Preparation and Characterization of Polystyrene Microspheres in the Presence of β-Cyclodextrin

Wei Wang1, Yan Deng1,2,*, Liming Zhang1,2, Juan Fu1, Zhuoxuan Lu1,2, and Lijian Xu1

1 Key Laboratory of Green Packaging and Application of Biological Nanotechnology, Hunan University of Technology, Zhuzhou 412007, China
2 State Key Laboratory of Bioelectronics, Southeast University, Nanjing 210096, China

Using styrene as raw material, potassium persulfate as an initiator, β-cyclodextrin as a stabilizer, polystyrene microspheres were successfully prepared with nice monodisperse feature by means of soap-free emulsion polymerization method. Experimental studies were performed in detail to check the effect of the synthesis process of the microspheres, the stabilizer dosage, monomer concentration, and initiator dosage on the particle size and distribution, the microstructures were characterized with SEM, TEM, infrared (IR) and the particle size distribution investigation. The results show that the appropriate changes in amount of stabilizer and monomer concentration and dosage of initiator can result in a different particle size and polystyrene microspheres with good monodispersity were finally obtained.

Keywords: Styrene, β-Cyclodextrin, Soap-Free Emulsion Polymerization, Polystyrene.

1. INTRODUCTION

Monodisperse polystyrene microspheres have a large surface area,1,2 high mechanical strength and microsphere surface is easy to give varieties of functional groups, etc. Due to these characteristics, the PS microspheres have been widely used in the ion exchange,3 chromatography,4 biological separation,5 immobilized enzyme,6 and immunology fields.7

Due to the special structure of hydrophobic cavity, the β-cyclodextrin (β-CD) can make hydrophobic monomer solubilized in the water system,8 and avoids the use of surfactants such as sodium dodecyl sulfate9,10 or organic solvents such as methanol and polyethylene pyrrolidine copper.11-13 The β-CD is an environmentally friendly green material used in polymerization reactions. Rinner and Glockner reported that by adding β-CD in the methacrylate polymerization,14,15 the monomer reaction rate and, therefore, the final conversion rate can be greatly improved. In Comparison with the traditional emulsion polymerization, this new type of β-CD-mediated polymerization method is quite different. And the new method in polymer synthesis research is still in its infancy.

This paper used water as the dispersion medium, styrene as raw material, potassium persulfate as an initiator, β-CD as a stabilizer, did not add any surfactants or organic solvents. And the monodisperse PS microspheres were prepared by means of soap-free emulsion polymerization method. The factors to influence the microsphere size and distribution of PS microspheres were researched, and the surface characteristics were characterized.

2. MATERIALS AND METHODS

2.1. Materials

Styrene (St) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Potassium persulfate (KPS) was purchased from Shantou Guanghua Chemical Factory Co., Ltd. (Guangdong, China). β-cyclodextrin (β-CD) was purchased from Mengzhoushi hongkey biological Co., Ltd. (Henan, China). Others were deionized water and absolute ethyl alcohol, etc. Before use, a 5% NaOH solution was applied to treat styrene for three times to get rid of the polymerization inhibitor, and deionized water was used to wash the styrene to make sure that the pH was neutral.

Scanning electron microscopy (SEM, Hitachi S-3000N, Japan), Transmission electron- microscopy (TEM, JEM-2000, Japan), Zetasizer Nanos90 (ZSNanos90, Malvern, Britain) and Fourier transform infrared spectroscopy (FTIR, Nicolet5700, American) were applied to characterize the obtained materials.

*a Author to whom correspondence should be addressed.
2.2. Preparation of Polystyrene Microspheres

10 mL of styrene, 90 mL of deionized water and 1.25 g of β-CD were added to a three-neck flask equipped with a reflux condenser and a mechanical stirrer, followed by stirring to form a homogeneous system, and then to get rid of oxygen by introducing nitrogen for 15–30 min. Then 0.25 g of potassium persulfate aqueous solution (0.25 g KPS dissolved in 10 mL of deionized water) was added to allow the polymerization for 6 h under nitrogen atmosphere at 75 °C. After the polymerization reaction, the microspheres were treated under ultrasound and the supernatant was removed, followed by washing the lower fluid with deionized water and absolute ethyl alcohol, then the centrifuging, washing and dispersion were repeated and finally a vacuum drying step was performed.

