Progress in Preparation of Monodisperse Polymer Microspheres

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Abstract. The monodisperse crosslinked polymer microspheres have attracted much attention because of their superior thermal and solvent resistance, mechanical strength, surface activity and adsorption properties. They are of wide prospects for using in many fields such as biomedicine, electronic science, information technology, analytical chemistry, standard measurement and environment protection etc. Functional polymer microspheres prepared by different methods have the outstanding surface property, quantum size effect and good potential future in applications with its designable structure, controlled size and large ratio of surface to volume. Scholars of all over the world have focused on this hot topic. The preparation method and research progress in functional polymer microspheres are addressed in the paper.

1. Introduction

In the vast universe there are numerous super balls like the sun, the earth which keep moving. And there are many small balls, such as football, basketball, volleyball and other balls. The size of these sports balls are mostly decimeter (dm), and the size of the sand are millimeter (mm). If the sand shrinks thousands of times, the size will become nan-scale (10^{-6}mm), and the naked eye is difficult to distinguish the microspheres. Polymer microspheres are polymer particles or polymer composite particles having a particle size in the order of nanometers to microns (typically 10^{-5}-10^{-2} mm) and shaped like spherical or other geometries.

Monodisperse polymer microspheres are those that have uniform particle size and are stable. Monodisperse micrometer microspheres are functional polymer materials with strong adsorption, large specific surface area and surface reaction ability. They are widely used in standard measurement, intelligence information, analytical chemistry, biomedicine, colloid science and chromatographic separation. It has a wide range of uses, especially in some high-tech areas (such as liquid crystal display, drug and catalyst carrier, etc.), so the study of such materials attracted more attention.

2. Monodisperse polymer microspheres

The traditional methods of preparing polymer microspheres are emulsion polymerization and suspension polymerization, the former can only prepare particles less than 0.5μm, and the latter in the size of 100-1000μm. Monodisperse particlals are difficult to prerare and contro by these two methods. In 1955 Vanderhoff Brodford succeed to synthesize monodisperse polystyrene microspheres with a particle diameter of 2-30 μm using the of emulsion polymerization in weightless state. The
development of polymer science has opened up new research areas, but this method is too expensive to achieve industrialization promotion. Vanderhoff followed by continuous seed polymerization, 1-10μm polymer microspheres were synthesized by two-steps swelling, but the steps were long and inconvenient. Soap-free or low-soap emulsion polymerization can prepare a monodisperse polymer microsphere with particle size close to 1μm, but for many applications the scale is too small. Since 70 years, foreign scholars have developed a variety of effective synthesis methods, such as dispersion polymerization, suspension polymerization, modified precipitation polymerization method, distillation-precipitation polymerization method to obtain 1-10μm particle size and monodisperse polymer microspheres.

2.1. Soap-free emulsion polymerization
Emulsion polymerization is the most commonly used microsphere preparation method which microspheres are uniformly dispersed in water to form a very stable polymeric emulsion. Emulsion polymerization system was generally comprised by the monomer (such as styrene), water (dispersion medium), water-soluble initiator and emulsifier (such as sodium dodecyl sulfate) and other four parts. The polymerization consists mainly of three stages: in the first stage, the free radicals enter the monomer micelles to swell and the nuclei swell the monomer to form micelles. In the second stage, the monomer droplets diffuse into the aqueous phase, and then generate the nuclei to absorb and polymerize, the nucleus continues to grow into microspheres until the oil droplets disappear; in the third stage, the monomer microspheres continue to converge until the reaction ends. The nuclear reaction ends in a short period of time during the use of nuclear growth [1]. Therefore, the main advantage of emulsion polymerization is the convergence rate. Dozens of nano-microspheres can be more easily got, and micro-ball system is very good dispersed.

However, the emulsion polymerization product contains emulsifiers that are difficult to completely remove and affect the performance of the product. And the volume of the emulsion polymerized particles is small, so its application is limited. With the development of polymerization technology, the demand for polymer emulsion products is increasing. Emulsion polymerization technology develop many new emulsion polymerization methods such as soap-free emulsion polymerization, microemulsion polymerization, fine emulsion polymerization, inverse emulsion polymerization Technology [2].

