

FORMATION OF PMMA MICROPARTICLES IN SUPERCRITICAL CARBON DIOXIDE

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Poly(methyl methacrylate) (PMMA) microparticles have been made by dispersion polymerization using PDMS-g-pyrrolidone carboxylic acid, a CO₂-philic stabilizer, in supercritical carbon dioxide. The effect of pressure, temperature, monomer content, surfactant content, initiator content, and reaction time on the yield, molecular weight, molecular weight distribution, particle size, and particle size distribution of PMMA has been thoroughly investigated. The polymerization reaction conditions are as follows: the surfactant content between 5 to 20% of monomer, the initiator content between 0.5 to 2.0% of monomer, the monomer content between 10 to 20% of CO₂, the pressure between 207 to 414 bar, the temperature between 333 to 343 bar, and the reaction time was up to 7 hours. The yield was higher than 90% and the molecular weights of PMMA were almost the same for all the surfactant concentrations between 5 to 20 % of monomer. However, the particle size got smaller and the size distribution became narrower as the concentration increased. The yield of PMMA has maximum at the initiator content of 1% of monomer, but the molecular weight decreased and the size distribution got wider at higher concentrations. As the monomer concentration increased, both the yield and molecular weight increased rapidly. The yield and molecular weight increased with pressure up to 310 bar but they leveled off and the particle sizes also showed near uniform distribution at higher pressures. The two quantities increase rapidly as temperature increased forming a maximum and then slowly decreased. The yield of polymer increased sigmoidally with time but the molecular weight increased along with different curves. The size of the polymer particles increased with time.

INTRODUCTION

In the conventional polymerization processes, polymer microparticles have been obtained through emulsion polymerization, dispersion polymerization, precipitation polymerization, or suspension polymerization using water as the reaction medium and surfactants as stabilizers. The particle size was a few millimeters in the early years, but as time has been passed it has been greatly reduced to a few submicrometers ~ micrometers due to the development of new polymerization methods and new surfactants. Some methods to make particles with wanted sizes and methods not to use surfactant have been developed. However, separation of the reaction medium from the product particles is not easy and what makes it worse is that the medium contains hard-to-separate surfactants. To overcome these drawbacks there have been attempts in the 90s, including one using supercritical fluid.

Supercritical carbon dioxide has been investigated as an alternative medium to the solvents that are used in the conventional polymerization processes [1-5]. PMMA that is widely used as glazing, lighting, and decorative materials and has been prepared by various polymerization methods, such as bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization, and dispersion polymerization. Except for the bulk polymerization, all other methods that are using water, solvents or organic diluents are

are harmful to our environments, whereas the supercritical CO₂ process [1-4,6-7,9-10] is environmentally benign. As CO₂ is gaseous at the atmospheric condition, we can get dry polymer by simple depressurization of the reaction product. Elimination of the energy-consuming drying process that is necessary in the conventional method reduces costs for the drying equipment and the energy required for drying. Polymers are swollen and plasticized in supercritical fluid process, lowering the glass transition temperature [7-8]. Therefore, the removal of residual monomers, mixing of additives, and formation of foams may be easily achieved using supercritical fluid process. Also, polymerization rate is promoted as the diffusion of monomer in the polymer particle is enhanced due to the plasticization [7].

The particle size of polymer could be tailored to meet the requirement in both conventional and supercritical fluid processes. In the latter process, we can get particles of desired size, from sub-microns to microns, by changing the types and amounts of surfactants [5]. PMMA particles are not stable in supercritical CO₂[1] and thus easily precipitated. To promote the stability of the particles in supercritical CO₂ they must be covered with a CO₂-philic polymeric surfactant. Though polymers are not soluble in CO₂, certain type of fluoro- and siloxane polymers are fairly soluble in supercritical CO₂ due to favorable interactions between CO₂ and these polymers[6]. A CO₂-soluble fluoropolymer was synthesized by DeSimone et al. in 1992[1] and used as a stabilizer in polymerization of methyl methacrylate (MMA) in supercritical CO₂. In the presence of CO₂-philic stabilizer, polymer particles are covered with this stabilizing barrier that prevents particles from being agglomerated. CO₂ also plasticizes polymers, lowering the glass transition temperature. Using this properties we may extract residual monomers from polymer, impregnate certain additives into polymers, fractionate polymers, and make polymeric foams. During the polymerization, the growing polymer particles are swollen and the diffusion of monomer in the particle is promoted, increasing the polymerization rate. Swelling of polymer depends on the reaction temperature and pressure.

