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Review on Preparation of Polystyrene Microspheres

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Abstract. The traditional preparation methods of polystyrene microspheres are emulsion polymerization and suspension polymerization. The diameter of the microspheres prepared by the former is generally less than 0.5 μm, and the diameter of the microspheres prepared by the latter is about several hundred microns and is difficult to control. With the continuous development of science and technology, scientists have found multiple methods to prepare micron-sized monodisperse polymer microspheres in recent years. Such as soap-free or low-soap emulsion method, dispersion polymerization method, liquid-phase synthesis method. The four preparation methods of dispersion polymerization, emulsion polymerization, liquid-phase synthesis, suspension polymerization and their respective advantages and disadvantages are discussed in detail, and the prospect of synthetic application is prospected.

Keywords: Dispersion Polymerization, Polystyrene Microspheres, Emulsion Polymerization, Liquid-phase synthesis, Suspension Polymerization.

1. Introduction

In 1971, Vanderhofl and Brodford first reported the preparation method of polystyrene (PS) microspheres with narrow particle size distribution [1-2]. The preparation and research of polymer microspheres have become a new field of polymer science.Polystyrene microspheres have excellent relative stability, strong hydrophobicity, low adhesion and excellent performance, as well as low production costs. And in recent years, functionalized polystyrene microspheres have been widely used in various fields such as immunoassays, high throughput drug screening, biological probe and microelectronics technology [3-5]. However, how to synthesize PS microspheres with controllable particle morphology, surface features and density and develop new monomers, stabilizers, initiators and dispersion media for the preparation of microspheres to prepare PS microspheres with special functions. These are questions that are still being studied intensively in the field of synthetic PS microspheres. At the same time, in the field of polymer microspheres, people are actively seeking methods to prepare micron-scale PS microspheres with uniform particle size distribution and controllable particle morphology and surface characteristics. In this paper, starting from the preparation method of micron-scale PS microspheres, the latest research progress in recent years is reviewed.

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2. Method for preparing polystyrene microspheres

2.1. Emulsion Polymerization

The one of most common methods for preparing PS microspheres is emulsion polymerization. However, the disadvantage of the emulsion polymerization method is that it is difficult to synthesize monodisperse macromolecular microspheres with a large particle size, the particle size of which is generally less than 0.5 μm.

In this article, Prepare 60 ml of deionized (DI) water in a 250 ml round-bottom flask and disperse approximately 0.1 g of sodium dodecyl sulfate (SDS) in it. Add 10 g to the round bottom flask and sonicate the flask for 10 min. After that, add 0.03 g KPS in it. At 80°C, the reaction mixture was refluxed under nitrogen atmosphere for 6 hours, and demulsified with anhydrous $CaCl_2$ after the reaction was completed. Filtering to get precipitate, the pellet is then washed repeatedly washed with deionized water and methanol. Finally, the washed precipitate was placed in a vacuum oven at 60°C overnight to give the final product as a white powder. [6] The polystyrene microspheres they prepared had an average diameter of 69 nm.

In [7], a similar method was used to prepare PS microspheres with an average particle size of about 35 nm and good dispersion.

2.2. Dispersion Polymerization

A variety of monomers, easy to control, and easy to obtain uniformly dispersed polymer microspheres can be synthesized by dispersion polymerization. It is the main method for the synthesis of monodisperse, micron-sized polystyrene microspheres [8].

In reference [9], Prepared with St 20mL, AIBN0.2g, PVP1.50g, EtOH95mL, H_2O3mL as raw materials. Then, PVP(1.50g), EtOH(95mL)and Deionized Water(3mL) was added to a 250mL four-necked flask equipped with mechanical stirring, a condenser tube and a nitrogen inlet and outlet, stirred at a rate of about 120r/min, and nitrogen was passed for 15min, and then placed at 70°C. Ready to use in water bath. In addition, a predetermined amount of St and AIBN were weighed into the beaker, and after shaking and dissolving, they were added to a four-necked flask to maintain stirring and N_2 flow, and the reaction was performed for 12 h, and the cooling was terminated to obtain an emulsion product. The emulsion obtained by the reaction was centrifuged at 4000 r/min, the supernatant was poured out, anhydrous ethanol was added to disperse by ultrasonic, and then centrifuged again; this was repeated three times to remove unreacted monomers and dispersion stabilizer. Finally, it was dried under vacuum at 60 °C for 8 h to obtain PS microspheres as a white powder product.

In order to simplify the experimental operation, conduct a series of comparative experiments and reduce the difference in system operation, a single-neck round-bottom flask was used as the reactor in Reference [10]. After nitrogen purging and feeding, the flask was sealed and placed in an electric constant temperature shaking tank to start the polymerization . The Polymerization starts at 70 °C, the shaking frequency was 80 r/min, and the reaction was carried out for 24 hours, and the comparative experiments could be carried out simultaneously in an electric constant temperature shaking tank. After the synthesis was completed, the obtained product particles were repeatedly washed with ethanol and water in a centrifuge, and finally dried at 60 °C under vacuum for 8 h to obtain polystyrene microspheres.