3. RESULTS AND DISCUSSION

3.1. Infrared Spectroscopic Analysis

Shown in Figure 1 are the infrared spectra of PS nanoparticles prepared without addition of β-CD (A) and with addition of β-CD (B). It could be seen from the figure that curve A and curve B are basically the same with each other, indicating that β-CD only acted as a stabilizer, did not participate in the polymerization reaction. For curve B, the 1600.7, 1492.6, 1452.0 cm⁻¹ were the skeleton vibration bands of benzene ring. 2921.2, 3025.0, 3059.4 cm⁻¹ were the C-H bond stretching vibration bands of benzene ring. 1938.7, 1872.4, 1797.7 cm⁻¹ were the C-H bond bending vibration bands of benzene ring. 756.5, 697.0 cm⁻¹ were the single substituted derivatives of benzene, simultaneously may also prove that this reaction had generated polystyrene. While the 3441.3 cm⁻¹ band may be attributed to the absorption of the reagent water, approving that the produced polystyrene did not contain impurities.

3.2. SEM and TEM of Microspheres

As shown in the SEM image in Figure 2 and in the TEM image of Figure 3, when the styrene was 10 mL, deionized water was 90 mL, β-CD was 1.25 g, respectively, it could be seen that the microspheres presented a smooth surface and the particle size had a very narrow distribution.

3.3. Effects of the β-CD Dosage on the Size of PS Microspheres

As shown in Figures 4 and 5, increasing the stabilizer dosage could reduce the particle size of polystyrene microspheres, but the particle size uniformity still remained. This is because, on one hand, the inside of β-CD molecule is hydrophobic owing to a large number of carbon-hydrogen bonds and ether bonds, while, on the other hand, the outside of β-CD is hydrophilic due to the large number of hydroxyl bonds. That is to say, the exterior cavity of β-CD is hydrophilic, and the interior cavity of β-CD is hydrophobic. Because of this special structure, β-CD is easy to form inclusion complexes with styrene monomer (hydrophobic objects), so that the solubility of the styrene monomer increased in the water, the initial...
monomer concentration was improved during polymerization, the nucleation was speeded and the time of nucleation was shortened, leading to a smaller particle size. On the other hand, because the β-CD and styrene monomer formed inclusion complexes, resulting in the stabilizing effect of the initial particles increased and the particles cohesion hindered, so that the particle size of polystyrene microspheres became smaller.

In addition, when the β-CD was introduced to the system, the blue opalescence appeared only after several minutes, contrary to that 10 minutes were taken before the blue opalescence appeared without β-CD. As time increased, the blue opalescence will disappear and the solution will become milk-white instead. When the β-CD dosage increased, the time for the system to present as a white emulsion will become shorter, which means that the β-CD can modify the speed of the entire polymerization owing to that the β-CD has an effect on the solubilization of the styrene monomer, making the initial monomer concentration increase and the whole reaction system significantly to be promoted, so that the initial conversion rate increased and the speed of the polymerization reaction was accelerated, as a result the time required for the entire reaction was reduced.

3.4. Effects of the Styrene Monomer Concentration on the Size of PS Microspheres

As shown in Figure 6, increasing styrene monomer concentration could allow a bigger particle size of polystyrene microspheres. This is because when the monomer content is low, the growth of polystyrene microsphere particle is restricted, so the particle size becomes smaller. With the increase in the monomer content, the solubility of the new generated nuclei increased in the system, polymer chain was got longer and the population of the formed-primary particles was decreased, that is, more monomers reacted at less active centers, so the diameter of the microspheres increased.

3.5. Effects of the KPS Dosage on the Size of PS Microspheres

As shown in Figure 7, increasing KPS dosage could reduce the particle size of polystyrene microspheres. This is because when the KPS dosage was very low, the free radicals concentration in the system was greatly reduced, the reaction to initially form reactive centers reduced and the nucleation extended, so the particle size of PS
microspheres increased. With the increase of the KPS dosage, the free radicals concentration in the system greatly increased, the reaction to initially trigger reactive centers increased, which made the monomers react at more active centers for polymerization and therefore, to form more small particles with small size.

4. CONCLUSIONS

Monodisperse polystyrene microspheres were prepared by soap-free emulsion polymerization method. By changing the monomer concentration, initiator dosage and stabilizer dosage, the particle size of the microspheres could be controlled from 100 nm to 400 nm, and the particle size uniformity unchanged. The results showed that the increase in monomer concentration can bring about a bigger size of the polystyrene microspheres, whereas the increase in stabilizer dosage or initiator dosage can reduce the size of the polystyrene microspheres. Moreover, the β-CD, as a stabilizer, not only changes the size of the microspheres, but also accelerates the polymerization reaction speed and therefore, shortens the time required by the whole system. In addition, the cost is not high and has less pollution. From above, the β-CD is the ideal choice of the stabilizer. Recently, PS and various nanoparticles have found application in biomedical and many other fields, our research provides people a cost-effective approach with details to prepare PS nanoparticles good in quality.

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References and Notes
