Environmentally Benign Precipitation Copolymerization of Methacrylate Ester and Styrene to Make Polymeric Microspheres in Supercritical Carbon Dioxide

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ABSTRACT: The polymeric microspheres were synthesized by the precipitation copolymerization of glycidyl methacrylate (GMA) with methacrylic acid(MAA) or 2-hydoxyethyl methacrylate (2-HEMA) containing styrene (ST) in SC-CO_2. Scanning electron microscopy (SEM) showed that the products were spherical microparticles, with the addition of MAA and/or 2-HEMA as the monomer, with diameter of 0.2–2 μm. The effects of copolymerization pressure, temperature, and ratios of GMA/MAA, ST, and/or GMA/2-HEMA, on the particle size and morphology were investigated in detail. A new experiment setup is proposed for the large amount of production, based on the rule of lower monomer concentration, more stable system, and better use of the present polymerization apparatus. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2425–2431, 2007

Key words: polymeric microsphere; supercritical carbon dioxide; polymerization; powder coating

INTRODUCTION

To reduce the release of harmful volatile organic compounds to environment from the coatings and chemical industry, powder coating has been attracting much attention as environmentally benign coating systems.[1,2] In powder coating, a polymeric powder with no solvent is baked at a high temperature to melt and fuse the particles into a coherent coating film. For a powder coating system, it is often desirable to produce globular polymer microparticles in the order of several micrometers in diameter. For microparticles smaller than 100 μm, production methods such as *in situ* polymerization are widely used.[3–7] However, this method often requires harmful organic solvents and/or ionic surfactants, and needs a removal process of the residual ionic surfactants on the small particles because of the voids in the polymer film caused by the residual ionic surfactants, which costs a large amount of water for washing the particles and thermal energy for drying the particles. Thus, an environmentally benign method to make polymer microparticles needs to be developed, avoiding the use of toxic organic solvents and/or surfactants.

It is well known that supercritical carbon dioxide (SC-CO_2) possesses interesting solvent properties, which has been applied to a range of separation and extraction processes, as well as in organic reaction and polymer industry. SC-CO_2 may be utilized as an environmentally benign solvent substitute, as it is nontoxic, nonflammable, and has easily accessible critical conditions, i.e., T_c = 304 K and P_c = 7.37 MPa. Recently, several principles based on the use of supercritical CO_2 for polymerization reaction have been attracting much attention as an environmentally benign procedure. SC-CO_2 offers the possibility of developing new polymerization methodologies with near-zero waste production.[8] The homogeneous polymerization of several fluorous monomers in supercritical CO_2 was reported.[9] However, as the fluorous monomers are expensive, the commercialization of promising CO_2-based processes has met with only limited successes. It is desired to develop an environmentally benign polymerization technique in SC-CO_2, using nonfluorous monomers from low-cost raw materials.[10] In fact, a number of groups conducted such kind of work, for example, Romack et al.[11] reported the preparation method of polyacrylic acid microparticles in SC-CO_2 without fluorous surfactants; Xu et al.[12] investigated the effect of acetic acid and ethanol as a cosolvent on the product morphology by precipitation polymerization of acrylic acid in supercritical CO_2; Otake[13] has reported the copolymerization of acrylic acid and/or
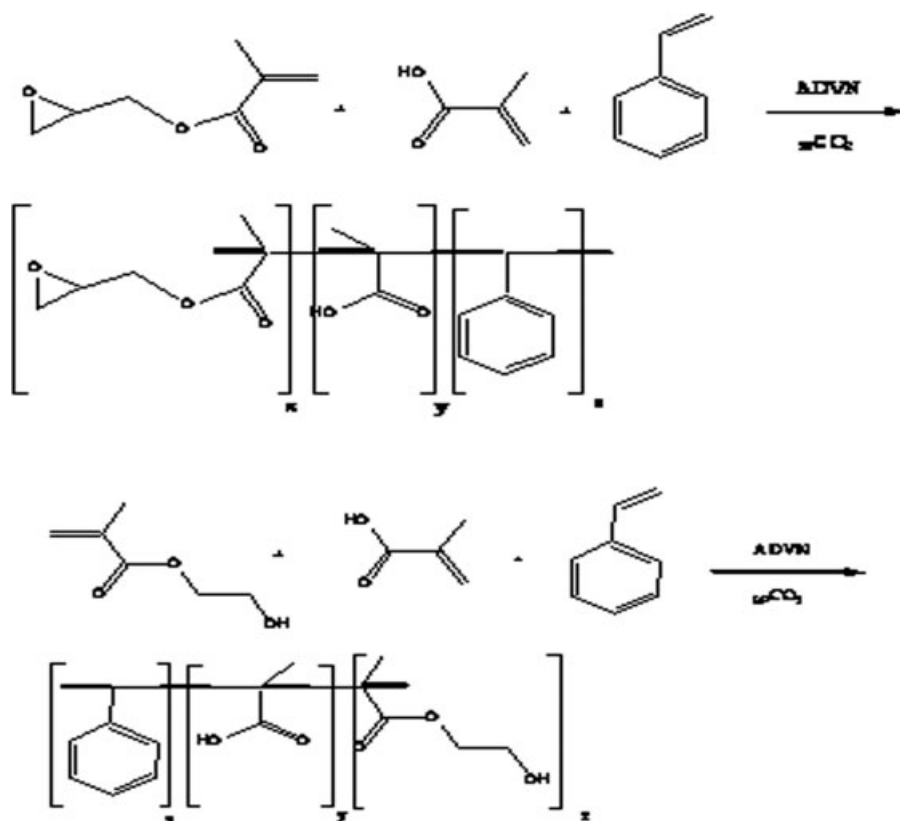
Figure 1 Scheme of the copolymerization.

