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RESEARCH ARTICLE

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Poly(styrene-acrylic acid) magnetic polymer microspheres

Abstract Magnetic polymer microspheres have been considered as a kind of new biopolymer materials with great advantages in bioseparation engineering and biomedicine engineering because they have not only polymer functional groups but also magnetic characteristics. Styrene-acrylic acid copolymer (p(S-AA)) magnetic microspheres were synthesized by dispersion polymerization with Fe_3O_4 as core and p(S-AA) as shell. The microspheres were characterized by SEM, size analysis, molecular weight and solid content measurement. All of them indicate that the microspheres are small in size, narrow in distribution, stable in chemistry and rich in functional groups on their surface.

Keywords poly(styrene-acrylic acid), microspheres, dispersion polymerization, magnetic fluid

The method of targeting drug delivery by magnetic polymer microspheres has been developed by the ICI company of Britain since the 1970s and research on magnetic polymer microspheres as a new drug delivery approach has become one of the active fields in drug research and development. Magnetic polymer microspheres are particles which possess magnetic response characteristics. The particles can be endowed with some functional groups (such as –OH, –COOH, –CHO, $–NH_2$ etc.) by copolymerization and surface modification. They can be separated easily in outer magnetic fields and the separation is faster and cheaper compared with traditional separation methods. Magnetic polymer micropheres can be moved in a fixed direction in an outer field and this is favorable for use in cell separation, enzyme immobilization, immune disease diagnosis, tumor targeting treatment, DNA separation and nucleic acid crossbreeding [1]

Dispersion polymerization is a special precipitation polymerization occurring in a homogeneous system involving monomers, stabilizers and initiators before reaction. When the length of the polymer chains increases up to its critical value, the polymer will precipitate and form small particles suspended in the reaction medium with the aid of stabilizers [2]. In order to increase the adsorption of functional monomers on the magnetic fluid, acrylic acid (AA) and styrene (S) were used as monomers to form a core-shell structure by dispersion polymerization which is useful for ligand bondage [3].

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1 Experiments

1.1 Materials

Styrene (Beijing Chemical company) acrylic acid (Shanghai Chemical Limited Company), polyethylene glycol (PEG4000, Beijing Chemical Reagent Company), ethylene glycol, ethanol, potassium persulfate were used as received.

1.2 Preparation of p(S-AA) magnetic polymer microspheres

The microspheres were synthesized by dispersion polymerization [4] with Fe_3O_4 magnetic particle as core and styrene-acrylic acid polymer as shell. The monomers are styrene and acrylic acid and the dispersion media are anhydrous alcohol and distilled water. The initiator is inorganic potassium persulfate. 0.1 g of magnetic fluid was dispersed in 30 mL of PEG4000 (50%) aqueous solution, then scattered by ultrasound for 30 min. 30 mL of anhydrous alcohol and 6 mL water were added into the mixture. The mixture then was transferred into a 250-mL 3 mouth flask with a stirrer, a cooling pipe and N_2 pipeline, and stirred for 30 min at 75°C under nitrogen. Then, 20 ml styrene and 5 mL acrylic acid were added into the reaction mixture and reacted for 8 h. The reactant was separated and washed by distilled water.

1.3 Characterizations

Gravity analytical method was used to measure the solid content. The molecular weight was measured by

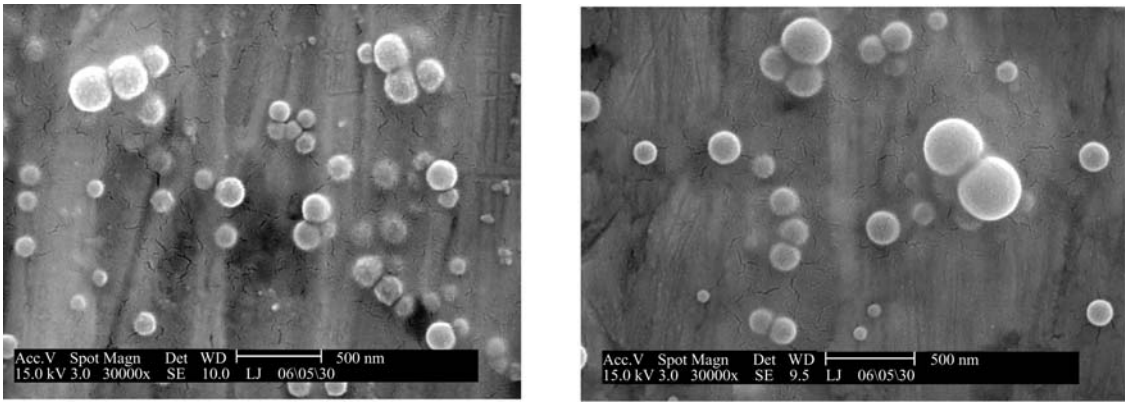

Fig. 1 SEM images of poly(styrene-acrylic acid) magnetic polymer microspheres

viscometry. The SEM images of the microspheres were obtained with a microscope (XL-30, American FEI company)

2 Results and discussion

2.1 The appearance of magnetic polymer microspheres

The size and appearance of magnetic polymer microspheres were determined with SEM as shown in Fig. 1. The styrene-acrylic acid polymer microspheres appear globular and regular with no damage. The average diameter of particles is about 200 nm.