Soap-free emulsion polymerization refers to the absence of emulsions for emulsion polymerization or only tracking emulsifiers, but the effects of some emulsifiers are completely different from conventional emulsion polymerization. On the polymer chain or end groups, the ionic groups and the hydrophilic groups are bonded together to stabilize the latex particles. Microspheres are characterized by monodisperse dispersion of soap-free emulsions, and the size of the microspheres is greater than that of conventional emulsion polymerization. (1) The surface of the microspheres is "clean", avoiding many of the drawbacks of conventional emulsion polymerization, such as the consumption of emulsifiers, rather than being completely removed from the polymer, so that the surface of the microspheres is "clean". Opposed to conventional emulsion polymerization processes which affect the purity and performance of the product. (2) The surface hydrophilic functional groups can also be prepared on the core shell hydrophobic-hydrophilic microspheres. (3) Latex particles are well dispersed, and the particle size is larger than the traditional emulsion polymerization. The size can be approximated to the micron level. The disadvantage of this method is that the polymerization rate is slower and the solids content is low. The micrometer size of the monodisperse polymer microspheres can be aggregated by soap-free emulsion, and the particle size is also small for many applications.

Soap-free emulsion copolymerized styrene and various hydrophilic monomers such as acrylamide (AAM), hydroxyethyl methacrylate (HEMA), N-acryloylpyrrolidine (APr), etc. which were studied by Kawakuchi. When the hydrophilic copolymer monomer N-acryloylpyrrolidine (APr) is used, if the temperature of polymerization is low, the microspheres show a three-layer structure, and inner layer and the outer layer the core are mainly composed of APr-shell structure microspheres.
2.2. Multi-step seed polymerization
The seed polymerization is a seed of a small particle size monodisperse polymer particle that is polymerized or dispersed by polymerization or dispersion polymerization. With the monomer, the crosslinking agent, the inert component swells, the particles become larger, and then polymerized, thereby making the large diameter monodisperse polymer microspheres. According to different methods, the seed polymerization method can be divided into conventional expansion method, gradual expansion method, activation and expansion method, dynamic expansion method and droplet expansion method. The conventional puffing method is limited in the amount of adsorbed monomer, and the particle size of the particles is relatively small. This gradual expansion of the process can produce new small particles at each step, resulting in the gradual dissolution of the individual dispersed polymer microspheres.

Ugelstad et al. have developed an activated swollen seed agglomeration method, which opens up a new milestone seed polymerization [3]. The specific method is to use a certain molecular weight oligomer or low molecular weight compound (such as 16 alkane) swollen seeds, and then swell and polymerize the monomer and initiator to obtain the large diameter of the monodisperse microspheres. The use of this technique to activate the swelling, can be porogen, crosslinking agent and functional monomer into the seed microspheres to prepare porous microspheres, cross-linked microspheres, and other functional groups with microspheres.

Okubo [4] has developed a method of swelling in order to disperse the development of seed polymerization. In this method, the monodisperse polymerized microspheres with particle size are prepared by dispersing the polymerization method, and then seed polymerization is carried out by dispersing polymerization. First, the seeds of microspheres, monomer, hydrophobic initiator dispersed in the alcohol / water medium, and then slowly dripping, so the monomer in the solubility reduction, forcing more monomer polymer particles, the last warming polymerization. The gradually reduced monomer was dissolved in a continuous stage, and the 1.8 μm seed could multiply by 100 times the monomer to obtain 6.1 of polystyrene microspheres. Cao Tongyu found that the key to success is the dynamic swelling method of adding water. If the water drops directly, the stability of the system instantaneously decline, which is due to excessive water, and the formation of new particles. In order to overcome these shortcomings, water and solvent in the polymer particles are generally used in the semipermeable membrane which cannot pass through the water, so that the system of water slowly increased [5].