methacrylic acid (MAA) in SC-CO_2. He also reported the effect of acrylic acid and/or MAA on the particle morphology, and it indicated the carboxyl group in monomer to act as the stabilizer in SC-CO_2; Matsuyama et al.[14] in our group reported the copolymerization of several monomers, using SC-CO_2 as solvent. During the copolymerization of glycidyl methacrylate (GMA) with MAA and/or 2-hydroxyethyl methacrylate (2-HEMA) in SC-CO_2, it was found that MAA and 2-HEMA served as a stabilizer for GMA in SC-CO_2. The particle size and morphology were affected by the copolymerization pressure, temperature, and initial GMA/MAA, styrene (ST), and/or GMA/2-HEMA concentration ratio. The initial concentration ratio was more effective than the other factors in controlling the particle size. The obtained polymer particles were applied as powder coatings and a toner of a copying machine, exhibiting a smooth and coherent film. These reports indicated the possibility of environmentally benign polymerization and particle formation in SC-CO_2 without fluorous surfactants.

This is a continuous work, we added one more monomer, ST, in the copolymerization of GMA with MAA and/or 2-HEMA for enhancing some properties of the polymer microparticles, and considering the effect of ST concentration on the mean particle size. Also, a new polymerization reactor was proposed for a large amount of production to ensure the monomer

concentration in the system as low as possible and as stable as possible, as well as avoiding explosive polymerization. Additionally, the effects of copolymerization pressure and temperature on the particle morphology were considered in detail.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA), methacrylic acid (MAA), 2-hydroxyethyl methacrylate (2-HEMA), and styrene (ST) were obtained from Wako Pure Chem. Their purities were believed to be greater than 98%. The initiator, 1,2,2′-Azobis (2,4-dimethylvaleronitrile) (ADVN) was purchased from Wako Pure Chem., and recrystallized twice from methanol before use. Its purity was believed to be greater than 95%. Carbon dioxide (CO_2), with a 99.9% minimum purity, was purchased from Fukuoka Sanso. The molecular structure and copolymerization scheme are shown in Figure 1.

Copolymerization

All copolymerizations were carried out in a 50 mL stainless steel high-pressure cell equipped with a magnetic stirrer. For the copolymerization, a known amount of monomers and initiator (ADVN) were charged into the cell, which was then purged with carbon dioxide
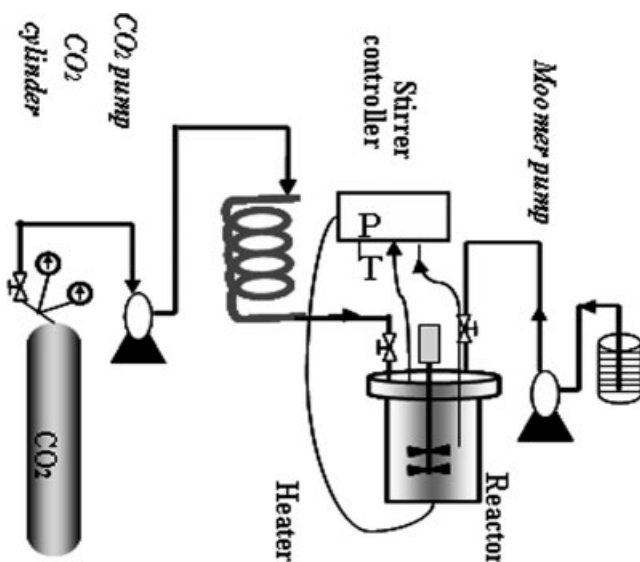
Figure 2 Experimental setup.