2.2 Analysis of the solid content

The solid content of the microspheres was carried out by gravity analytical method and the results are shown in Figs. 2–5. The solid content increases with increasing amount magnetic fluid and monomers which means the transfer ratio is also increasing. The solid content decreases with increasing amount of anhydrous alcohol which means an increase in the solid dissolving reference.

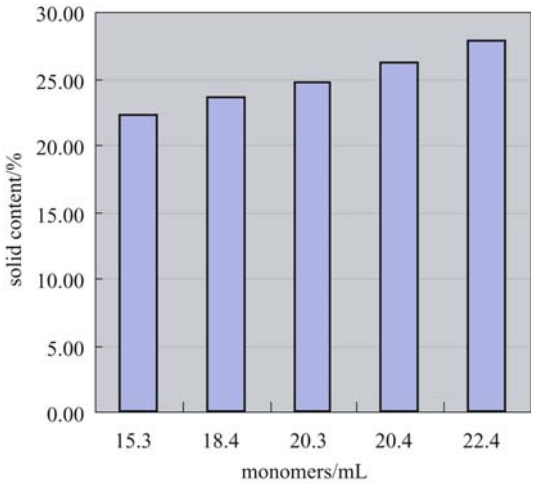

Fig. 3 The effect of the monomer amount on the solid content of the microspheres

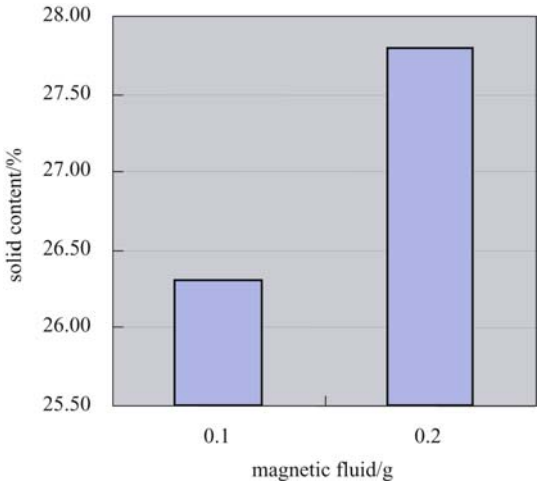

Fig. 2 The effect of the magnetic fluid amount on the solid content of the microspheres

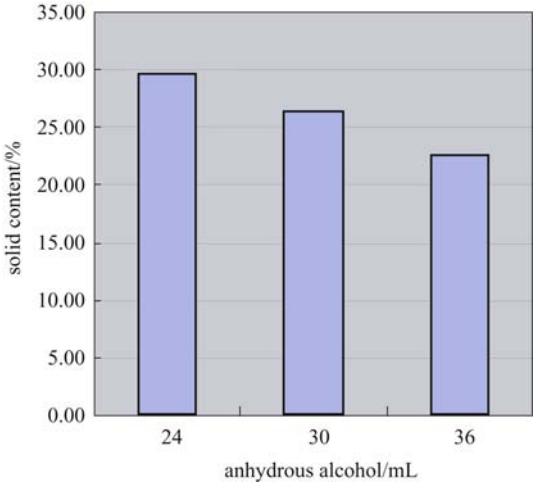

Fig. 4 The effect of the alcohol amount on the solid content of the microspheres

The solid content increases with increasing amount of stabilizer which means the stabilizer functions well to stabilize the dispersion polymerization and increase the transfer ratio of the monomers.

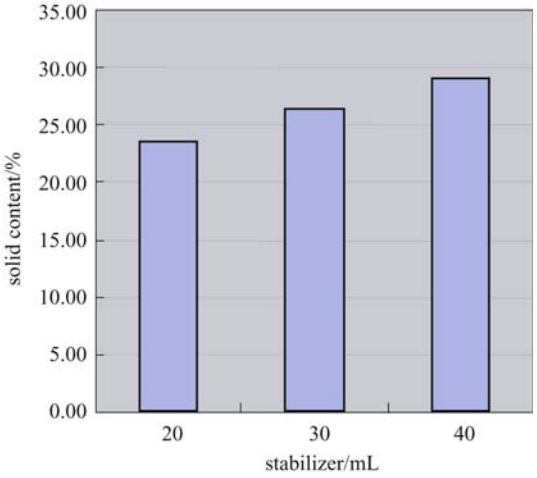

Fig. 5 The effect of the stabilizer amount on the solid content of the microspheres

2.3 Molecular weight analysis

The changes of molecular weight of the polymer with the magnetic fluid, monomer, anhydrous alcohol and stabilizer amount are shown in Figs. 6–9. The molecular weight of the polymer decreases with increasing amount of the magnetic fluid. This means that the number of polymerization points increase leading to a decrease in the molecular weight. The molecular weight of the polymer increases with increasing monomer amount. On the other hand, it decreases with increasing amounts of anhydrous alcohol and stabilizer.