Omi et al. developed a droplet swelling method, and homogenized hydrophobic seed droplets were prepared by SPG (Shirasu Porous Glass) membrane emulsification method, and homogeneous emulsifiers were used to prepare secondary small droplets with strong hydrophilicity. After mixing the two, the secondary droplets are small, nonuniform and hydrophilic, and the monomer is rapidly dissolved in the aqueous phase and absorbed by the seed droplets. The advantages of this swelling method are as follows: first, only one step polymerization process, swelling speed, swelling large; second, uniform size of the porous, high degree of cross-linking or other functions of the polymer micro ball can be easily prepared. During the preparation process, the hydrophobic additive may be added to the droplet seed, and the hydrophilic functional monomer may be added to the secondary droplets. With this effective polymerization method, uniform microspheres having a particle size of at most 100 μm or more can be prepared.

2.3. Glass film emulsification method
Glass film emulsification is a new method to prepare monodisperse microspheres, which is combined with SPG membrane emulsification and suspension polymerization. The oil phase containing the hydrophobic initiator is first pressed into the aqueous phase through a glass membrane and then subjected to suspension polymerization in a suitable environment. Because the aperture of the SPG membrane is very uniform, the particle size of the oil droplets is also very uniform (the variation coefficient of the particle diameter is about 10%). Microspheres having a particle size of 3μm m to 100μm or more can be prepared by glass film emulsification.
The advantages of the preparation of microspheres by glass film emulsification are as follows:
1. Biodegradable polymer microspheres that cannot be achieved by free radical polymerization can also be synthesized by this method;
2. Functional polymer microspheres with high embedding rate were prepared;
3. The diameter of the microspheres is controlled by the membrane pores with high experimental reproducibility;
4. Do not use organic solvents, no pollution, green;
5. The modified SPG membrane can be used for the preparation of hydrophilic natural macromolecule materials such as natural polymer aqueous solution, microspheres and microcapsules for emulsifying proteins and polysaccharides.

The preparation of microspheres is preceded by the preparation of microspheres by the glass film emulsification method and the use of special equipment in the emulsification process. Therefore, the cost of this method is high.

3. Dispersion polymerization method
Dispersion polymerization is a widely used polymerization method for obtaining a formically controllable polymer dispersion system, which was first proposed by ICI researchers in the 1970s. Dispersion polymerization can be easily synthesized by one-step method to obtain particles with a particle size of 0.1 microns to tens of microns. This monomer is widely used, so it has great application prospect, especially the success of polar medium in the 1980s Polymerization, attracting people's attention; in the 90's supercritical CO2 media dispersion polymerization solved the solvent reaction medium pollution of the environment. Therefore, in recent decades, the research and application of decentralized basic research has shown a vigorous development trend.

Dispersed polymer system features:
1. Low viscosity, no wire drawing, drying rate, not to rust and deformation of the substrate, can be used in low temperature environment, have better construction performance;
2. The polymer particles have a good spherical shape, narrow particle size distribution, large particle size (compared with emulsion polymerization) and other characteristics;
3. Low toxicity and the use of hazardous dispersion media to reduce environmental pollution, so it is particularly suitable for the preparation of various types of coatings, dyes and so on.

4. Precipitation polymerization method
The control of the size of the polymer microspheres and the control of the particle size distribution of the polymer microspheres are difficult. These two technical difficulties exist in the process of micron monodisperse polymer microspheres. Conventional methods for preparing polymer microspheres include suspension polymerization, emulsion polymerization and dispersion polymerization. However, in the conventional process, it is necessary to use a surfactant such as polyvinylpyrrolidone (PVP) or a dispersion stabilizer in the preparation of the polymer microspheres which make it difficult to control the particle size and particle size distribution of the microspheres. The 1993 precipitation polymerization method was developed by Stover et al., Which is a novel method for preparing monodisperse, particle size homogeneous microspheres. The system does not add any emulsifier and stabilizer, and the polymer microspheres are precipitated in the form of precipitates by simply shaking the reaction system. The most significant advantage of the precipitation polymerization method is the preparation of high cross-linking polymer microarray because of the addition of more crosslinking agents in the precipitation polymerization and the crosslinking agent plays a crucial role in the formation of the polymer microspheres ball.