for 15 min to get rid of oxygen. The cell was then sealed and enough liquid CO_2 was added using a CO_2 pump (SCF-get, JASCO) to a required reaction pressure. The temperature was then gradually increased to the desired reaction temperature. The polymerizations were allowed to proceed for reaction time varying from 1 to 8 h. After the polymerization, the reactor was immersed in a cold water-bath and the CO_2 was immediately vented through a needle valve into methanol to collect a sample of the intact polymer particles that sprayed out of the reaction cell. A new experiment setup as shown in Figure 2 was proposed for the large amount of production, to make the monomer concentration in the reaction system as low as possible and as stable as possible, and good use of the present polymerization apparatus.

Characterization

The particle morphologies were analyzed and imaged using a scanning electron microscopy (SEM) (Hitachi, S-2100B). The sample was sputter-coated with silver-palladium to an approximate thickness of 200 Å. The particle size and particle size distribution were determined by SEM and a laser diffraction particle size analyzer (Shimadzu, SALD-2000). To analyze the particle size and distribution by SALD, the sample was dispersed in water with surfactant, and sonicated before the analysis. The reproducibility of the primary particle diameter and geometric standard deviation of the sample particle diameter was within ±5%.

RESULTS AND DISCUSSION

Phase behavior

Before the copolymerization experiment, the phase behavior of the monomer–CO_2 system was observed

by using a high-pressure cell equipped with sapphire windows. The phase behavior was observed at 10 MPa and 338 K, because the precipitation copolymerization of the methacrylate ester was carried out at 338 K in the pressure range from 10 to 25 MPa. The mixtures of CO_2 and the methacrylate ester or methacrylic acid formed a single supercritical fluid phase at 10 MPa and 338 K. A similar phase behavior has been observed in other CO_2–monomer systems, such as CO_2–ST,[15] CO_2–GMA,[16] CO_2–MMA, and CO_2–MAA.[17] Experiments also showed that the ADVN, as the initiator in the system, dissolved in the mixtures of CO_2 and methacrylate ester or methacrylic acid. The polymerization is regarded as conducting in homogenous phase, for the minor polymer produced will precipitate and the effect to the phase can be omitted.

Copolymerization of GMA, MAA, and ST in SC-CO_2

The copolymerization conditions, monomers ratio, and polymer morphologies from the copolymerization in SC-CO_2 for all the experiments are shown in Table I. We ever tried the experiment with monomers ratio of GMA : MAA : ST = 1 : 1 : 1, but failed to obtain fine polymer particles. The obtained products were like oligomer with a low glass transition temperature. It may be considered that MAA acts as not only a monomer, but also as a stabilizer during the copolymerization of GMA with MAA in SC-CO_2, that was consistent with our previous experimental results.[14] Then the methacrylic acid molar ratio was increased to GMA : MAA : ST = 1 : 5 : 1. White particles were observed in the high-pressure cell, after venting CO_2. The polymer particles were collected and weighed, the yields were more than 95%. The SEM photograph of the poly(GMA-MAA-ST) copolymer microparticles obtained at 338 K and 20 MPa is shown in Figure 3 to indicate that the polymeric particles had the size of several hundreds of nanometers and exhibited spherical shape. The particle size distribution of the poly(GMA-MAA-ST) copolymer microparticles was fairly monodispersed as shown in Figure 4. Furthermore, the residual monomer in the polymeric microspheres was measured by recording the weight loss after heating a sample at 413 K for 2 h to show that the residual monomer was less than 0.1 wt %. It may be considered that the residual monomer was removed through the CO_2 venting process after copolymerization in SC-CO_2. Though the similar product morphologies have been observed for the dispersion polymerization of GMA using poly(1,1-dihydroperfluorooctyl acrylate) (poly(FOA)) as a stabilizer,[18] it had the disadvantage of the high cost of poly(FOA).

