

Polymer Synthesis in Supercritical Fluid

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ABSTRACT

Since polymers were first synthesized by DeSimone et al. in early 1990s, a lot of research has been made worldwide. In our laboratory polymers such as poly(methyl methacrylate)(PMMA), poly(2-ethylhexylacrylate)(PEHA), polystyrene(PS), and poly(vinyl acetate)(PVAc) were synthesized by dispersion polymerization in supercritical CO₂ (scCO₂). A surfactant was used to stabilize polymer particles in the scCO₂. The effects of initiator and surfactant concentrations as well as the monomer concentration were investigated experimentally. The effect of pressure and temperature on the polymerization was measured and discussed.

INTRODUCTION

Polymerization in scCO₂ has been received significant attention as a clean reaction process during the past 10 years as an alternative to the conventional polymerization process [1,2,5]. Conventionally, PMMA, PEHA and PS have been prepared by bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization, or dispersion polymerization. These processes, apart from bulk polymerization, are harmful to human beings and environment due to the using of water, solvents or organic diluents.

However, these polymers can be produced by using environmentally benign scCO₂ [1,3,4,6] and easily separated from the reaction medium by depressurization. It helps to eliminate the energy-consuming drying step that is necessary in the conventional methods. In supercritical fluid (SCF), the polymers are swollen and plasticized, lowering the glass transition temperature [7,8]. Therefore, the removal of residual monomers, mixing of additives, and the formation of foams may be easily achieved. Due to the plasticization in SCF, the diffusion of monomer into the polymer particle is enhanced and the rate of polymerization is promoted.

Since DeSimone et al. synthesized a CO₂-philic fluoropolymer surfactant, various fluoro- and silicone-macromonomer, homopolymer, and copolymer surfactants have been developed [6]. Yates et al. [2] synthesized PMMA and PS using poly(di-methyl siloxane)(PDMS)-derivative block copolymer surfactants which could be inexpensive but not commercially available. Christian et al. [3] prepared dilute latexes of copolymers of MMA and dimethyl aminoethyl methacrylate with Krytox 157 FSL carboxylic acid terminated perfluoropolyether surfactant at 20°C in scCO₂. However, the fluorine based polymer surfactants are very expensive.

PVA is a polymer containing hydroxyl groups, extremely hygroscopic organic gel and is difficult to obtain from direct polymerization of vinyl alcohol. Therefore, it is prepared by saponification of vinyl ester derivative polymers, such as poly(vinyl acetate)(PVAc) (Figure 1), polyvinyl pivalate(PVPi), polyvinyl trifluoroacetate(PVTFA), and polyvinyl tri-chloroacetate(PVTCAc). Although the monomers such as VPi, VTFA and VTCAc are used in the manufacture to produce excellent syndiotactic PVA, they are expensive and the polymers are hard to be hydrolyzed [11]. Therefore, PVAc is the most popular intermediate.

In this study, PMMA and PVAc were synthesized through dispersion polymerization in scCO₂. A commercially-available inexpensive CO₂-philic stabilizer, PDMS-g-pyrrolidone carboxylic acid which was adopted in the synthesis of PEHA by Shim et al. [4,9], was used. The effects of stabilizer and initiator concentrations on the morphology, the yield and the molecular weight were investigated.

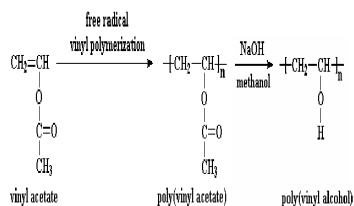


Figure 1: The polymerization of vinyl acetate to poly(vinyl acetate), followed by saponification to produce poly(vinyl alcohol).

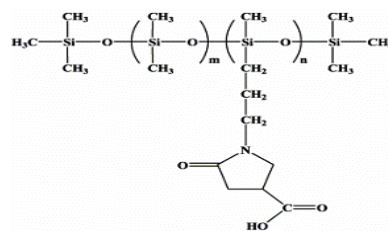


Figure 2: The molecular structure of Monasil PCA.

