared under certain complicated reaction conditions or by multi-step synthesis, but the FPC poly(St-*co*-VEIB) microspheres composed of many small poly(St-*co*-VEIB) nanospheres with the average diameter of 40 nm are obtained by a very simple self-assembly method of common free radical initiated emulsion polymerization. The formation mechanism of FPC poly(St-*co*-VEIB) microspheres is proposed by investigating the influence of reaction conditions on their morphologies and observing their growth process. It can be well convinced that VEIB not only acted as a kind of monomers which participated in the polymerization and provided electropositivity for FPC poly(St-*co*-VEIB) microspheres, but also acted as emulsifier and reactive stabilizer. Furthermore, the FPC poly(St-*co*-VEI[SO$_3$CF$_3$]) microspheres obtained by anion-exchange between $^-$SO$_3$CF$_3$ of HSO$_3$CF$_3$ and Br$^-$ in FPC poly(St-*co*-VEIB) microspheres showed the higher catalytic activity for hydration of 1,2-epoxypropane with H$_2$O and esterification between acetic acid and ethanol than that of H$_2$SO$_4$.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.11.183.

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