Progress in polystyrene microspheres

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Abstract. The preparation methods of polystyrene (PS) microspheres were reviewed, and the effects of monomer, dispersant, initiator, reaction medium and temperature on the particle size and size distribution of PS microspheres were discussed. Finally, the application prospect of polystyrene microspheres was prospected.

1. Introduction
In 1955, Vanderhoff and Bradford of Lehigh University and USA et al. Successfully synthesized the monodisperse polystyrene microspheres with particle size at 2~30 µm by weight loss. Since then, the preparation of monodisperse polymer microspheres has become a research hotspot. Monodispersed polystyrene microspheres are functional materials with excellent properties, such as high cohesion, large specific surface area, high mechanical properties, strong adsorptivity and surface reactivity. Therefore, they are widely used in the fields of medicine, standard metrology, analytical chemistry and information.

2. Preparation of polystyrene microspheres
The commonly used methods for preparing polystyrene microspheres include emulsion polymerization, Surfactant-free Emulsion Polymerization, dispersion polymerization, seed swelling polymerization, etc. Different methods are suitable for the preparation of microspheres with different particle sizes. Generally, emulsion polymerization and Surfactant-free Emulsion Polymerization are suitable for preparing nanoscale microspheres. Seed Swelling Polymerization and Dispersion Polymerization Suitable for the Preparation of Micron Microspheres. The particle size of microspheres prepared by suspension polymerization is larger, in the order of millimeter, and the dispersion is poor.

2.1 Emulsion polymerization
Emulsion polymerization is a polymerization method in which latex particles are produced in water or other liquids as medium, and micelles or oligomers are used to form latex particles in each other, and radical polymerization or ion addition polymerization is used to produce polymers. The emulsion polymerization method mostly uses water as the medium, so that the viscosity of the system is not high, the heat transfer effect is good, and it will not cause partial overheating. At the same time, emulsion polymerization avoids the use of expensive solvents, resulting in waste. Emulsion polymerization has higher reaction rate than other methods. Polymerization system is mainly composed of hydrophobic monomers, surfactants, emulsifiers (such as sodium dodecyl sulfate), dispersing media (usually water) and water-soluble initiators. Emulsion polymerization is suitable for preparing polystyrene microspheres with particle size of 50~700 nm. Dube et al. Studied the emulsion...
polymerization of BA/MMA/VAc three system. The effects of monomer feed composition, initiator type, initiator concentration, chain transfer agent concentration, emulsifier concentration and temperature on monomer conversion, polymer composition and molecular weight and latex particle size were investigated. Xu Bingwen et al. studied the effect of emulsifier concentration on the formation mechanism of polystyrene microspheres using sodium dodecyl sulfate as emulsifier and potassium persulfate as initiator.

The mechanism of emulsion polymerization is recognized by two kinds. For hydrophobic monomers, when the emulsifier concentration is higher than the critical micelle concentration (CMC), the explanation is based on the theory of micelle nucleation. For monomers with strong hydrophilicity, when the emulsifier concentration is lower than CMC, the homogeneous nucleation theory is used to explain.

2.2 Surfactant-free Emulsion Polymerization

Surfactant-free Emulsion Polymerization means that the emulsifier is added without adding emulsifier or less than the critical micelle concentration in the reaction process. Compared with emulsion polymerization, it is an environmentally clean method for preparing microspheres. The obtained microspheres have good monodispersity, large particle size and close to micron scale, but it is difficult to prepare particles with diameters greater than 1 µm.

Surfactant-free Emulsion Polymerization has been widely applied in the field of colloidal particles, coatings, adhesives, additives for waterborne coatings and so on. Dou K et al. successfully synthesized monodisperse polystyrene microspheres with a particle size between 50~400 nm and emulsifier free emulsion polymerization. Zhu Wen et al. used Surfactant-free Emulsion Polymerization with styrene as monomer and potassium persulfate as initiator, successful preparation of polystyrene microspheres with particle size of 100-200 nm, monodisperse, uniform particle size and good sphericity, the effects of monomer, initiator and temperature on the particle size of microspheres were also studied. The nucleation mechanism of Surfactant-free Emulsion Polymerization can be divided into two types: homogeneous nucleation mechanism and oligomer micelle nucleation mechanism.

2.3 Dispersion polymerization

Dispersion polymerization was first proposed by ICI scientists in the early 1970s. Before the reaction, the system was homogeneous. Monomers, initiators and stabilizers were all dissolved in the dispersing medium. After the reaction started, the resulting polymer was insoluble in the dispersing medium. With the help of steric hindrance, micro-crosslinking or charge interaction, microspheres suspended in the dispersing medium were formed. The dispersion polymerization method is suitable for preparing monodisperse polystyrene microspheres with particle size of 0.5~10 µm.