2.3. Liquid-phase synthesis

The temperature required for liquid-phase synthesis is much lower than that of solid-state synthesis, and can generally be carried out below 300 °C [10]. Cationic PS particles with positive zeta charge were produced using (2,2-azobis(isobutyra-midine) dihydrochloride (AIBA)) as the cationic initiator. The polymerization was performed using a batch reactor system under nitrogen atmosphere with stirring at 600 rpm and heating to about 60°C. When the reactor is under anaerobic conditions, styrene monomer is added to the reactor for polymerization, and the dispersion of styrene is kept uniform during the polymerization process. When the reaction is sufficient, bringing the temperature of the liquid down to room,and finally the product polymer is obtained Styrene Microspheres[11-14].

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2.4. Suspension Polymerization

Suspension polymerization is the methods for producing polystyrene microspheres [15]is described that BPO is used as the initiator, and the mass ratio of initiator to styrene is controlled to be 1.5:100 to obtain the best microspheres. Pour 0.2 g gelatin, 0.3 g SDBS, and 100 mL deionized water into a 250 mL flask equipped with thermometer, condenser, and an anchor stirrer. The resulting mixture was heated and stirred for 10 minutes at 40°C. And the purpose of this is to fully disperse them. Then, the dispersed product was added to styrene (22 mL) along with an appropriate amount of BPO. After 15 minutes of nitrogen purging, the mixture was heated to 85°C with stirring for 12 hours. The product was washed twice with alcohol and deionized water. Finally, the polystyrene microspheres were placed in a vacuum oven at 50 °C to dry.

However, these microspheres produced by traditional suspension polymerization methods are generally 100-1000 μm in size and polydisperse.

In this study [16] by improving the reaction conditions, monodispersed PS microspheres with a particle size of about 40 μm were prepared by suspension polymerization. The synthetic steps in as follows. Take a certain amount of water, A certain amount of hydroxyethyl cellulose was added under stirring, and the stirring was continued for 24 h and the resulting solution is clear; take another certain amount of water and heat it to 50 °C, add a certain amount of gelatin under constant stirring, dissolve and cool to room temperature; Prepare a certain amount of sodium chloride solution, and then mix the above three solutions to make an aqueous phase. The aqueous phase was added to a three-necked flask with a stirrer, a condenser tube and a nitrogen-passing tube, 30 g of St and 1.2 g of DVB were mixed, and 0.3 g of benzoyl peroxide was added to it under stirring, and then A certain amount of toluene and heptane were added to form the dispersed oil phase; nitrogen was introduced for 30 min to drive off the air; the stirrer was started, the oil phase was added to the water phase, and stirred for 10 min; the rotational speed was adjusted to 500 r/min , heated to 60 °C in an oil bath for 24 h. Finally, when the temperature of the reaction mixture is close to room temperature, filter under reduced pressure, transfer the obtained polymer into a flask containing distilled water, heat to 50° C. while stirring, and filter under reduced pressure while hot after one hour. Repeat this operation until the unreacted monomer and solvent were completely washed away. Using a 70 °C vacuum oven to dry the polymer for 24 h. And the best St suspension polymerization conditions are summarized as follows: maintain a 1:4 volume ratio of organic phase to aqueous phase, At a polymerization temperature of 60 °C and a stirring speed of 500 r/min, a crosslinking agent with a monomer mass fraction of 4%, a dispersant with a water phase volume fraction of 0.6%, and a water phase mass fraction of 20% of the monomer and monomer were used. 1% mass fraction of initiator.

The PS microspheres synthesized by the suspension polymerization method have no impurities on the surface, simple post-processing, no pollution to the environment, and have broad application prospects [16].

3. Conclusion

Polystyrene microspheres have the advantages of excellent mechanical properties, large specific surface area and strong adsorption force, so they have a wide range of application prospects in biomedicine, information engineering, polymer synthesis and other fields. Different methods can prepare polystyrene microspheres with different particle sizes and different excellent properties, and a suitable method can be selected to prepare the required microspheres. The influence of reactive monomers, initiators, dispersants, etc. on the particle size and properties of polystyrene microspheres has also been widely studied recently, and with the improvement of synthesis technology and synthesis raw materials and equipment, the performance is better and the cost is lower. The synthetic route of polystyrene microspheres is expected to be the focus of future research. However, the above-mentioned preparation methods still have many deficiencies and difficulties in preparing micron-scale PS microspheres with uniform particle size distribution, controllable particle morphology and surface characteristics. It has also attracted the attention of more and more scientists.These are all conducive to the expansion and renewal of the application range of polystyrene microspheres.

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