EXPERIMENTAL

Materials

Pure CO₂ (99.99%) was purchased from Korea Specialty Gases. Methyl methacrylate, vinyl acetate (99%), 2,2'-azobis-isobutyronitrile(AIBN), potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were obtained from Aldrich. Polydimethyl siloxane-g-pyrrolidone carboxylic acid (Monasil PCA, Uniquema), whose structure is shown in Figure 2 and molecular weight is 8500 g/mol, was used as a CO₂-philic surfactant. KPS, SDS, and Monasil PCA were used without any further purification.

Equipment and Procedures

The apparatus was set up as shown in Figure 3. The reactor was a variable-volume view cell equipped with an automatic syringe pump (ISCO Model 260D) and a piston to keep the pressure constant throughout the reaction. After putting an accurately measured amount of initiator and surfactant (± 0.0001 g) into the cell, it was capped and purged with carbon dioxide for 10 minutes. A small amount of monomer was then injected into the cell by a graduated syringe. Carbon dioxide was supplied to the cell and agitated with a magnetic bar. The cell was placed in the constant temperature water-bath and heated to the desired temperature while agitated. After the reaction time, the cell was quenched by placing in an ice bath to stop the polymerization. When the temperature was fully lowered, the pressure was reduced by venting the rear chamber of the cell to remove monomer and CO₂. The polymer and surfactant deposited at the bottom of the chamber were collected. The remaining polymer attached to the wall was also collected by dissolving with acetone solvent. These polymer samples were dried at room temperature for 24 hours to remove the remaining monomer.

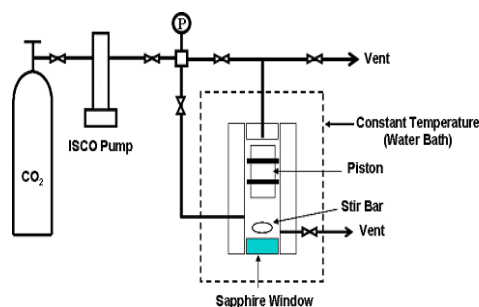


Figure 3: Schematic diagram of the supercritical fluid polymerization equipment.

The polymer was dissolved in tetrahydrofuran(THF) to determine the molecular weight by gas permeation chromatography (GPC). The system consists of Waters 515 Pump, Waters 2410 Differential Refractometer, Rheodyne 7725I Injector and Waters Strygel HR5E column. As reference materials, the Showadenko's polystyrene standards (Mw = 1310, 3370, 13900, 303000, 52400, 205000, 736000, 1190000, 2060000, 3850000) were employed. The column temperature was room temperature and the flow ratio is 1 ml/min.

RESULTS AND DISCUSSION

Effect of Initiator on Polymerization

MMA was polymerized using different amount of initiator, AIBN, at the same amount (10%) of Monasil PCA. Figure 4 shows that the entire polymer samples have similar particle sizes and narrow size distribution. There was no appreciable aggregation of particles in all samples (a), (b) and (c) and the amount of initiator AIBN was not a major factor in determining the morphology of PMMA. It can be seen that 0.5 ~ 1.0% initiator is efficient to obtain uniform and non-agglomerated particles.

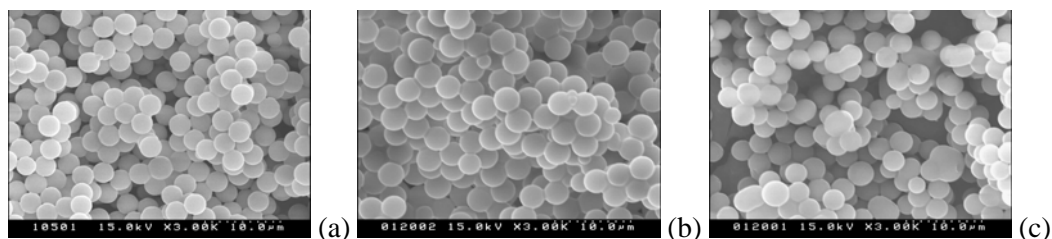


Figure 4: Scanning electron micrographs of PMMA particles produced by different amount of AIBN: (a) 1.0, (b) 1.5, and (c) 2.0 wt%.

