



Preparation of slightly crosslinked monodisperse poly(maleic anhydride-cyclohexyl vinyl ether-divinylbenzene) functional microspheres with anhydride groups via precipitation polymerization



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ABSTRACT

Slightly crosslinked monodisperse poly(maleic anhydride-cyclohexyl vinyl ether-divinylbenzene) (MA-CHVE-DVB) microspheres were prepared via precipitation polymerization while using 2,2-azobisisobutyronitrile as an initiator in a mixture of methyl ethyl ketone and n-heptane without any stabilizer. The number-average diameter of the resultant poly(MA-CHVE-DVB) microspheres ranged from 0.478 to 1.386 μm with a polydispersity index of 1.00 to 1.02 that depended on the feed ratios of the MA/CHVE/DVB monomers. The introduction of one electron donor monomer cyclohexyl vinyl ether strongly affected the yield, size, and morphology of these slightly crosslinked microspheres. Quinoline-type chelating resins were obtained after combining the poly(MA-CHVE-DVB) with 8-hydroxyquinoline; the adsorption properties of these materials were measured through their ability to remove Cu^{2+} ions from water. The poly(MA-CHVE-DVB) microspheres with low degrees of crosslinking provided more effective functional groups and therefore better ion removal capabilities. These slightly crosslinked microspheres may have applications in water treatment as well as in sensing and drug delivery.

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Introduction

Crosslinked monodisperse polymer microspheres have attracted much attention across a wide range of applications, including information technology, electric and electronic sciences, and biochemical and biomedical technologies (Covolan, Mei, & Rossi, 1997; Fudouzi & Xia, 2003; McDonald, Bouck, Chaput, & Stevens, 2000; Serpengüzel, Kurt, & Ayaz, 2008; Solorio, Fu, Hernández-Irizarry, & Alsberg, 2010; Ugelstad et al., 1992; Zhao et al., 2012) due to their superior strength, thermal and solvent resistance, and anti-slip properties. Exerting precise control over the properties of these polymer particles has become increasingly important as their applications have expanded (Dai et al., 2014;

Horák & Shapoval, 2000; Sanders et al., 1984). The crosslinking degree, size, size distribution, functionality of the base polymer, morphology of the polymer beads, among others are the most important controlling properties (Hattori, Sudol, & El-Aasser, 1993; Horák & Shapoval, 2000; Tunc & Ulubayram, 2009; Sanders et al., 1984). Interestingly, a low degree of crosslinking density generates polymer microspheres with good swelling performances, facilitating modification (Ding, Aklonis, & Salovey, 1991; Gupta & Jabrail, 2006).

Emulsion, suspension, and dispersion polymerization are well-known methods used to prepare crosslinked polymer microspheres (Gibanel, Heroguez, & Forcad, 2001; Kawaguchi, Winnik, & Ito, 1996). However, these synthetic processes require an emulsifier or particle stabilizer, such as poly(N-vinyl pyrrolidone) or poly(vinyl alcohol) (Marumoto, Suzuta, Noguchi, & Uchida, 1978; Paine, Luymes, & McNulty, 1990; Uchida, Hosaka, & Murao, 1982). These stabilizers cannot be easily removed from the polymer, often generating adverse consequences in many applications, particularly biological applications. Furthermore, the three synthetic

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methods described above are usually performed in water, making them inappropriate for monomers containing functional groups that are either reactive or labile in water, such as maleic anhydride (MA). Precipitation polymerization is an alternative approach that produces crosslinked polymer particles with uniform sizes and shapes in the absence of any additional stabilizer or water (Downey, Frank, Li, & Stöver, 1999; Li & Stöver, 1993b). During precipitation polymerization, a homogeneous mixture of a monomer, initiator, and solvent becomes heterogeneous during the reaction as insoluble polymer chains aggregate, forming a separate polymer phase (Bai, Yang, Zhao, & Huang, 2005; Li & Stöver, 1993a; Sosnowski, Gadzinowski, & Slomkowski, 1996).

MA, which contains both double bond and anhydride groups, offers dual functionality while providing maximum freedom and flexibility during polymer design (Dispenza, Tripodo, LoPresti, Spadaro, & Giammona, 2009). Polymers microspheres derived from MA are attractive as a reactive starting material when designing compounds with various functional groups (Croll, Stöver, & Hitchcock, 2005; Jeong, Byoun, & Lee, 2002; Qiu, Zhu, & Xu, 2005; Trivedi, Shah, & Indusekhar, 1996; Wehrens & Tomaschewski, 1996). Naka and Yamamoto (1992) reported the preparation of copolymer microspheres of MA with diethylene glycol dimethacrylate (2G) by precipitation polymerization; the yield, size, and the crosslinking degree of microspheres remained unaffected by the concentration of MA. Therefore, the crosslinking degree of the copolymer MA microspheres cannot be decreased by adjusting the amount of MA monomer. While keeping the same number of double bonds in MA and DVB, Croll and Stöver (2003a) obtained copolymer microspheres containing MA and divinylbenzene-55 (DVB-55) via precipitation copolymerization; they proposed that MA copolymerizes with DVB in an alternating pattern. The poly(DVB-MA) microspheres formed spherical tectocapsules that could be used for the controlled release of pharmaceutical and agricultural agents. However due to the high cross-linking density of the microspheres, the links between the hard microspheres were relatively fragile and unstable, restricting the applications of crosslinked microspheres that contain anhydride groups (Croll and Stöver, 2003b).