Shim et al.[9] synthesized poly(2-ethylhexyl acrylate) (PEHA) using a CO₂-philic Monasil PCA stabilizer, PDMS-g-pyrrolidone carboxylic acid, in supercritical CO₂. The resulting polymer suspension in supercritical fluid was expanded rapidly to make surface coatings and stable aqueous latexes. There have been many reports on the synthesis of PMMA using supercritical CO₂, however, it is hard to find a detailed research on the effects of all the reactions variables involved. In the synthesis of PMMA particles through dispersion polymerization in supercritical CO₂, we have used the same stabilizer that was adopted in the synthesis of PEHA by Shim et al.[9-10]. In this research, the effect of pressure, temperature, monomer content, surfactant content, initiator content, and reaction time on the yield, molecular weight, molecular weight distribution, particle size, and particle size distribution of PMMA will be thoroughly investigated.

EXPERIMENTAL

Materials

Pure CO₂ with purity of 99.99% were purchased from Korea Specialty Gases. Inhibitor in methyl methacrylate (Aldrich) was removed by passing through alumina column (Aldrich)⁵. 2,2'-azobisisobutyronitrile (AIBN) was used as an initiator and purified by recrystallization in methanol[9]. PDMS-g-pyrrolidone carboxylic acid (Monasil PCA, Uniquema) was used as a CO₂-philic surfactant. The molecular weight of Monasil PCA is 8500 g/mol.

Polymerization equipment and procedure

The polymerization equipment is shown in Figure 1, where a variable-volume view

cell was used as the polymerization reactor. The pressure in the reactor is kept constant using a syringe pump (ISCO Model 260D). After placing known amounts of initiator (0.5~2.0% of monomer) and surfactant (5~20% of monomer), air in the reactor was removed by flushing with CO₂ for about 20 minutes. Methyl methacrylate (MMA, 10~20% of CO₂) was then injected into the reactor using a syringe and about 10 g of CO₂ was charged into the reactor. These materials that were placed in the reactor were then mixed by stirring with a magnetic stir bar for ten minutes, while the pressure in the reactor was maintained at a certain value in the range between 207 and 414 bar by ISCO Model 260D syringe pump. While keeping the pressure, the polymerization reaction began in the water bath that was maintained at a temperature between 333.2 and 343.2 and controlled to ± 0.1 K by an immersion thermostat (LAUDA Model E-100). After certain time (1~7 hours) of polymerization at a fixed condition, the reactor was quenched and depressurized to atmospheric pressure. The polymer powder collected from the reactor was dried in the vacuum oven overnight to remove the remaining monomers. The morphology of polymer particles was imaged with a Hitachi Model S-420 scanning electron microscope (SEM). The molecular weight and molecular weight distribution were measured with a gel permeation chromatograph (Waters Model GPC 2000) equipped with a refractive index detector and a micro styragel column (American Polymer Standards).

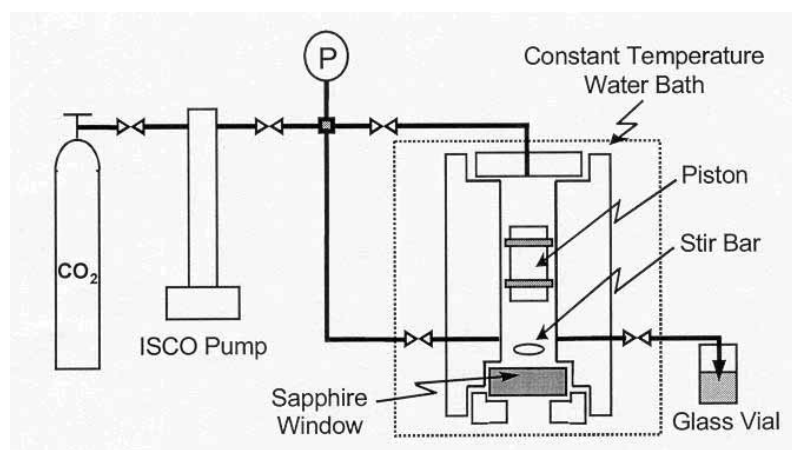


Figure 1. Schematic of the Polymerization Equipment.

RESULTS AND DISCUSSION

Effect of CO₂-philic Surfactant on the Particle Morphology and the Molecular Weight

Using CO₂-philic surfactant, Monasil PCA, uniform and micron-sized PMMA particles were obtained from the polymerization reaction in supercritical CO₂. For each reaction the amount of surfactant was set in a range between 5.0 and 19.9 wt% of MMA, while other conditions are fixed: AIBN 1.0 wt% of monomer, MMA 20 wt% of CO₂, temperature 338.2 K, pressure 345 bar, and reaction time 5.5 hours. The particle size decreased as the amount of surfactant increased but leveled off when it goes over 15% (Table 1 and Figure 2), while the polydispersity index does not change much. This may be because when the amount of surfactant is small, the number of polymer particles is small and they grow large until all the monomers are consumed. When it goes over 10%, the number of particles does not increase much and all the surfaces of the particles are fully covered. The molecular weight of the polymer is in the range between 173,000 and 190,000 but the molecular weight distribution reduced from 3.44 to 1.60 and the yield of the polymer Table 1. The particle size, PDI, molecular weight and its distribution, and the yield of PMMA produced by polymerization with AIBN 1.0 w% of monomer, and MMA 20 w% of CO₂ in