The above-mentioned precipitation copolymerization in SC-CO_2 is an environmentally benign forma-

TABLE I
Copolymerization Conditions and Monomer Ratio with Obtained Particles Characteristics

No.	ADVN (g)	2-HEMA (g)	MAA (g)	Styrene (g)	GMA (g)	Temp. (K)	Pressure (MPa)	Time (h)	D_p (µm)[a]	Geometric SD[b]
1	0.03	0	0.172	0.21	0.284	338	20	6		
2	0.03	0	0.172	0	0.284	338	20	6		
3	0.03	0	0.43	0.105	0.142	338	20	6	0.7	0.3
4	0.03	0	0.43	0.05	0.142	338	20	6	0.36	0.28
5	0.03	0	0.43	0.02	0.142	338	20	6	0.3	0.25
6	0.03	0	0.43	0	0.142	338	20	6	0.56	0.28
7	0.03	0.13	0.43	0	0	338	20	6	0.5	0.34
8	0.03	0.13	0.43	0.02	0	338	20	6	0.28	0.24
9	0.03	0.13	0.43	0.05	0	338	20	6	0.35	0.28
10	0.03	0.13	0.43	0.105	0	338	20	6	0.66	0.32
4	0.03	0	0.43	0.05	0.142	338	10	6	0.54	0.3
12	0.03	0	0.43	0.05	0.142	338	15	6	0.48	0.3
13	0.03	0	0.43	0.05	0.142	338	25	6	0.32	0.28
14	0.03	0	0.43	0.05	0.142	338	30	6	0.3	0.28
15	0.03	0	0.43	0.05	0.142	348	20	6	0.4	0.3
16	0.03	0	0.43	0.05	0.142	358	20	6	0.42	0.28
17	0.03	0	0.43	0.05	0.142	368	20	6	0.42	0.28
18	0.03	0.13	0.43	0.05	0	338	10	6	0.66	0.34
19	0.03	0.13	0.43	0.05	0	338	15	6	0.56	0.36
20	0.03	0.13	0.43	0.05	0	338	25	6	0.32	0.28
21	0.03	0.13	0.43	0.05	0	338	30	6	0.28	0.24
22	0.03	0.13	0.43	0.05	0	348	20	6	0.38	0.3
23	0.03	0.13	0.43	0.05	0	358	20	6	0.45	0.4
24	0.03	0.13	0.43	0.05	0	368	20	6	0.54	0.46

[a] D_p = mean particle diameter.
[b] Standard deviation, $\ln \sigma = \sqrt{(1/\sum n)(\sum n(\ln D - \ln D_p))^2}$, where n is the number of particle, D is the particle diameter, and D_p is the mean particle diameter.

tion technique for the production of polymer microspheres when compared with a routine *in situ* polymerization. The technique does not require harmful organic solvents and/or ionic surfactants, hence does not need a removal process of the residual

ionic surfactants on the small particles, that cost a large amount of water for washing the particles and thermal energy for drying the particles, and the residual surfactants and impurities may cause adverse effect on the resin film in the powder coating. On
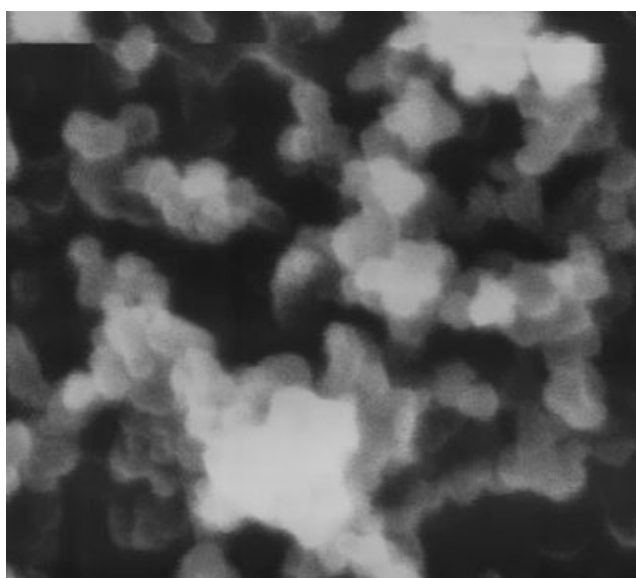

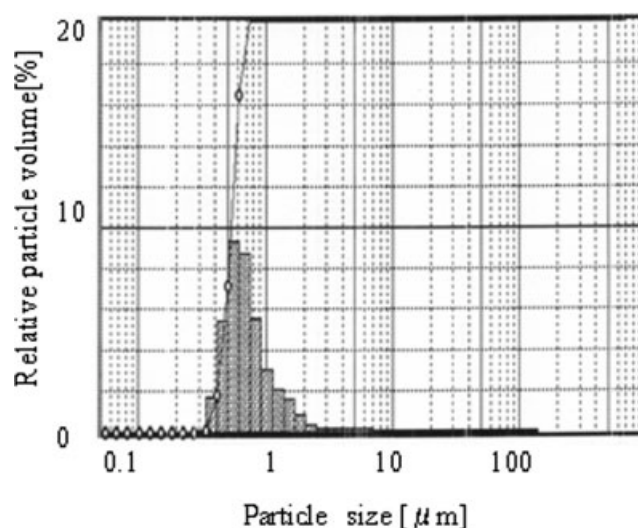
Figure 3   Copolymer particles GMA + MAA + ST.

