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SHORT COMMUNICATION

The synthesis of polyacrylamide nanoparticles in supercritical carbon dioxide

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Abstract Polyacrylamide nanoparticles, 50 to 200 nm, were created by inverse emulsion polymerization of acrylamide in supercritical carbon dioxide. The cross-linked polyacrylamide was produced by intermolecular imidization.

Keywords Inverse emulsion polymerization · Nanoparticles · Polyacrylamide · Supercritical fluids · Synthesis

Introduction

Synthetic water-soluble polyacrylamides have come into widespread usage [1–7]. According to the final application, the monomer can be easily co-polymerized with different monomers, cross-linked, etc. The polyacrylamide can be chemically modified to make them cationic, anionic or amphoteric. Their hydrophobicity or hydrophilicity can also be controlled by chemical modification or by co-polymerization. They can be made into gels or beads. The monomers can be polymerized in several solvents including water and by inverse emulsion polymerization. By inverse emulsion polymerization, high-molecular-weight linear or cross-linked polyacrylamides can be made in a relatively low viscosity medium.

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Inverse emulsion polymerization consists in reacting the monomers in surfactant-stabilized water-in-oil (w/o) emulsion. There are several advantages to conducting acrylamide polymerizations in an inverse w/o emulsion. These include the high reaction rates, solids levels, polymer molecular weights, lower solution viscosities and higher heat removal rates [8]. However, with these advantages, there are also several disadvantages. The disadvantages include the presence of oil and the eventual phase separation of the oil due to inherently unstable emulsions. The oil is an undesirable contaminant in most applications. Therefore, the oil is post-polymerization removed, replaced or emulsified in the final application.

A way to bypass the problems associated with the oil phase is to carry out the reaction in supercritical fluids. Supercritical fluids offer the advantages that they exhibit "liquidlike" densities and solvent powers while having "gaslike" viscosities. Furthermore, their solvent properties can be tuned by varying the pressure. Using these advantages, Beckman and Smith [9, 10] conducted inverse polymerization of acrylamide in supercritical ethane/propane mixtures at 65 °C. This was followed by Adamsky and Beckman [11], who carried the inverse emulsion polymerization of acrylamide in supercritical carbon dioxide. Supercritical carbon dioxide has the attraction of being inexpensive, non-toxic and non-flammable and exhibits a critical temperature of 31 °C [12–14]. Both techniques produced high-molecular-weight linear polyacrylamides at high reaction rates. Using supercritical carbon dioxide, Cooper et al. [15] were the first investigators to synthesize cross-linked microspheres (100 nm to 10 μm) of poly (divinylbenzene) with and without stabilizing surfactants.

Interest has shifted to the use of micro- and nano-polyacrylamide particles [16, 17]. Nanoparticles of polyacrylamide have found uses in the papermaking industry

[18] and in the medical field (embedded iron oxide in 100 nm polyacrylamide particles) as contrast agents for molecular imaging using magnetic resonance imaging [19, 20]. Polyacrylamide polymer probes encapsulated by biological localized embedding (PEBBLE) sensors [21, 22] consist of sensor molecules entrapped in chemically inert 30- to 500-nm polyacrylamide particles. A fluorescent ionophore can be covalently reacted with or embedded in the polyacrylamide matrix. Then, the particles can be used as optical nanosensors for intracellular chemical analysis [23–25], as a center for the photochemical production of singlet oxygen for treatment of cancer cells [26, 27], etc.

All of the previous applications relied on synthesizing the polyacrylamide nanoparticle by conventional inverse w/o emulsion polymerization. It is the purpose of this investigation to demonstrate the synthesis of polyacrylamide nanoparticles in supercritical carbon dioxide.

Experimental section

The reagents acrylamide and potassium persulfate were purchased from Aldrich and used without further purification. The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was obtained from Sigma. It was purified using the method described by Williams et al. [28]. The co-surfactant perfluoropolyether-phosphate (PFPE–PO_4) was acquired from Ausimont. The CO_2 (SFE grade) was obtained from Oxarc. The polymerization of acrylamide initiated with potassium persulfate has been previously described [29, 30].