supercritical CO₂ at 338.2 K and 345 bar for 5.5 h

Entry Number	Surfactant (wt% of monomer)	D_n^a (?)	PDI ^b	Mw	MWD ^c	Yield (%)
1	5.0	5.04	1.11	190000	3.44	89.8
2	10.2	2.86	1.0	180000	1.76	96.6
3	15.2	2.41	1.05	173000	1.68	98.8
4	19.9	2.44	1.07	188000	1.60	97.8

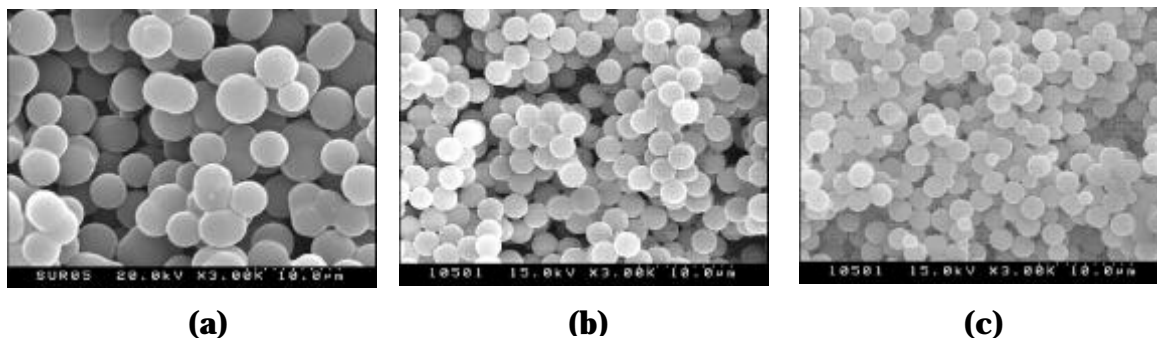


Figure 2. Scanning electron micrographs of PMMA produced by polymerization with AIBN 1.0 w% of monomer and MMA 20 w% of CO₂ in supercritical CO₂ at 338.2 K and 345 bar for 5.5 h and with Monasil PCA of (a) 5.0, (b) 10.2, and (c) 15.2 wt% of monomer.

increased from 89 to 98% as the amount of surfactant increased. The average particle size was measured the size of more than 50 particles in the SEM pictures and averaged. The particle size distribution (PDI) was calculated with the measured particle sizes. We can see here that the amount of surfactant influence the size of the particles but does not influence the molecular weight and and yield of the polymer.

Effect of Initiator on the Particle Morphology and the Molecular Weight

For each reaction the amount of initiator was set in a range between 0.5 and 2.0 wt% of MMA, while other conditions are fixed: surfactant 10.0 wt% of monomer, MMA 20 wt% of CO₂, temperature 338.2 K, pressure 345 bar, and reaction time 5.5 hours. Figure 3 shows that as the amount of initiator increases, molecular weight decreases monotonically, while the yield of PMMA has a maximum at the initiator concentration of 1.0%. As the amount of surfactant increases, the number of radicals and thus the number of polymer chains also increase, producing shorter polymer chains when the reaction terminates. The reason that the yield of polymer is small when the initiator concentration is 0.5% may be that at this low concentration the termination reaction is faster than the initiation reaction.

Effect of Monomer Concentration on the Particle Morphology and the Molecular Weight

As the monomer concentration increased from 10 to 20% of CO₂, the particle diameter, molecular weight, and the yield of polymer increased (Figure 4). The last two may have increased as the propagation reaction continued until all the monomers were consumed.

Effect of Pressure on the Particle Morphology and the Molecular Weight

When the pressure was changed from 207 to 414 bar, a gel shape product was obtained at low pressures and spherical particle shape products were obtained at high pressures. As pressure increased, the particle size, the yield, and the molecular weight of polymer increased

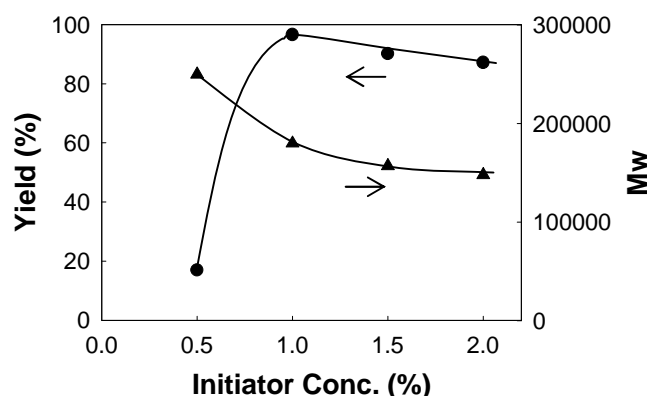


Figure 3. The yield and molecular weight of PMMA produced by polymerization of MMA with monomer 20 w% of CO₂ and surfactant 10.0 % of monomer in supercritical CO₂ at 338.2 K and 345 bar for 5.5 h.

