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Magnetic polymer nanospheres with high and uniform magnetite content

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Abstract

Magnetic polymer nanospheres with high and uniform magnetite content were synthesized using a new process based on miniemulsion polymerization, where a stable water-based dispersion of sodium dodecyl sulfate (SDS)/oleic acid bilayer coated magnetite aggregates was first synthesized and mixed with monomer styrene miniemulsion. Then another miniemulsification was performed for the full encapsulation of magnetite into monomer droplets. Subsequent polymerization generated magnetic polymer nanospheres. Extensive characterization of magnetic polymer particles by transmission electron microscopy (TEM), dynamic light scattering (DLS), thermogravimetric analysis (TGA) and Vibrating Sample Magnetometer (VSM) showed that up to 40 wt% of 8 nm superparamagnetic magnetite particles could be uniformly encapsulated into polystyrene nanospheres with an average diameter of 80 nm.

Keywords: Magnetite particles; Magnetite aggregates; Magnetic polymer nanospheres; Miniemulsion polymerization; Superparamagnetic

1. Introduction

Magnetic polymer particles have been widely applied to various aspects in biotechnology and biomedicine fields, such as immobilized enzyme, cell separation, protein purification, immunoassay, targeting drug, NMR and hyperthermia [1–7]. To be successfully used in the above areas, they should fulfill such requirements as no sedimentation, near-nano-sized distribution, high and uniform superparamagnetic content, no iron leaking and non-toxicity.

The common route for synthesizing magnetic polymer particles is monomer polymerization by dispersing magnetite particles directly in the liquid phase of a polymerizable formulation and polymerizing the monomer in the presence of the magnetite particles to form magnetic polymer particles. Several processes have been developed

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including emulsion polymerization [8], dispersion polymerization [9], suspension polymerization [10], microemulsion polymerization [11] and miniemulsion polymerization [12]. To obtain a good dispersion, reaction conditions must be such that all the magnetite particles are transferred uniformly into the resulting particles, or the magnetite particles must provide the only site for precipitation of polymers. However, it often carries the risk of incomplete and non-uniform encapsulation, in which the resulting particles are usually of uneven sizes, lack homogeneity and the distribution of magnetite in the polymer particles is not uniform.

Another important challenge in the preparation of magnetic polymer particles, especially for their biological applications, is that the magnetite content of the polymer particles should be large enough for quick magnetic separation. However, it is difficult to disperse high concentrations of hydrophilic magnetite particles into droplets of hydrophobic monomers by those processes based on direct monomer polymerization. Therefore, the magnetite content in the polymer sphere is usually limited [13,14].

To avoid these problems and obtain nano-sized magnetic polystyrene spheres with high and uniform magnetite content, a novel indirect process based on miniemulsion polymerization [15–17] is introduced in this paper. Oleic-acid-coated magnetite particles were firstly synthesized and dispersed into octane. Then the dispersion was miniemulsified into water using sodium dodecyl sulfate (SDS) as a second emulsifier and hexadecane as an osmotic agent. By the evaporation of octane, a water-based SDS/oleic acid bilayer coated magnetite aggregates' dispersion was obtained. For the encapsulation, the magnetite aggregates dispersion was mixed with monomer styrene miniemulsion, and then a second miniemusification was carried out by co-sonicating the mixture. Subsequent polymerization generated polymer particles with magnetite fully encapsulated. The effect of weight ratio of magnetite to monomer on the properties of the magnetic polymer particles was studied, and the characterization of magnetic polymer particles with high magnetite content was further discussed, including size and size distribution, magnetic content and magnetic properties.

2. Experimental

2.1. Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), ammonium hydroxide (25% NH_3), SDS, potassium peroxodisulfate (KPS), and oleic acid (90%) were purchased from Shanghai Chemical Reagents Company, China. Octane (98%) and hexadecane (99%) were purchased from Acros. All were used as received. The monomer styrene from Shanghai Chemical Reagents Company was distilled under reduced pressure and at 40 °C. The purified monomer was stored at −5 °C before use.

2.2. Preparation of the ferrofluid

24.3 g of $FeCl_3 \cdot 6H_2O$ and 16.7 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 200 ml distilled water and heated to 90 °C. Then 60 ml of ammonium hydroxide and 4 g of oleic acid were sequentially added rapidly. After 3 h, the sediment was washed with distilled water until neutrality was achieved. After drying, the coated magnetite particles were dispersed in the octane with a magnetite content of 14 wt% to form to a ferrofluid.

2.3. Preparation of magnetite aggregates' dispersion

14 g ferrofluid as synthesized above with 0.3 g hexadecane constituted the oil phase and was added to 24 g water containing 0.7 g SDS. The mixture was stirred for 1 h, and then the emulsion was subjected to sonication for 5 min with a Hongxing Sonifer at 100 W power in an ice-cooled bath to form a miniemulsion. Then octane was carefully evaporated at 80 °C to obtain a stable water-based magnetite aggregates' dispersion.

2.4. Preparation of monomer miniemulsion

The monomer styrene miniemulsion was prepared using the following recipe: 3.0 g of styrene and 120 mg of the hydrophobic agent hexadecane were added to a surfactant solution containing 36 mg of