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Dispersion polymerization of styrene in supercritical CO_2 stabilized by random copolymers of 1*H*,1*H*-perfluorooctyl methacrylate and 2-dimethylaminoethyl methacrylate

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Abstract

The dispersion polymerizations of styrene in supercritical CO_2 employing random copolymers composed of 1,1-dihydroperfluorooctyl methacrylate (FOMA) and 2-dimethylaminoethyl methacrylate (DMAEMA) (poly(FOMA-*co*-DMAEMA)) as stabilizers were investigated with two different compositions. It was demonstrated that micron-sized, free-flowing, spherical polystyrene (PS) particles could be obtained in high yields by poly(FOMA-*co*-DMAEMA) containing as low as 50% (w/w) FOMA. Results indicate that DMAEMA units in the stabilizer, as an anchor group with its special characteristics, can be adsorbed on PS particles to provide an enough colloidal stability. The initial concentration of styrene and the stabilizer affected the molecular mass, polymerization yield, and the morphology of PS particles. The PS particles could be redispersed in buffered water (pH 2.1) by an ionic stabilization mechanism provided by DMAEMA units on the surface. Dynamic light scattering (DLS) measurements of aqueous latexes gave similar particle sizes as those from SEM analysis.

Keywords: Supercritical carbon dioxide; Stabilizer; Dispersion polymerization; Random copolymer; 2-Dimethylaminoethyl methacrylate; Polystyrene

1. Introduction

An intense research activity concentrated in the last decade has demonstrated that carbon dioxide is an attractive alternative replacement for the aqueous and organic solvents traditionally employed by the polymer industry because it is inexpensive, non-toxic, non-flammable, and environmentally benign [1–4]. Additionally, products are separated from the polymerization by simply depressurizing CO_2, which can reduce a large amount of cost for product recovery at industrial scale. Due to the solubility of wide range of monomers and insolubility of most polymers in supercritical carbon dioxide, a majority of the work in heterogeneous radical polymerizations has focused on dispersion polymerizations. Dispersion polymerization is one in which the monomer and initiator are soluble in the reaction medium, while the polymer formed is insoluble. For a successful dispersion of polymer product in $scCO_2$, specially designed stabilizers have to be used. These amphiphilic stabilizers should have CO_2-philic segments which extent out into CO_2 medium while CO_2-phobic segments which anchor onto growing polymeric particles and ensure the steric stabilization on the latexes; prevent flocculation and precipitation of the reaction product. DeSimone et al. reported the first dispersion polymerization of methyl methacrylate in $scCO_2$ by using highly CO_2 soluble 1,1-dihydroperfluorooctyl acrylate (PFOA) as the stabilizer [5]. Since then, a number of other stabilizers mostly based on block and graft copolymers have been described [6–8]. However, block and graft copolymers are often difficult to synthesize and fluoropolymers are uneconomical and often cannot be characterized in usual solvents due to their poor solubility. A reactive macromonomer system has been reported based on poly(dimethylsiloxane) (PDMS), which acts as a effective stabilizer for the dispersion polymerization in $scCO_2$ [9–11]. The drawback to the use of such stabilizers is that they are necessarily incorporated into the final product. Alternatively, random copolymers are of interest because they

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have many industrial applications and can be synthesized more easily and affordably than block or graft copolymers [12,13]. Shiho and DeSimone reported that the random copolymers composed of 1,1-dihydroperfluorooctyl methacrylate (FOMA) and styrene could be effective stabilizers in the dispersion polymerization of styrene in $scCO_2$ when the incorporated ratio of fluoroacrylates was above 92% (w/w) [14]. Recently Ding and Olesik synthesized a series of random copolymers consisting of (2-perfluorooctyl)ethyl methacrylate and poly(propylene glycol)methacrylate poly(FOEMA-*co*-PPGMA) which were shown to be effective stabilizers in the dispersion polymerization of MMA [15] and styrene [16] in $scCO_2$ with an optimal 52% (w/w) PPGMA composition. Random copolymers composed of heptadecafluorodecyl acrylate (HDFDA) and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (SiMA), poly(HDFDA-*co*-SiMA) were also found to be effective stabilizers in the dispersion polymerization of MMA [17] and styrene [18]. More recently, we have shown that random copolymers which consist of FOMA and DMAEMA, poly(FOMA-*co*-DMAEMA), with as low as 34% (w/w) FOMA content, provided abnormally large stabilization on the dispersion polymerization of MMA in $scCO_2$ to form micron-sized spherical PMMA particles [19]. This class of stabilizers offers several advantages over fluorinated stabilizers previously used in the dispersion polymerization, including cost-effectiveness by extremely reducing fluorine content and the ease of preparation and characterization compared to block or graft copolymers. With all these additional advantages of poly(FOMA-*co*-DMAEMA), we hypothesized that the random copolymeric stabilizer could also work for styrene. In this study, we investigated the dispersion polymerization of styrene using a series poly(FOMA-*co*-DMAEMA) containing different ratios of DMAEMA structural units with reduced fluorine content up to 50% (w/w) FOMA. Additionally, the effect of particle size, morphology, and molecular weight of PS as a function of the concentration of the copolymeric stabilizer and monomer was presented.