The molecular weight of PVAc decreased whereas the yield increased with the increasing of the amount of initiator (Figure 5). As the initiator concentrations lower than 1 wt%, the molecular weight decreased sharply; however the decreasing rate became much smaller thereafter. When the initiator concentration was more than 5 wt%, the yield was continually increasing but very slowly. Thus, the amount of initiator necessary in the polymerization of vinyl acetate is 1.0 wt%. There was some research that used KPS and V-50 (2,2'-azobis(2-amidinopropane)dihydrochloride) as initiators [12] in the polymerization of vinyl acetate at atmospheric pressure. However, when KPS or V-50, which was not even dissolved well in CO₂, was used, no polymer was formed.

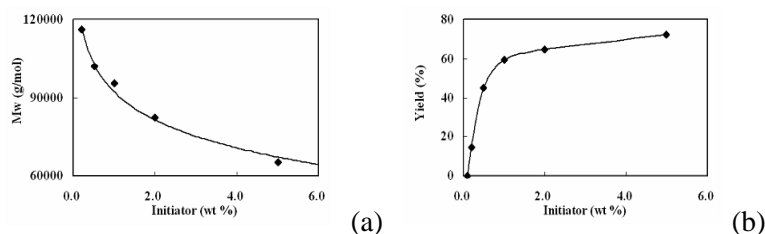


Figure 5: Variation of molecular weight (a) and yield (b) of PVAc upon the amount of initiator in the polymerization of vinyl acetate at 345 bar and 338.15 K for 10 hours.

Effect of Surfactant on Polymerization

As the amount of surfactant increased, the particles size and the overlapped portion of the particles decreased (Figure 6). The PMMA particles conglomerated to form larger particles when 5.1 wt% of Monasil PCA (Fig.6(a)) was used for the reaction. Each agglomerated mass contains up to several primary particles. Fig.6(b) to 6(e) show the particles have a small common volume. It is clearly seen that the particles in Fig.6(f) exist independently. The average size of primary particles that was estimated from 100 particles in each SEM micrograph was approx. 4.2 μm for 5.1 % surfactant (Fig. 6(a)), whereas it was greatly reduced to approx. 2.6 μm when 15.1% surfactant was used (Fig.6(f)). The synthesis of PMMA with Monasil PCA in scCO₂ required the surfactant of 15% of the monomer to cover all the particles completely.

The number average molecular weight, weight average molecular weight and molecular weight distribution were also measured for PMMA synthesized at the same condition but with different

amount of surfactant Monasil PCA. The number average molecular weight was in the range of 72,000 and 118,000 g/mol, while the weight average molecular weight was between 167,000 and 248,000 g/mol. The molecular weight distribution decreased from 2.40 to 2.10 as the amount of surfactant increased, except for the polymer with 10.2% surfactant.

