ELSEVIER

Colloids and Surfaces A: Physicochem. Eng. Aspects 253 (2005) 217–221

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Micron-size crosslinked microspheres bearing carboxyl groups via dispersion copolymerization

Hongtao Zhang, He Huang*, Rui Lv, Min Chen

School of Chemistry and Materials Science, Hubei University, Wuhan 430062, China

Received 23 March 2004; accepted 11 November 2004
Available online 18 December 2004

Abstract

Micron-size crosslinked polystyrene microspheres in the range of 2–33 μm, bearing carboxyl groups were prepared via dispersion copolymerization of styrene (St), acrylic acid (AA) and ethylene glycol dimethacrylate (EGDMA) in water/ethanol media, using poly(*N*-vinylpyrrolidone) (PVP) as stabilizer and 2,2′-azo-bisisobutyronitrile (AIBN) as initiator. The effects of concentration of functional monomer (AA) and crosslinking monomer (EGDMA), as well as water/ethanol ratio on particle size and distribution were investigated. It has been found that, increasing the concentration of AA and EGDMA would increase particle size and distribution. However, particle size decreased but particle size distribution increased, as the ratio of water/ethanol increased. The distribution of carboxyl groups was greatly affected by the concentration of reactants and the water/ethanol ratio in the media. The particles formed will be more hydrophylic in the core, but more hrdrophobic in the shell, with increasing AA or St concentration. This result is reversed when crosslinking monomer (EGDMA) concentration or water/ethanol ratio was increased.

Keywords: Dispersion copolymerisation; Micron-size microspheres; Particle size and distribution; Distribution of carboxyl groups; Water/ethanol ratio

1. Introduction

Uniform micron-size crosslinked polymer microspheres, as a supporting substrate in biology, medicine, chemical separation and solid-phase organic synthesis, etc., have many advantages over large-size ion-exchange resins. For example, it can take more functional groups, due to its larger exterior specific area. In addition, it has good mechanical properties, excellent solvent-resistance, and easy recyclization etc. [1].

Nowadays, functional groups-carrying micron-size uniform polymer microsphere becomes the center of this study due to its importance in the area of the biotechnological and biomedical applications, etc. The reactive functional groups, such as carboxyl, hydroxyl, amine, amide and chloromethyl groups, could be incorporated onto the microspheres. Among them, the incorporation of carboxyl groups has attracted large attention since the carboxyl groups on the surface of particles can be easily activated for various applications. Also, the characterization on carboxyl groups is relatively easy.

Various methods can be used to prepare polymer particles, such as conventional emulsion polymerization [2], miniemulsion polymerization [3], concentrated emulsion polymerization [4], suspension polymerization [5], and seeded emulsion polymerization [6,7], etc. Polymer particles prepared by emulsion polymerization are normally in the range of tens to hundreds of nanometers, while that from suspension polymerization is in the range of 1–1000 μm, with multi-dispersity. In recent years, dispersion polymerization [8] has attracted much attention [9–18], because it can produce micron-size monodisperse particles. Of course, various seeded emulsion (co)polymerization techniques are also now well appropriate, especially for making narrow-size distributed particles with a high concentration of carboxylic groups. Moreover, it must be kept in mind that the presence of grafted hydrophilic polymer in dispersion polymerization,

* Corresponding author. Tel.: +86 2761206856; fax: +86 2761206856.
E-mail address: h99huang@yahoo.com (H. Huang).

0927-7757/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2004.11.008

PVP in this study, at the particle interface could be sometimes a disadvantage (steric effect) when carboxylated groups should be used for binding biomolecules, for instance.

We once prepared micron-size crosslinked microspheres with no functional groups [19–21]. In this study, we are going to apply batch dispersion polymerization to synthesize micron-size crosslinked polystyrene micronspheres carrying carboxyl groups. Using ethylene glycol dimethacrylate (EGDMA) as crosslinker, acrylic acid (AA) as functional monomer, poly(*N*-vinylpyrrolidone) (PVP) as stabilizer, and 2,2′-azo-bisisobutyronitrile (AIBN) as initiator, carboxyl-carrying polystyrene particles in the size range of 2–33 μm were obtained in ethanol/water medium. Particle size and distribution, and the distribution of carboxyl groups of the microspheres obtained were discussed in detail.