The general methodology for supercritical fluids has been previously reported [31]. Briefly describing this procedure, the high-pressure vessels were homemade. One of the vessels (9.5-ml volume) was connected by fiber optics to a charge-coupled device array UV–Vis spectrometer. The 50 °C, 150 atm or 25 °C, 200 atm acrylamide concentration was monitored by following its UV relative adsorption at 200 nm. The other high-pressure vessel (15-ml volume) was equipped with sapphire viewing windows. A schematic diagram is shown in Fig. 1. The vessels were isolated from each other by Valco high-pressure valves. The reverse-phase micellar solutions were made by using the surfactant AOT at a concentration of 12.8 mM with the co-surfactant PFPE–PO_4 at 25.3 mM. The water-to-surfactant ratio was 12. The acrylamide micellar solution was placed in the 9.5-ml high-pressure cell. The polymerization initiator micellar solution was made in the other high-pressure vessel (15-ml volume). Each pressure vessel was charged with liquid CO_2 by the use of an ISCO syringe pump. Then, the solutions were stirred for 1 h to ensure the formation of homogeneous colloidal optical transparent emulsions. The vessels were first charged to a pressure of 80 atm. After 1 h, the 15-ml vessel was pressurized to 200 or 150 atm. The vessels were brought up to the reaction temperature, and the initiators were pushed into the fiber-optic 9.5-ml cell by opening the interconnecting valve and the ISCO syringe pump. The reaction was monitored by following the disappearance of UV absorption of the acrylamide.

Results and discussion

The polymerization was carried out at 25 °C, 200 atm and at 50 °C, 150 atm. Regardless of temperature and pressure, the reaction was completed, as followed by the 200-nm UV relative absorption (acrylamide absorbs at 200 nm and

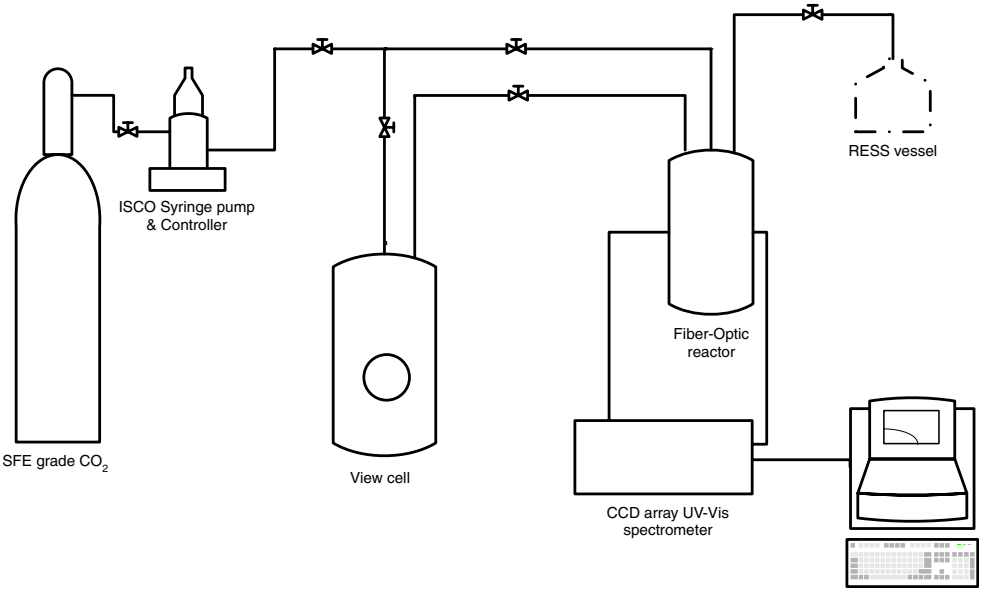

Fig. 1 Schematic diagram of the supercritical CO_2 micro-emulsion reaction system