5. Distillation - precipitation polymerization method
On the basis of precipitation polymerization, a distillation-precipitation polymerization method was developed, which began to react in the homogeneous system containing monomer and initiator. The solvent in the system was distilled off to form a monodisperse polymer microsphere system. The
surface prepared by the distillation-precipitation method is smooth and has regular spherical particles and the particle size can be controlled within a certain range. The nanometer / micrometer microsphere resin prepared by this technique is used as a carrier for the drug release and catalyst, a column packing, an optical array material, and a solid phase carrier as an immobilized biomolecule such as a biological enzyme, an antibody, etc. And other aspects have been widely used.

The following two types of monodisperse polymer microspheres can be easily prepared using a distillation-precipitation polymerization method: (1) monodisperse polydivinylbenzene or (poly)ethylene glycol dimethacrylate and its copolymer micro (2) two-step distillation-precipitation polymerization method for the synthesis of nuclear high cross-linked, shell is low cross-linked and contain different functional groups of monodispersed core-shell polymer microspheres.

6. Polymer microspheres
Large particle size monodisperse polymer microspheres have many characteristics, such as multifunction, high performance, different molecular weight, different structure, different surface characteristics and functions. Therefore, they can be applied in many fields, especially in some high-tech fields of the application prospects, at present, many of the world's advanced countries are exploring the development of polymer microspheres in its various fields of application:

(1) Polymer microspheres have been widely used in the field of medicine and biochemistry [16]. The encoded monodisperse polymer microspheres can be used for biological detection. Magnetic polymer microspheres can be combined with a variety of functional molecules to meet the different requirements, due to the role of magnetic field microspheres which can be targeted to a specific location or from the surrounding media quickly separated. These properties make it widely used in the fields of immobilized enzymes, immunoassays, cell isolation and classification.

(2) In the field of electronic information, gold-plated microspheres can be used as conductive particles of the isotropic conductive film, so that the electrode spacing is small, the combination is more reliable, the assembly is easier [17]. Monodisperse polymer microspheres can also be used as interstitial carriers between liquid crystal chips, which are applied between wafers to precisely control and maintain the spacing, thus greatly improving the clarity of the liquid crystal display.

(3) Polymer microspheres can be used as high-grade paint, the rheological properties of paint to facilitate control; can be used as a cosmetic lubricating material, can improve its adhesion and sweat absorption [18]; can also be used as electronic printing photographic materials and photoelectric toner [19]. In addition, the polymer microspheres are used for electrophotographic developer and toner, room temperature curing printing inks and photoconductive printing inks and the like.

(4) Monodisperse polymer microspheres with particle size in the range of 2-10μm can be used as high performance liquid chromatography fillers, which can not only reduce the column pressure but also improve the column efficiency remarkably. If the surface of the polymer microspheres is modified, such as according to the specificity of the enzyme-substrate, antigen-antibody, and hormone-receptor, one is immobilized on the surface of the microspheres, then high selectivity affinity chromatography filler, which in the separation and purification of biological components has a very important application value.

(5) Monodisperse micrometer microspheres can be used as standard particles for instruments such as electron microscopy, optical microscopy and Coulter particle size analyzers. They can also be used in the study of colloid and polymer emulsions and the determination of semipermeable membrane pore size. In addition, electronic industry testing equipment is also commonly used monodisperse micron-scale polymer microspheres as the standard material.

(6) In the field of environmental protection, polymer microspheres, especially molecularly imprinted microspheres, can be used as enrichment, separation and analysis of some kind of pollutants in natural water.

References
[1] G.H. Ma, Z.G. Su, Polymer microsphere material. Chemical Industry Press, Beijing, 2005, pp.
314-319.

