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Preparation of Hollow/Porous Polymeric Microspheres based on OH-HPEEK and PVA

Chunfeng Zhang [a], Guibin Wang [a], Xiujie Li [b], Shuling Zhang [a,*]

[a] Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
[b] 529 Factory, Fifth Research Institute, Aerospace Science and Technology Corporation, Beijing 100190, People's Republic of China

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ABSTRACT

The formation of polymer microspheres based on rigid polymer (hydroxyl-terminated trifluoromethylphenyl substituted hyperbranched poly ether ether ketone, OH-HPEEK) and flexible polymer (polyvinyl alcohol, PVA) in tetrahydrofuran/water (THF/H_2O) system was studied. The results of SEM and TEM showed that such a rigid-coil polymer pair could form the microspheres with hollow core/porous shell structure. Moreover, the formation of the hollow core/porous shell structure not only depended on the concentrations of PVA and OH-HPEEK, but also on the structure of OH-HPEEK. A formation mechanism (combination of self-assemble and solvent evaporation method) of the hollow/porous polymer microspheres was proposed based on the experimental process and results.

1. Introduction

Colloidal particles with a void in the center have been widely applied in some fields, like controlled release of drugs, contrast agents, cosmetics, inks, pigments, protection of biologically active species, and removal of wastes [1, 2]. Several approaches have been developed to fabricate hollow polymer microspheres, such as emulsion polymerization, acid/alkali swelling method [3], solvent swelling method [4, 5], template method [6], solvent evaporation [7], phase separation [8], and self-assembly [9]. Among the aforementioned methods, solvent extraction/evaporation method is relatively simple without the involvement of complicated chemical reactions. However, the mechanism of formation is quite subtle and closely related to several parameters, depending greatly on the nature of the system such as polymer, solvent and active agent.

Using solvent extraction/evaporation method to prepare hollow microsphere has received considerable attention recently. However, we have noticed that the polymers used in this method were mostly linear and flexible copolymers [10]. In this work, a novel hyperbranched rigid polymer (OH-HPEEK) was introduced into this method successfully. Up to now, hyperbranched macromolecules have received more and more considerable attention due to the expectation that their unique highly branched structure will impart unusual properties [11].

In order to explore the influence of polymer concentration and polymer structure on the formation of microspheres with hollow core/porous shell structure, we first synthesized a novel hyperbranched rigid polymer (OH-HPEEK), then discussed the formation of microspheres based on OH-HPEEK and PVA in tetrahydrofuran/water (THF/H_2O) system, and proposed a formation mechanism of the hollow/porous polymer microspheres.

2. Experimental

2.1. Synthesis of hydroxyl-terminated trifluoromethylphenyl substituted hyperbranched poly ether ether ketone (OH-HPEEK) and hydroxyl-terminated trifluoromethylphenyl substituted linear poly ether ether ketone (OH-LPEEK)

The synthesis route and characterization of OH-HPEEK are shown in supporting information (Scheme S1). 3-Trifluoromethyl phenyl hydroquinone (A_2) [12] (7.6200 g, 30 mmol), 2,4′,6-trifluorobenzophenone (BB'_2) [13] (2.3600 g, 10 mmol), K_2CO_3 (0.9636 g, 10.5 mmol) and Na_2CO_3 (1.4803 g, 21 mmol) were dissolved in NMP (40 ml) and toluene (25 ml) in a 100 ml three-necked flask fitted with a nitrogen inlet. The subsequent process could refer to a procedure reported by our group [13], and a gray solid was obtained, 63.7%.

The synthesis route and characterization of OH-LPEEK are also shown in supporting information (Scheme S2). A_2 (3.8100 g, 15.00 mmol), B_2 (2.182 g, 10.00 mmol), and K_2CO_3 (2.1735 g, 11.03 mmol) were dissolved in NMP (24 ml) and toluene (15 ml) in a 100 ml three-necked. The subsequent process was the same to the preparation of OH-HPEEK, and the yield was 53.2%.

* Corresponding author. Tel./fax: +86 0431 85168199.
E-mail address: zsl@jlu.edu.cn (S. Zhang).

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2.2. Preparation of polymer microspheres with hollow core/porous shell structures

A typical procedure of preparation is as follows: first, two kinds of polymer solutions were prepared. 0.2 g PVA was dissolved in 50 ml deionized water (H_2O) as solution A, and 0.1 g OH-HPEEK was dissolved in 10 ml tetrahydrofolate (THF) as solution B. Then, 1 ml A was diluted with 30 ml H_2O in a beaker, and 1 ml B was dropped in the aforementioned beaker containing diluted A within 30 s under strong stirring. After 18 h, a slightly brown solution was obtained.

2.3. Characterization

Scanning electron microscopy (SEM) observations were made on an SSX-550 electron microscope at an accelerating voltage of 15 kV. For the sample preparation, a drop of the aggregate solution was dropped on a piece of aluminum foil, and then was dried in the air at room temperature. The specimens were coated with gold before SEM observations. Transmission electron microscopy (TEM) observations were made on a JEM-1200EX electron microscope.