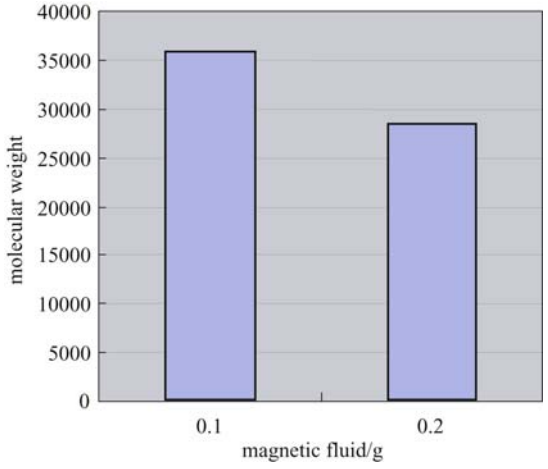

Fig. 6 The effect of the magnetic fluid content on the molecular weight of the polymer

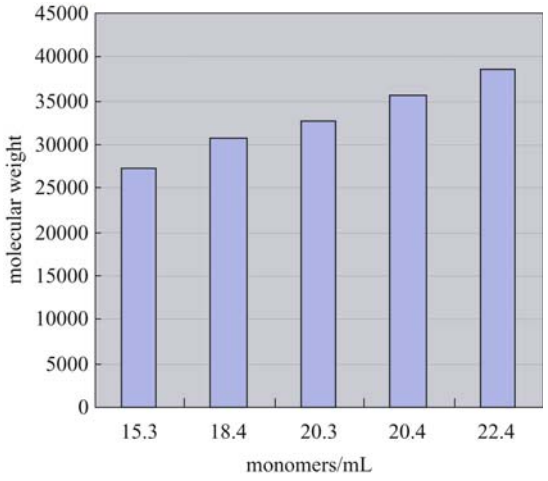

Fig. 7 The effect of the monomer content on the molecular weight of the polymer

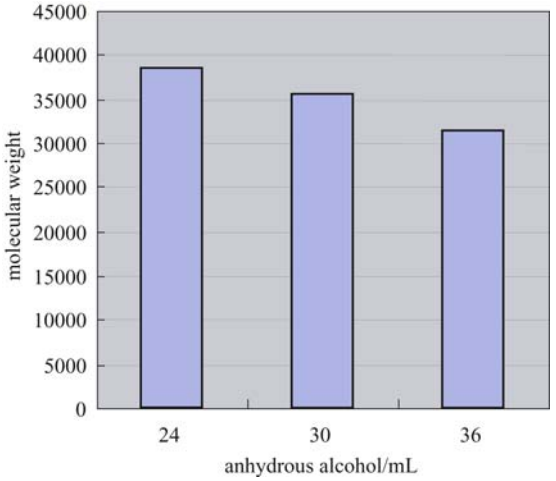

Fig. 8 The effect of the alcohol content on the molecular weight of the polymer

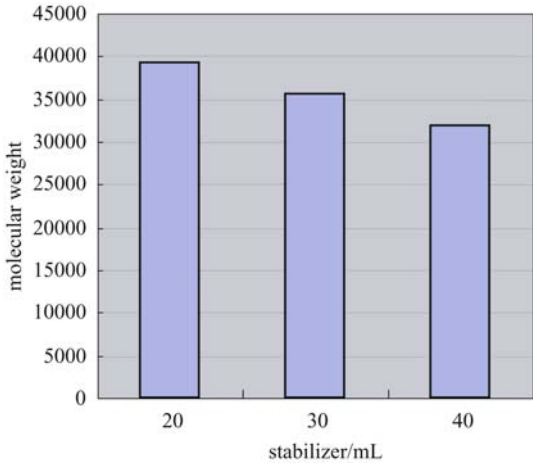

Fig. 9 The effect of the stabilizer content on the molecular weight of the polymer

3 Conclusions

The styrene-acrylic acid magnetic microspheres were synthesized by dispersion polymerization. As the –COOH group is led into the surface of the polymer and the average diameter of the microspheres reaches about 200 nm, microspheres which have high drug delivery ability and adaptability can be obtained. In addition, as the microspheres are magnetic, they can be used in targeted drug release in an outer magnetic field improving the curative effect at the same time decreasing the side effects.

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