Stabilizer is an important component of dispersion polymerization. Polymer particles are dispersed in the medium by means of the steric hindrance effect of stabilizers to form a stable dispersion system. The commonly used stabilizers are polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyacrylic acid (PAA), lactic acid and hydroxypropyl cellulose. Wang Guangsheng et al. successfully prepared monodisperse polystyrene microspheres with particle size of 2.22~4.15 µm using PVP as stabilizer, lactic acid as co-stabilizer, dibenzoyl peroxide as initiator and isopropanol/ethanol as dispersion medium. Jeongwoo Lee et al. synthesized monodisperse polystyrene microspheres by dispersion polymerization using amphiphilic initiator (VA-057). Compared with traditional initiators such as AIBN and BPO, the polymerization reaction is more stable and the size of microspheres is more uniform. First, the amphiphilic initiator decomposes faster, so the initial polymerization speed becomes faster and the nucleation time is reduced. Second, the initiator itself can stabilize the primary particles and replace the role of some stabilizers, so more uniform microspheres are obtained.

Dispersion polymerization is generally divided into three stages: nucleation stage, nucleation stage and microsphere growth stage. The nucleation stage follows the homogeneous nucleation mechanism. There are different opinions on the mechanism of nucleation and microsphere growth. There are two
mechanisms widely recognized by researchers, namely the oligomer precipitation mechanism and the graft copolymer coalescence mechanism. The precipitation mechanism of oligomers is that stabilizers gather on the surface of particles by physical adsorption to form a surface hydration layer, which makes it difficult for particles to gather and suspend stably in the medium. The coalescence mechanism of graft copolymer shows that the stabilizer molecules react with oligomers through active hydrogen sites to form graft copolymers. The graft copolymers "anchor" on the surface of polymer particles, thus preventing the flocculation and coagulation of polymer particles in the formation stage. It is generally believed that the above two mechanisms exist at the same time, and the oligomer precipitation mechanism is the main one

2.4 Seed swelling polymerization
The seed swelling polymerization method is to use other polymerization methods, such as soap free emulsion polymerization or dispersion polymerization, to prepare smaller size and monodisperse microspheres as seeds, then swelling the seed microspheres with swelling agent, and then initiating polymerization to prepare monodisperse large particle size (1~100 µm) microspheres.

Vanderhoff\textsuperscript{14} first proposed the seed swelling polymerization method to prepare large size monodisperse microspheres, but due to the use of water-soluble initiator, new microspheres were formed, which made the dispersion worse. Two-step seed swelling polymerization was proposed by Ugelstad\textsuperscript{15} in the 1980s to improve the column efficiency of chromatographic columns. It has better swelling effect and higher efficiency, but the subsequent treatment is relatively cumbersome. Subsequently, Okubo\textsuperscript{16} proposed the dynamic swelling method in the 1990s. The dynamic swelling method does not need any swelling agent, but uses monomer and initiator to further swell the seeds directly.

2.5 Suspension Polymerization
Suspension polymerization is a process in which monomers are dispersed into numerous droplets under the action of mechanical stirring and dispersants, usually suspended in water and initiated by oil-soluble initiators.

Suspension polymerization systems are generally composed of hydrophobic monomers, oil-soluble initiators, amphiphilic dispersants and dispersing media. The main oil-soluble initiators are azo initiators and peroxide initiators. Dispersants are divided into organic and inorganic substances, including polyvinyl alcohol; inorganic substances include calcium carbonate, magnesium carbonate, barium sulfate and so on. Suspension polymerization was first proposed by Hoffman\textsuperscript{17} in Germany in the early 20th century. The traditional suspension polymerization method is suitable for the preparation of particles of 100-1000 µm with multi-dispersity. Qi Dongming\textsuperscript{18} et al. successfully prepared polystyrene microspheres with small particle size and narrow distribution by combining ultrasonic homogenization with polymer dispersant when preparing polystyrene microspheres by micro-suspension polymerization. The size of microspheres can be controlled by changing the intensity of ultrasound.

3. Influencing factors of particle size and distribution of polystyrene microspheres
Take the dispersion polymerization method as an example, the effects of monomer content, initiator, dispersion stabilizer and dispersion medium on the particle size and distribution of microspheres were studied.

