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European Polymer Journal 42 (2006) 2088–2097

EUROPEAN POLYMER JOURNAL

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Preparation of narrow or monodisperse poly(ethyleneglycol dimethacrylate) microspheres by distillation–precipitation polymerization

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Received 16 January 2006; received in revised form 30 March 2006; accepted 30 March 2006

Abstract

Highly crosslinked narrow or monodisperse poly(ethyleneglycol dimethacryltae) (polyEGDMA) microspheres were prepared by distillation–precipitation polymerization in neat acetonitrile with 2,2′-azobis(2-methyl propinitrile) (AIBN) as an initiator. The polymer microspheres with clean surfaces due to the absence of any added stabilizer in the reaction system were formed simultaneously through a precipitation manner during the distillation of acetonitrile off the reaction system. The effects of the solvent, initiator concentration, monomer concentration and comonomer (divinylbenzene, DVB) fraction on the formation of the microspheres were investigated. Narrow- or monodisperse particles with spherical shape and smooth surface were obtained with diameters between 1.18 and 2.50 μm with monomer loading lower than 3.13 vol%. The surfaces of the microspheres became rougher, some elliptic particles and doublet or triplet appeared with the increase of monomer concentration (as high as 3.75 vol%). The yield of polymer microspheres was increased from 31% to 75% with the increase of EGDMA fraction from 0 to 100% when EGDMA was copolymerized with DVB. The resulting polymer microspheres were characterized with scanning electron microscope (SEM) and Fourier transform-IR spectra.

Keywords: Poly(ethyleneglycol dimethacrylate); Monodisperse; Polymer microspheres; Distillation–precipitation polymerization

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1. Introduction

Recently, crosslinked polymer microspheres have received increasing attention in many fields of scientific research as well as for industrial importance due to their wide applications, including supporting phases for separation science [1,2], biomedical devices [3], casting additives [4], controlled release reservoirs [5,6], capillary electrochromatography of macrolide antibodies [6] and supports for metallic nano-colloids [7]. Control of the polymer particle size and its uniformity has been a major area of interest, especially for particles in the micron-size range. Emulsion polymerization, suspension polymerization, and dispersion polymerization are well-known as methods for the preparation of polymer microspheres [8–12].

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0014-3057/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.eurpolymj.2006.03.030

However, these synthetic processes involve the utilization of a surfactant or a particle stabilizer, such as poly(*N*-vinyl pyrrolidone) [11,12]. Precipitation polymerization is unique to prepare monodisperse polymer microspheres of uniform size and shape in absence of any added surfactant or stabilizer [13–16].

We have previously reported the distillation–precipitation polymerization as a novel technique to afford monodisperse poly(divinylbenzene) (poly-DVB) [17] and poly(divinylbenzene-*co*-chloromethylstyrene) (poly(DVB-*co*-CMSt)) [18] microspheres in neat acetonitrile without stirring in absence of any additive. These polymer microspheres are entirely styrenic in nature and highly hydrophobic. It is essential to get the hydrophilic property of the surface of the microspheres with wider ranges of polarity and functionality rather than those achievable with styrenic monomers for the applications of the microspheres in various fields, such as solid carriers for the immobilization of biological substances of enzymes and antibodies [19,20]. Emulsification technique [21] and seeded suspension polymerization [22, 23] have been used to incorporate ethyleneglycol dimethacrylate (EGDMA) with various comonomers in different ratios, such as hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GMA), methylmethacrylate (MMA). All these emulsion polymerizations require the utilization of suitable ionic or steric stabilizers. Recently, monodisperse polymer microspheres with various functional groups, such as aldehyde, imide and amide, were obtained by a radiation precipitation polymerization without stirring in the absence of any stabilizer or catalyst [24,25]. However, the irradiation polymerization technique needs a special γ-ray source of Co-60 and special equipment to perform the polymerization.

In the present work, the preparation of monodisperse poly(ethyleneglycol dimethacrylate) (poly-EGDMA) microspheres with polarity has been investigated in detail by distillation–precipitation polymerization in neat acetonitrile with AIBN as initiator, in which the microspheres are formed by a one step process without stirring in the absence of any additive or stabilizer.

2. Experimental

2.1. Chemicals

Ethyleneglycol dimethacrylate (EGDMA) was chemical grade available from Heshibi Chemical Eng. Co., Ltd., Shanghai, China and used without further purification. Divinylbenzene (DVB, technical grade, containing 80% DVB isomers) (Shengli Chemical Factory, Shandong, China) was washed with 5% aqueous sodium hydroxide and water, and then dried over anhydrous magnesium sulfate prior to use. 2,2′-Azobisisobutyronitrile (AIBN) (analytical grade, available from Chemical Factory of Nankai University) was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagents II Co.) was dried over 4 Å molecular sieves and purified by distillation before use. The other reagents were analytical grade and used as received without any further purification.

2.2. Distillation–precipitation polymerization

The basic polymerization procedure is similar to that described previously for the synthesis of poly-DVB and poly(DVB-*co*-CMSt) microspheres by distillation–precipitation polymerization [17,18]. A typical procedure for the distillation–precipitation polymerization: EGDMA (2.0 ml, 2.04 g, 14.1 mmol, 2.5 vol% relative to the reaction medium) and AIBN (0.041 g, 0.24 mmol) 2 wt% relative to the total monomer) were dissolved in 80 ml of acetonitrile in a dried 100-ml two-necked flask, attaching with a fractionating column, Libieg condenser and a receiver. The flask was submerged in a heating mantle and the reaction mixture was heated from ambient temperature till boiling state within 30 min and then the solvent began to be distilled. The initially homogeneous reaction mixture became milky white after boiling for 10 min. The reaction was ended after 40 ml of acetonitrile was distilled from the reaction system within 90 min. The boiling point of the reaction mixture was determined by the thermometer at the top of the fractionating column, which was near the boiling point of acetonitrile: 82 °C. After the polymerization, the resulting poly-EGDMA microspheres were separated by vacuum filtration over a G-5 sintered glass filter and washed successively with THF, acetone and ether for three times. The polymeric particles were dried in vacuum oven under 50 °C till constant weight to afford 1.59 g of microspheres with 78% yield.

The procedures for the other distillation–precipitation polymerizations were much similar as that for the typical one by altering either the solvent used, or EGDMA concentration, or initiator concentration, or the EGDMA fraction in the comonomer feed in the case of copolymerization of EGDMA and