2. Experimental

2.1. Materials

Styrene (Sigma–Aldrich), DMAEMA (Sigma–Aldrich), and FOMA (SynQuest) were purified by passing through a neutral alumina column to remove an inhibitor. Then they were stored over CaH_2 below 0 °C and distilled prior to use. $CFCl_3$ (Sigma–Aldrich), 2,2′-azobisisobutyronitrile (AIBN) (Sigma–Aldrich), and research-grade CO_2 (Daeyoung Co., 99.99%) were used as received.

2.2. Preparation of polymeric stabilizer

Statistical random copolymers of poly(FOMA-*co*-DMAEMA) (Fig. 1) were prepared by charging 0.5 g of FOMA, 0.5 g of DMAEMA, and 0.01 g of AIBN into a 25 mL flask equipped with a Teflon-coated stir bar. The flask was then closed and purged with argon. The flask was heated to 65 °C and the reaction was carried out for 24 h. After completion of the reaction, the mixture was dissolved in mixed solvent of $CFCl_3$ and chloroform and precipitated into hexane. The product collected was dried and weighed.

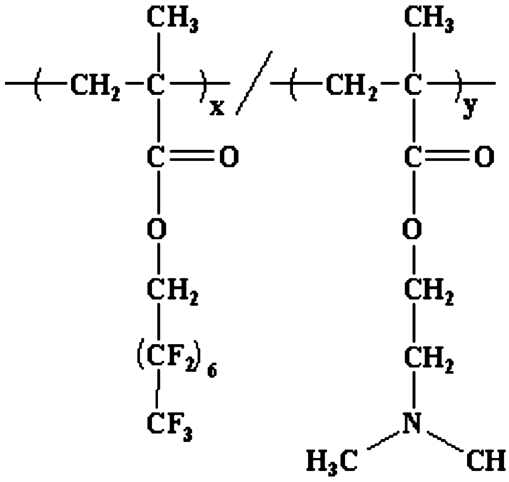

Fig. 1. The structure of copolymeric stabilizer poly(FOMA-*co*-DMAEMA).

2.3. Dispersion polymerization of styrene in $scCO_2$

The dispersion polymerization of styrene in $scCO_2$ was conducted in a 4 mL high-pressure view cell. For a typical experiment, 0.6 g of styrene (15%, w/v, to CO_2), 0.03 g of poly(FOMA-*co*-DMAEMA) (50:50) (5%, w/w, of monomer), 0.006 g (1%, w/w, of monomer) of AIBN, and a Teflon-coated stir bar were put into the view cell reactor. The reactor was pressurized by ISCO syringe pump (Model 260D) containing compressed CO_2 at the pressure of 70 bar, then it was heated to 65 °C. As the reactor was heated, the remaining CO_2 was added into the reaction mixture until the desired pressure of 345 bar was reached. The reactor was sealed, and the polymerization was allowed to continue with stirring for 40 h. After polymerization, the reactor was cooled in an ice water bath and residual styrene was extracted with ~20 mL of liquid CO_2 at 138 bar and ambient temperature. At the end of extraction, the remaining CO_2 was slowly vented out and the product was collected and weighed.

2.4. Characterization

Size-exclusion chromatography (SEC) was carried out with a HP1100 apparatus equipped with a set of four columns (10^5–10^4–10^3–10^2 Å: polymer standards service) with THF as the eluent. Polystyrene samples were used as standards to construct the calibration curve. The ratio of monomers incorporated in the copolymer was determined by ^1H NMR spectra using a JNM-ECP 400 (JEOL) NMR spectrometer with $CDCl_3/CFCl_3$ (v/v = 1/3.5) as the solvent. Microscopic images of PS particles were obtained from a Hitachi S-2400 scanning electron microscope. The number–average particle size and particle size distributions were determined by measuring the diameter of 100–150 particles. Dynamic light scattering (DLS) measurements were made using an electrophoretic light scattering