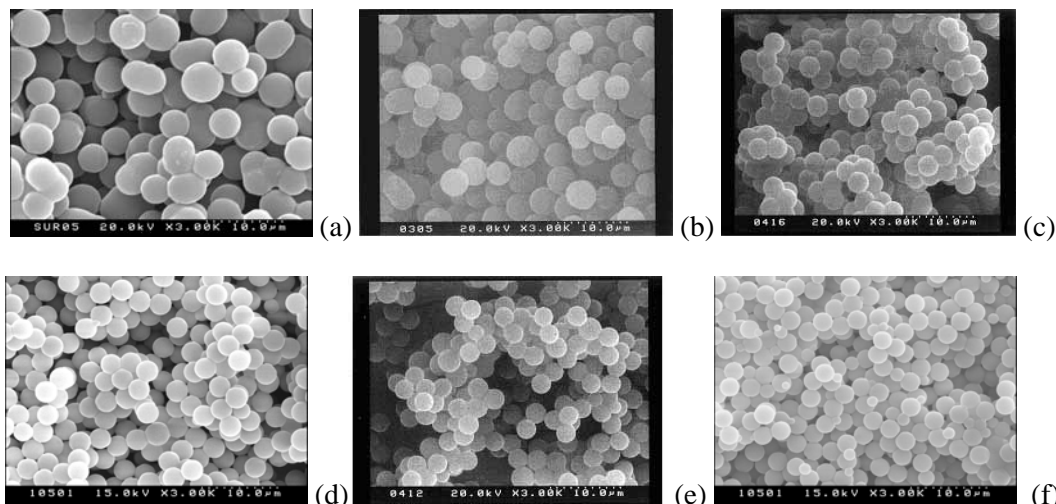


Figure 6: Scanning electron micrographs of PMMA particles produced by reaction in $scCO_2$ with Monasil PCA for 5 hours. The amounts of Monasil PCA in the reactor were (a) 5.1, (b) 6.1, (c) 7.7, (d) 10.2, (e) 12.7, and (f) 15.1 wt%, respectively, based on the monomer content.

Figure 7 shows that the molecular weight decreased with increasing the amount of surfactant up to 10.0 wt%. While the yield of PVAc showed the increasing with the concentration of surfactant. We observed the effect of surfactant in the reaction mixture: (1) when was no surfactant, the reaction mixture was only a little opaque but (2) when Monasil PCA was used in the reaction, the reaction mixture became white milky state.

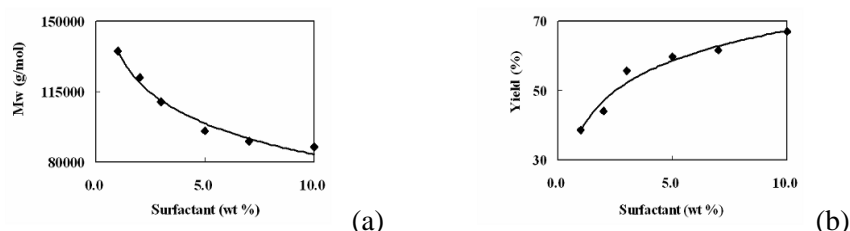


Figure 7: Variation of molecular weight (a) and yield (b) of PVAc upon the amount of surfactant at 345 bar and 338.15 K.

Effect of Monomer Concentration on Polymerization

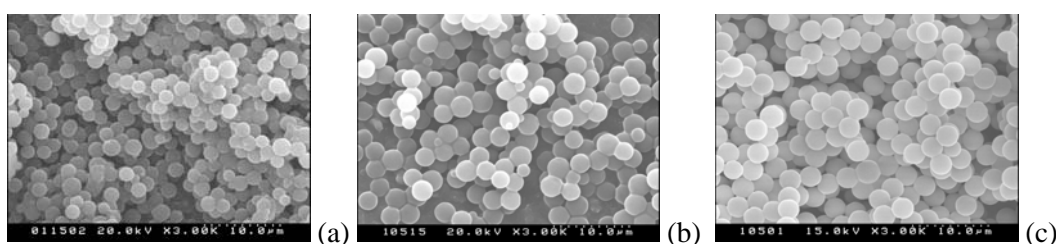


Figure 8: Scanning electron micrographs of PMMA particles produced by reaction in $scCO_2$ with Monasil PCA for 5 hours for different amount of monomer ((a) 12.5, (b) 15, and (c) 20 wt% of CO_2).

The polymerization with 1.0 wt% AIBN (of monomer) and 10 wt% Monasil PCA surfactant (of monomer) in scCO₂ at 338.2 K and 345 bar for 5 h and with different amount of monomer was performed. Figure 8 shows that the size of the polymer particles increased from 1.99 μm to 2.86 μm when the concentration of monomer increased from 12.5 wt% to 20 wt% of CO₂. The molecular weight of PMMA obtained also became greater with the amount of monomer.

Effect of Pressure on Polymerization

The effect of pressure on the polymerization of PMMA was investigated. The reactions with 1.0 wt% AIBN (of monomer), 20 wt% monomer (of CO₂) and 10 w% Monasil PCA surfactant (of monomer) in scCO₂ at 338.2 K for 5 hours were done. Figure 9 shows that the pressure has the same effect with the concentration of monomer on particle size and molecular weight. The particle size of PMMA enhanced from 2.68 μm to 2.99 μm while the molecular weight increased from 179,000 g/mol to 184,000 g/mol when the pressure increased from 310 bar to 414 bar.

