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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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ABSTRACT

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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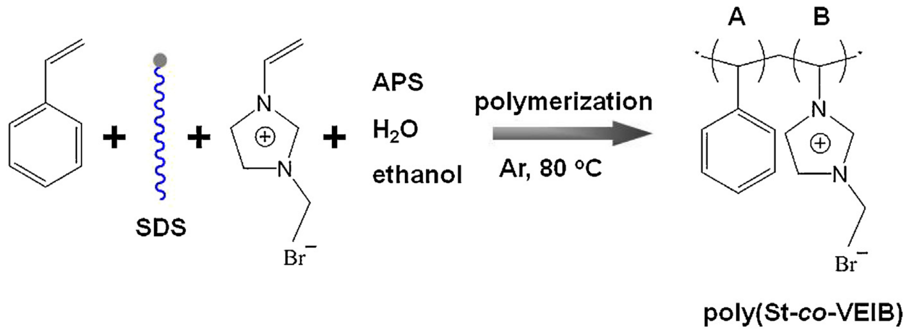


Scheme 1. Polymerization of St and VEIB.

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%).

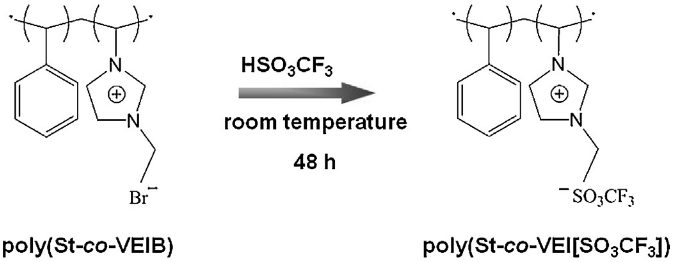
2.2. Preparation of FPC poly(St-co-VEIB) microspheres

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 ^1H 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_3CF_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.