To broaden the applications of these functional microspheres, an electron donor monomer cyclohexyl vinyl ether (CHVE) (Dodgson & Ebdon, 1977; Kharas & Ajbani, 1993; Kokubo, Iwatsuki, & Yamashita, 1968; Kokubo, Iwatsuki, & Yamashita, 1970) was introduced into a MA and DVB copolymer. The purpose of this introduction is to obtain monodisperse microspheres with less crosslinking, more effective anhydride groups and improved swelling properties compared to poly(MA-DVB) microspheres. In this work, slightly crosslinked poly(MA-CHVE-DVB) microspheres were successfully prepared via precipitation polymerization at various monomer concentrations. The effects of the CHVE concentration on the morphology, particle size, size distribution and MA content of the final microspheres were presented and investigated.

Experimental

Materials

Cyclohexyl vinyl ether (CHVE), divinylbenzene (DVB, 80% divinylbenzene isomers), maleic anhydride (MA), 8-hydroxyquinoline (HQ), sodium hydroxide (NaOH), hydrochloric acid (HCl), and phenolphthalein indicator were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The solvents, i.e., methyl ethyl ketone (MEK), n-heptane (Hp), and tetrahydrofuran (THF), were all analytical grade and used as received from Shanghai Chemical Reagents Co. Ltd. (Shanghai,

China). 2,2-Azobisisobutyronitrile (AIBN, analytical grade) was supplied by Shanghai Chemical Agent Fourth Factory (Shanghai, China) and purified via recrystallization from ethanol.

Preparation of P(MA-CHVE-DVB) and P(MA-DVB) microspheres

During a typical polymerization, MA (1.568 g, 16 mmol) was first dissolved in 16 mL of MEK in a 100 mL three necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. Afterwards, 24 mL of Hp was introduced into the glass reactor (i.e. the three necked flask) before 2.016 g of CHVE (16 mmol), 1.043 g of DVB (8 mmol, 20 mol% relative to the total monomer), and 0.0463 g of AIBN (1 wt% relative to the total monomer) were loaded to the glass reactor. After purging with N₂ for 30 min, the reactor was placed into a 70 °C water bath for 6 h.

At the end of the reaction, the particles were separated from the reaction medium by filtration, before being washed in a Soxhlet extractor with acetone for 48 h. Afterwards, the material was dried at room temperature under vacuum until a constant weight was achieved. The polymerization yield was determined gravimetrically as the mass ratio of the resulting polymer to the feed monomers.

Characterization

The Fourier transform infrared (FT-IR) spectra of poly(MA-CHVE-DVB) and poly(MA-DVB) samples were taken in KBr pellets with a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer (Perkin-Elmer Co., USA). The particle morphologies were observed on a Hitachi S-2500 scanning electron microscope (SEM) under a low vacuum. The particle size and size distributions were measured using the Scion Image Analyzer software. One hundred individual particles would be measured from the SEM microphotographs to calculate the SEM size data by using the following equation:

$$D_n = \frac{\sum_{i=1}^n D_i}{n}, \quad (1)$$

$$D_w = \frac{\sum_{i=1}^n D_i^4}{\sum_{i=1}^n D_i^3}, \quad (2)$$

$$PDI = \frac{D_w}{D_n}, \quad (3)$$

$$\varepsilon = \frac{[\sum_{i=1}^n (D_i - D_n)^2 / (n - 1)]^{1/2}}{D_n}, \quad (4)$$

where D_n is the number-average diameter, D_w is the weight-average diameter, D_i is the particle diameter of the determined microspheres, PDI is the polydispersity index, n is the total number of the measured particles, and ε is the deviation coefficient.

Metal ion adsorption kinetics experiments

Quinoline-type chelating resins were obtained when using the poly(MA-CHVE-DVB) and poly(MA-DVB) microspheres as a reaction substrate. During a typical experiment, HQ (1.773 g) was dissolved in 20 mL of tetrahydrofuran (THF) before the HQ solution was dropped through a burette into a gently shaken poly(MA-CHVE-DVB) solution; this solution was prepared by soaking 3 g of the poly(MA-CHVE-DVB) microspheres in 60 mL of THF at 30 °C for 12 h with stirring. Next, a mixture of HQ and a poly(MA-CHVE-DVB) solution was heated to reflux for 10 h with stirring, forming a quinoline-type chelating resin. After the reaction, the quinoline-type chelating resin was separated by filtration and washed with

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