[2] T.Y. Cao, Q.P. Liu, J.S. hu, Principle, Performance and Application of Polymer Emulsion Synthesis. Chemical Industry Press, Beijing, 1997, pp. 78-85.

[3] Y.C. You, B.L. Chang, Z.M. Lin, J.F. Huang, P.D. Ding, Studies on grafting copolymerization of methyl methacrylate onto corn starch and biodegradability of copolymer, Polymeric Materials Science and Engineering. 1 (1994) 33-37.

[4] M. Okubo, M. Shiozaki, M. Tsujihiro, Preparation of micron-size monodisperse polymer particles by seeded polymerization utilizing the dynamic monomer swelling method, Colloid Polym Sci. 26 (1991) 222-226.

[5] T.Y. Cao, B. Dai, J.Y. Dai, Synthesizes and applications of monodisperse polymer microspheres with large size, Polymer Bulletin. 3 (1995) 174-180.

[6] M. Jose, Dispersion copolymerization of styrene and butyl acrylate in polar solvents, J. Polym. Sci. Polym. Chem. 3 (1996) 977-992.

[7] I. Capek, M. Yanriza, Dispersion copolymerization of poly(oxyethylene) macromonomers and styrene, J. Polym. Sci. Polym. Chem.. 3 (1997) 131-139.

[8] T.Y. Cao, B. Ding, J.Y. Dai, Y.J. Wang, C.D. Yuan, Preparation of monodisperse polystyrene microspheres with large size, Acta Polymeric Sinica. 2 (1997) 158-165.

[9] H.T. Zhang, J.X. Huang, B.B. Jiang, X.Q. Li, Studies on kinetics of copolymerization and particle size for preparing monodispersed crosslinked polystere microspheres, Chinese Journal of Applied Chemistry. 18 (2001) 726-730.

[10] T.Y. Cao, B. Dai, J.Y. Dain, Y.J. Wang, C.D. Yuan, Study of stability mechanism and kinetics of dispersion polymerization, Polymeric Materials Science and Engineering. 14 (1998) 31-34.

[11] H.T. Zhang, B.B. Jiang, J.X. Huang, Crosslinked polystyrene microsphere preparing by non-aqueous dispersion polymerization-effect of monomer content on polymerization rate and particle size, Polymeric Materials Science and Engineering. 18 (2002) 57-61.

[12] Y.J. Wang, J.M. Liu, C.D. Yuan, Chinese Chemical Society, Beijing, 8 (2000) 89-94.

[13] X.P. Chen, K.Y. Qiu, Study of “living” /controlled radical polymerization, Progress in Chemistry. 13 (2001) 224-233.

[14] C.H. Ho, S.A. Chen, Dispersion polymerization of styrene in alcohol media: Effect of initiator concentration, solvent polarity, and temperature on the rate of polymerization, J. Polym. Sci. Polym. Chem. 3 (1997) 207-215.

[15] S.F. Li, X.L. Yang, W.Q. Huang, Polystyrene N,O-diacyl-N-sulfonyl hydroxylamine. A new double- acyl transfer reagent for synthesis of the amide library, Chinese Journal of Organic Chemistry. 5 (2005) 59-64.

[16] X.Y. Lu, D. Huang, X.L. Yang, Preparation of monodisperse poly (divinylbenzene-co-acrylonitrile) microspheres by distillation precipitation polymerization, Acta Polymerica Sinica. 3 (2007) 103-107.

[17] L.R. Ma, Y.Q. Liu, Preparation and properties of Immunomicrosphere, Current Immunology. 1 (1982) 59-64.

[18] K. Zhang, Q. Fu, Y.H. Huang, D.H. Zhou, L.X. Jiang, Preparation of crosslinked polystyrene microspheres in anisotropic conductive films, Insulating Materials, 1 (2005) 14-16.

[19] S.J. Li, T. Yu, Z.Z. Shao, S.K. Fu, Hydroxyl terminated polysiloxane modified epoxy resin prepared by dispersion polymerization, Thermosetting Resin. 1 (1997) 8-11.