3. Results and discussion

As shown in Fig. 1, polymer microspheres with hollow core/porous shell structures are successfully prepared, and their size is about 0.5 μm–2 μm. In order to explore the formation mechanism of polymer microspheres with hollow core/porous shell structures and the role of rigid polymer with hyperbranched structure (OH-HPEEK) in the self-assemble process, we studied the influence of PVA concentration, OH-HPEEK concentration and OH-HPEEK structure on the polymer microspheres with hollow core/porous shell structures.

Only at the lower PVA concentration, polymer microspheres with hollow core/porous shell structures could be obtained. When we directly dropped B to A (without diluted with 30 ml H_2O) under strong stirring, no hollow core/porous shell structures were observed. Because the concentration of PVA and OH-HPEEK were considerably high, the self-assemble procedure between them could rapidly take place and no solvent evaporation happened. Meanwhile, six different concentrations of OH-HPEEK were tried, as shown in Fig. 2. It could be found that polymer microspheres with hollow core/porous shell structures appeared when the concentration of OH-HPEEK reached a certain value (0.080 g OH-HPEEK/10 ml THF). Moreover, if the concentration of OH-HPEEK is below the value, only the solid polymer nanospheres with about 100 nm diameter could be obtained. This suggested that the rich region of OH-HPEEK was more likely to form, when the concentration of OH-HPEEK was higher than the value (0.080 g OH-HPEEK/10 ml THF). As a result, polymer microspheres with hollow core/porous shell structures could form.

In order to study the influence of OH-HPEEK structure on the polymer microspheres with hollow core/porous shell structures, OH-LPEEK was synthesized. The difference between OH-HPEEK and OH-LPEEK was that OH-HPEEK is a hyperbranched structure, whereas OH-LPEEK was a linear structure. For OH-LPEEK, no hollow/porous polymer microspheres were obtained using the above method, namely only solid micelle-like particle could be obtained. In comparison with OH-HPEEK and OH-LPEEK, their molecular weights were similar, but the structure of OH-HPEEK was more loosely than that of OH-LPEEK, which meant that the movement of molecular chains of OH-HPEEK was easier, namely self-assemble of OH-HPEEK and PVA was easier. In addition, the interaction among the components of system (such as OH-PEEK, PVA, THF and H_2O) was also very important for

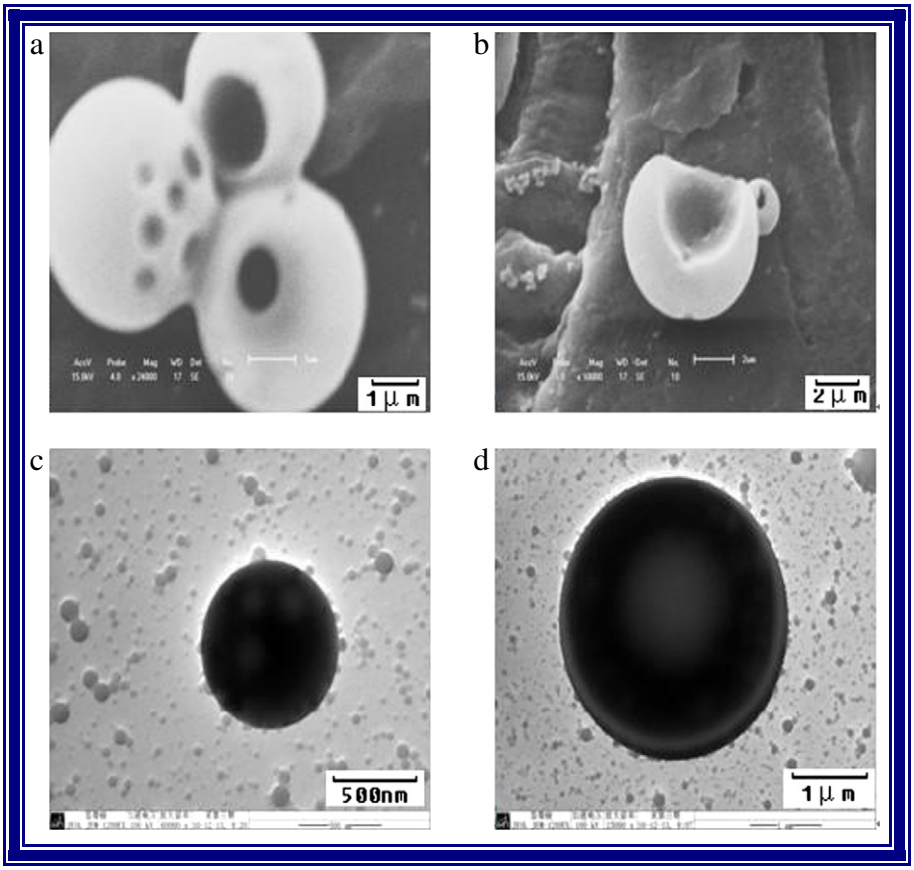

Fig. 1. The SEM (a and b) and TEM (c and d) micrographs of polymer microspheres with hollow core/porous shell structures (solution B was 0.100 g OH-HPEEK that was dissolved in 10 ml THF).