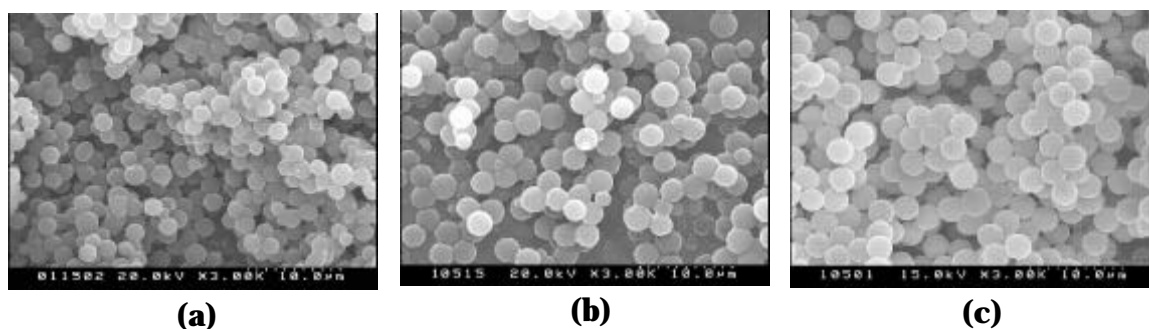


Figure 4. Scanning electron micrographs of PMMA produced by polymerization with AIBN 1.0 w% of monomer and Monasil PCA surfactant 10% of monomer in supercritical CO₂ at 338.2 K and 345 bar for 5.5 h and with different amount of monomer ((a) 12.5, (b) 15, and (c) 20 w% of CO₂).

due to the increase in the stability of the particles and the solubility of surfactant with pressure. At pressures higher than 300 bar, both the yield and the molecular weight were leveled off.

Effect of Temperature on the Particle Morphology and the Molecular Weight

When the temperature was changed from 333.2 to 343.2 K, the particle size, the yield, and the molecular weight of the polymer increased until the temperature reaches 338 K. After this temperature both values decreased and the particles became agglomerated forming cocoon shapes. So, it may be said that 65 C is the best polymerization temperature for MMA. At low temperatures, the reaction rate is slow. At high temperatures, the termination rate may be fast.

Effect of Reaction Time on the Particle Morphology and the Molecular Weight

Until 4 hours after the reaction started, there was no particle formed. After 3 hours, the polymer particles started to be formed but were heavily agglomerated. After then, segregated polymer particles were formed. The size, the molecular weight, and the yield of the polymer increased as the reaction time passed. The yield of the polymer increased with time forming a sigmoidal curve. It was smaller than 40% until 2 hours but suddenly increased to about 95% when 4 to 5 hours have passed. After 5 hours, the yield remained almost the same value (Figure 5). This type of curve is the result of the well known Trommsdorff effect.

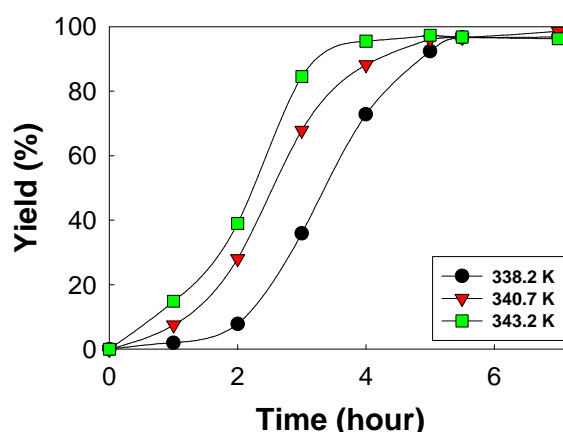


Figure 5. Yield of PMMA produced by polymerization with AIBN, 1.0 w% of monomer, MMA, 20 w% of CO₂, and Monasil PCA, 10 w% of monomer, in supercritical CO₂ at 338.2 K and 345 bar at different reaction times.

CONCLUSIONS

As the amount of surfactant increased, the polymer particles became smaller due to the complete coating of the particles with the surfactant. With more initiator, the molecular weight decreased. The particle size, the molecular weight, and the yield of the polymer increased as the amount of monomer or the reaction pressure increased. The size and the yield increased as the initiation reaction increased with temperature up to 338.2 K, but then decreased. As time passed, the size, the yield, and the molecular weight increased. The yield of polymer increased in a sigmoidal curve.

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