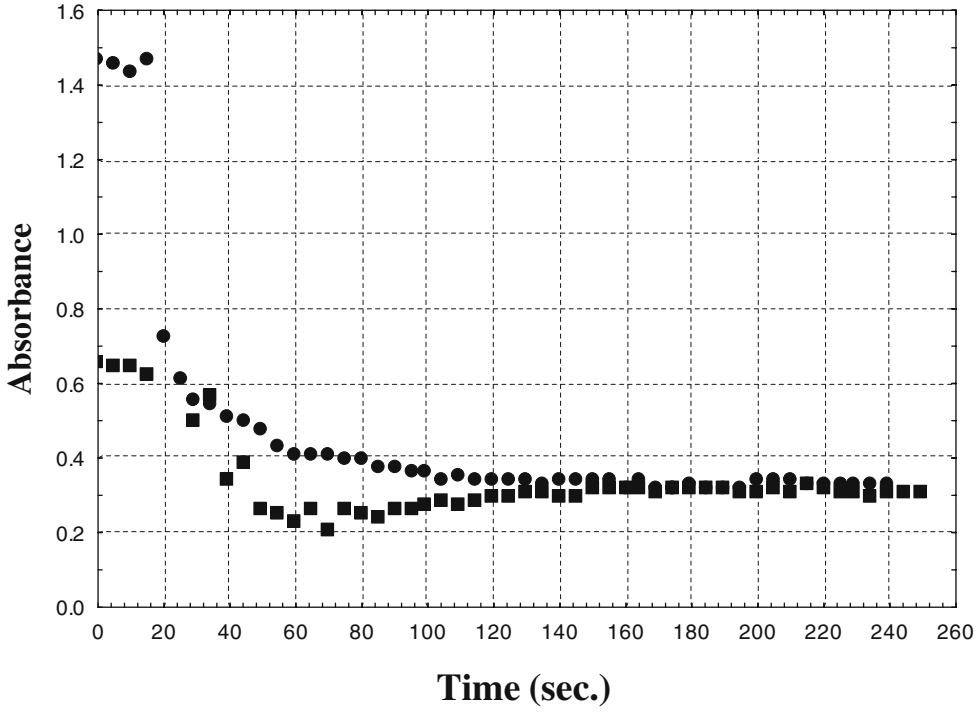

Fig. 2 Concentration of acrylamide as a function of time in supercritical CO_2. Absorbance vs time (s). *Filled circle*, 200 atm and 25 °C; *filled square*, 150 atm and 50 °C

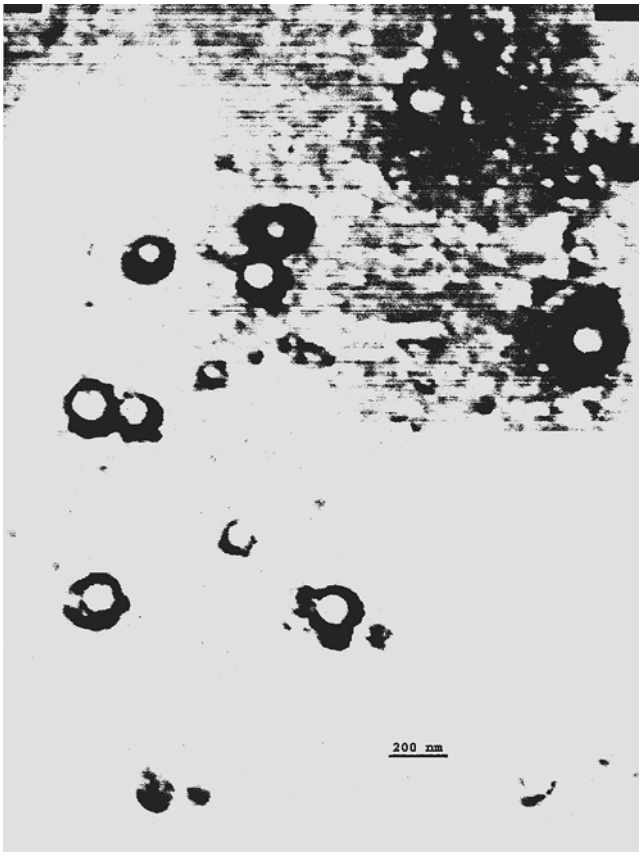

Fig. 3 TEM micrograph of polyacrylamide particles created in supercritical CO_2, 200 atm and 25 °C, collected on a copper grid using the RESS method

Fig. 4 TEM micrograph of polyacrylamide particles created in supercritical CO_2, 150 atm and 50 °C, collected on a copper grid using RESS method

polyacrylamide does not adsorb at this wavelength), in a matter of seconds. The relative absorbance, as a function of time, is given in Fig. 2. Furthermore, the starting absorbance of acrylamide at 200 atm was greater than the one at 150 atm. This could be due to higher acrylamide concentration in the reverse micelle. The time that is required for the absorbance-time curve to reach a plateau was used as a measure of the completion of the reaction. In this set of experiments, no attempt was made to control the rate of mixing of the reagents. It appears that the reaction rate increases with temperature. The polymerization at 25 °C, 200 atm was completed in less than 1 min, and the reaction at 50 °C, 150 atm was completed in less than 30 s. However, future research will be conducted to differentiate between the effects of temperature, pressure, concentration and mixing effects. Furthermore, we will design experiments to accurately measure these fast reaction rates.

Further investigations revealed that beads were created. Therefore, part of the reaction proceeded through an intermolecular imidization process that cross-linked the polyacrylamide chains. Rapid expansion of supercritical carbon dioxide method (RESS) was used to collect the polyacrylamide beads [32]. The beads were collected on a copper grid by the RESS method for transmission electron microscopy analysis. They are shown in Figs. 3 and 4. The observed size distribution was between 50 and 200 nm. Past experiences have shown that rapid expansion of the water in carbon dioxide microemulsion can cause some agglomeration of the nanoparticles [31].

In summary, polyacrylamide nanoparticles were produced by inverse emulsion polymerization of acrylamide in supercritical carbon dioxide. The mechanism involved intra- and intermolecular imidization for nano-bead formation.

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