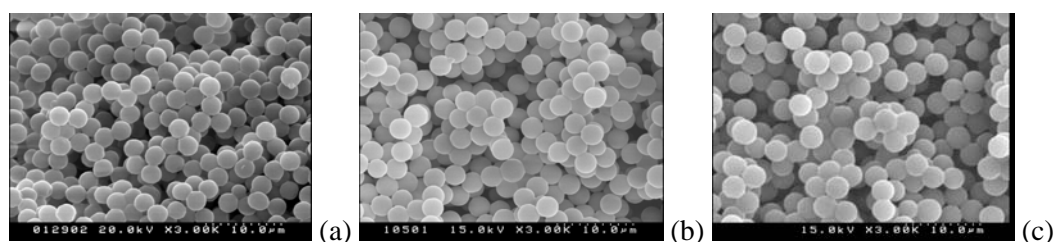


Figure 9: Scanning electron micrographs of PMMA produced by polymerization in scCO₂ by different pressure ((a) 310, (b) 345, and (c) 414 bar).

Effect of Temperature on Polymerization

Figure 10 shows the influence of temperature on polymerization PMMA. The reaction condition set at 1.0 w% AIBN (of monomer), 20 w% monomer (of CO₂) and 10 w% Monasil PCA (of monomer) in scCO₂ at 345 bar for 5 hours. The particle size has the same behaviour when the pressure and temperature were changed. As temperature was increased from 335.7 K to 340.7 K, the particle size enlarged from 2.22 μm to 3.64 μm . However, temperature does not affect much on the molecular weight. It was in the range of 130,000 g/mol to 148,000 g/mol.

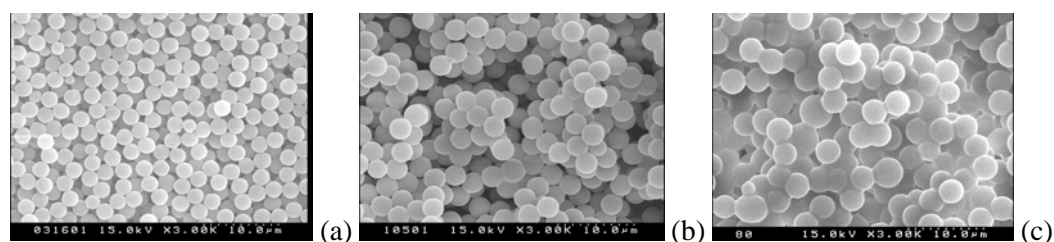


Figure 10: Scanning electron micrographs of PMMA produced by polymerization in scCO₂ at different temperature ((a) 335.7, (b) 338.2, (c) 340.7 K).

CONCLUSION

PMMA particles with diameters of about 2.5 and 4.2 μm were obtained by polymerization in scCO₂ using an inexpensive CO₂-philic surfactant, Monasil PCA. The polymer particles were stable in scCO₂ and their shape was remained spherical as their surfaces were covered with the surfactant. The average particle size decreased exponentially with increasing the amount of CO₂-philic surfactant, yielding the smallest and very uniform particles at 15% surfactant. The degree of agglomeration was also decreased with the amount of CO₂-philic surfactant. To obtain acceptable quality PMMA particles, at

least of 7 % of Monasil PCA must be used. The amount of initiator (AIBN) in the range of 1 ~ 2% did not significantly influence the morphology of PMMA though the particle size distribution became slightly wider. AIBN and Monasil PCA were functioning well as initiator and stabilizer, respectively, in the polymerization of VAc. The monomer concentration, the pressure and the temperature have the same affect on the particle size of PMMA. As these parameters increased, the particle size increased. However, the effect of temperature on the molecular weight was not significant.

The polymerization of PVAc also examined in scCO₂ medium. The results show that the yield of PVAc increased, however, the molecular weight decreased with the concentration of initiator and surfactant.

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