3.1 The influence of monomer dosage
With the increase of monomer content, the particle size of the prepared polystyrene microspheres increased, the particle size distribution became wider, and the uniformity of the microspheres became worse. The effect of monomer concentration on the particle size of microspheres is mainly due to the solubility of polymer chains in dispersing media. With the increase of monomer dosage, the solubility of polymer chains in dispersing media and monomers dissolved in dispersing media increases, which
increases the critical chain length of polymer, resulting in the decrease of the number of polymer particles and the increase of monomer dosage, so more monomers grow on the core, resulting in the increase of the particle size of microspheres. On the other hand, with the increase of monomer dosage, the reaction rate of polymerization in solution accelerates, the formation rate of oligomer radicals and dead polymers also accelerates, and the relative capture efficiency of particles decreases. Secondary particles in the system cannot effectively capture oligomer radicals and dead polymer chains in the continuous phase. These oligomer radicals and dead polymer chains which cannot be captured in time are from the continuous phase. There may be enough time for the precipitation to combine with enough dispersant to form new secondary particles which can continue to grow. This is called "secondary nucleation" or "multiple nucleation". The existence of "secondary nucleation" inevitably leads to the uneven growth of particles, resulting in the widening of the final particle size distribution. In a sense, the appearance of "secondary nucleation" is equivalent to prolonging the nucleation period of dispersion polymerization, which will lead to the deterioration of the final particle monodispersity and the broadening of particle size distribution.

3.2 Initiator
With the increase of initiator concentration, the particle size of the prepared polystyrene microspheres increased and the particle size distribution became wider. When the dosage of initiator increases, the termination rate of active chain increases with the increase of free radical concentration in the dispersing medium, and the graft chain segments in the stabilizer grafted copolymer molecules become shorter, which makes it easier to dissolve in the medium and slows down the adsorption rate to the polymer particles. Moreover, because of the high rate of free radical production and the fast nucleation rate in the initial stage, the absorption rate of stabilizer cannot keep up with it, which reduces the stabilization effect on particles, and the phenomenon of agglomeration among particles is serious, resulting in the reduction of the number of secondary particles and the increase of particle size. At the same time, due to the decrease of the number and total surface area of particles, the capture efficiency of free radicals and dead polymer chains of aligned particles is affected. It is easy to nucleate twice, and the coalescence of particles makes the particle size distribution wider.

3.3 Dispersion stabilizer
With the increase of the dosage of dispersing stabilizer, the particle size of microspheres decreases and the particle size distribution narrows. In the process of polymerization, the amount of dispersant is less stable, the initial microspheres are not stable enough to agglomerate easily, so the size of microspheres becomes larger. When the content of dispersing stabilizer increases, the concentration of dispersing stabilizer around the microspheres increases, the medium viscosity increases, the resistance of collision between microspheres increases, and the number of nucleation increases, which reduces the amount of monomers obtained by each nucleating particle, leads to the decrease of microsphere size, effectively inhibits the generation of secondary nucleation and narrows the particle size distribution. When the content of dispersant stabilizer is too high, the viscosity of the system is too high, which will hinder nucleation and nucleation, affect the growth of microspheres, and eventually lead to the widening of the size distribution of microspheres. Therefore, the dosage of dispersing stabilizer should be controlled within an appropriate range.

3.4 Disperse medium
Dispersion media selected for dispersion polymerization must be benign solvents for dispersion stabilizers, and have certain solubility for monomers, but cannot dissolve the synthesized polymer microspheres. The results of Liu Duan et al show that the dispersing medium with good solubility for PS is beneficial to the synthesis of microspheres with large particle size and narrow distribution. Water is an inert solvent for PS, so the addition of water will reduce the solubility of dispersing media, resulting in smaller particle size of the synthesized microspheres. The use of ethanol instead of methanol as a dispersing medium improves the solubility of polymer chains, increases the critical
chain length of polymer chains, decreases the settling rate of polymer chains, and decreases the number of nucleation. Finally, monodisperse microspheres with larger particle size are obtained.

4. Summary and Prospect
Monodisperse polystyrene microspheres, as a functional material with excellent properties, have attracted wide attention from researchers at home and abroad because of their strong adsorption, large specific surface area, high mechanical properties and strong surface reaction. It has shown very important application value in biomedicine, information engineering, chromatographic fillers, supercapacitor electrode materials and other fields. It is anticipated that the future research focus of monodisperse polystyrene microspheres will focus on the following points: (1) To explore a simpler preparation method and synthesize polystyrene microspheres with uniform particle size, good dispersion and high yield; (2) To develop new preparation technology or improve existing technology in order to obtain functional microspheres with better performance; (3) To further expand the application scope of microspheres.

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