2. Experimental

2.1. Materials

Acrylic acid (AA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Tianjing Bodi Chemical Ltd. Co., and Tianjing Chemical Reagents Institute, China, respectively. PVP (M_n: 40 000) was purchased from Wuhan Supply Station of Chemical Materials. Styrene monomer was distilled under vacuum and stored in refrigerator until use. AIBN was purified by recrystallization in ethanol. All other reagents were used as received without further purification.

2.2. Dispersion copolymerization

Dispersion colymerization was carried out in a 500 mL glass kettle equipped with a nitrogen inlet, a stirrer and "sealed" with Teflon gasket. As a typical procedure, PVP was dissolved in the solution of ethanol and water. Then, the mixture of AIBN, styrene, AA and EGDMA was added. The charge was stirred under nitrogen for 30 min until a homogenous solution was formed. The kettle was suspended in a water bath maintained at 70 °C, and the reaction was run for about 12 h before cooling. Latex particles were isolated via centrifuging the reaction mixture, decanting the supernatant, and then redispersing the particles in ethanol. This procedure was repeated three times in ethanol and three times in distilled deionized water. Basic recipe: [St + AA + EGDMA] = 20 wt.%, St/AA/EGDMA = 76.5/2.77/1(mol/mol/mol), [AIBN] = 0.8 wt.%, [PVP] = 1.6 wt.%, [H_2O] = 6 wt.%, [EtOH] = 70 wt.%.

2.3. Characterization

Morphology of particles was observed by using Transmission Electron Microscopy (TEM-100SX, Japan). Particle size (D_n) and distribution (PDI) were determined on the Shimadzu Centrifugal Particle Size Analyzer (SA-CP3). D_n represents the average diameter of particles, and PDI the polydispersity index of particles. The content of carboxyl groups on particle surface were measured by conductometric titration (DDS-11) as suggested in [22].

3. Results and discussion

3.1. Particle size and distribution

Table 1 shows the particle size and distribution (determined only by using the centrifugal particle sizer, as specified in Section 2; same is true for the size data in Tables 2 and 3) of the crosslinked microspheres under different concentrations of acrylic acid (AA).

When there were no functional and crosslinking monomers, PS particles obtained are uniform via dispersion polymerization. Increasing AA concentration increased the particle size and distribution. This can be clearly demonstrated by TEM photographs of particles obtained, as shown in Fig. 1. It can be seen from Table 1 and Fig. 1 that, when the amount of AA increased from 0 to 2.5%, the average particle size almost doubled, and the particle size distribution became broader. This is because AA is a water-soluble monomer. The incorporation of AA increases the water solubility of oligomer chains and the nucleation period, which increases the size of nuclei and therefore the final particles. In addition, the total surface area of particles decreases due to the increasing particle sizes, which reduces the ability of particles to absorb oligomer radicals and low-molecular-weight copolymer chains. These oligomer chains might precipitate from the continuous phase and form new secondary particles with the protection of stabilizer. In one word, the probabil-

Table 1
Effect of AA concentration [AA], on particle size and distribution

[AA] (wt.% of St)	D_n (μm)	PDI
0	4.61	1.013
2.5	8.9	1.128
5	14.16	1.228
7.5	33.72	1.248

Table 2
Effect of EGDMA concentration on particle size and PDI

[EGDMA] (wt.% of St)	D_n (μm)	PDI
0	4.27	1.010
1	5.47	1.110
2.5	8.90	1.128
4	12.45	1.198

Table 3
Effect of the mass ratio of water/ethanol on particle size and distribution

H_2O/EtOH (wt/wt)	D_n (μm)	PDI
0/76	9.18	1.133
6/70	8.90	1.128
10/66	7.52	1.245
15/61	7.43	1.256