Figure 4   Distribution of copolymer particles GMA + MAA + ST.
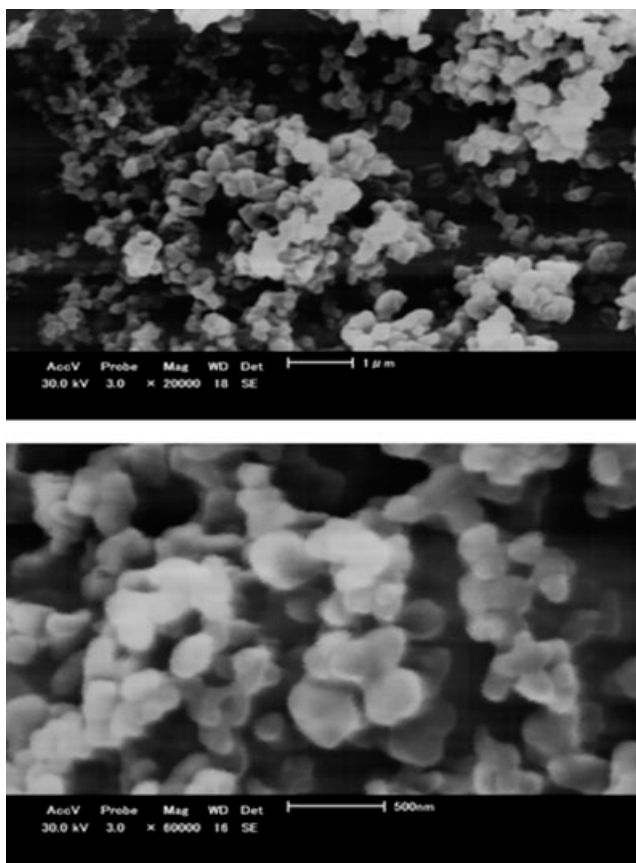
Figure 5 SEM photos for different monomer ratio. (a) MAA : GMA : ST = 5 : 1 : 0.5; (b) MAA : GMA : ST = 5 : 1 : 0.2.

the other hand, globular polymer microparticles in the order of several micrometers in diameter were obtained during the copolymerization of GMA, MMA, and 2-HEMA, the example SEM photo is shown in Figure 5.

The Figures 5 and 6 are the SEM photos of microspheres of PGMA-MAA-ST and PMAA-ST-2-HEMA, which reflect the effect of ST concentration on the polymer particle morphology. The effects of monomer ratio, copolymerization temperature, and pressure on the polymer particles were investigated hereinafter.

Effect of monomer concentration ratio on the particle morphology

The effect of molar ratio of MAA on the copolymer particle morphology for the PMAA-GMA and PMAA-2-HEMA system has been discussed in our previous work,[14] (that is the concentration of MAA play an important role for the produced particle morphology, the mean particle diameter decreases with an increase in the concentration of the MAA. Here, the same trend remained, for the monomers ratio (GMA : MAA : ST = 1 : 1 : 1), we failed to obtain fine polymer particles. When we increased the methacrylic acid molar ratio to GMA : MAA : ST = 1 : 5 : 1, a desirable result was obtained. It may be considered that

MAA acts as not only a monomer, but also as a stabilizer during the copolymerization of GMA with MAA in SC-CO$_2$. We mainly discussed the effect of ST concentration on the copolymer microparticle, the molar ratio of MAA to GMA was fixed to 5 : 1, and the copolymerization was conducted at 338 K and 20 MPa with the ratio of ST to MAA varying from 0.2 to 1.0, the mean particle diameters are listed in Table I, and the mean particle size against the concentration of ST is plotted in Figure 7. As shown in Figure 7, the small amount of ST is helpful to decrease the mean diameter of the particles, this may be explained the as the modification of the polymer by ST to make the system more stable, but with the increase of ST content in the system, the copolymer was more difficult to precipitate, resulting in a viscous copolymer.

Effect of copolymerization temperature on the particle morphology

The effect of the copolymerization temperature on the particle morphology was investigated with the specific monomers ratio of MAA : GMA : ST = 1 : 1 : 0.5 at 20 MPa. The mean diameters of the (MAA-GMA-ST) copolymer and the (MAA-2-HEMAA-ST) copolymer are displayed against the temperature in Figure 8.
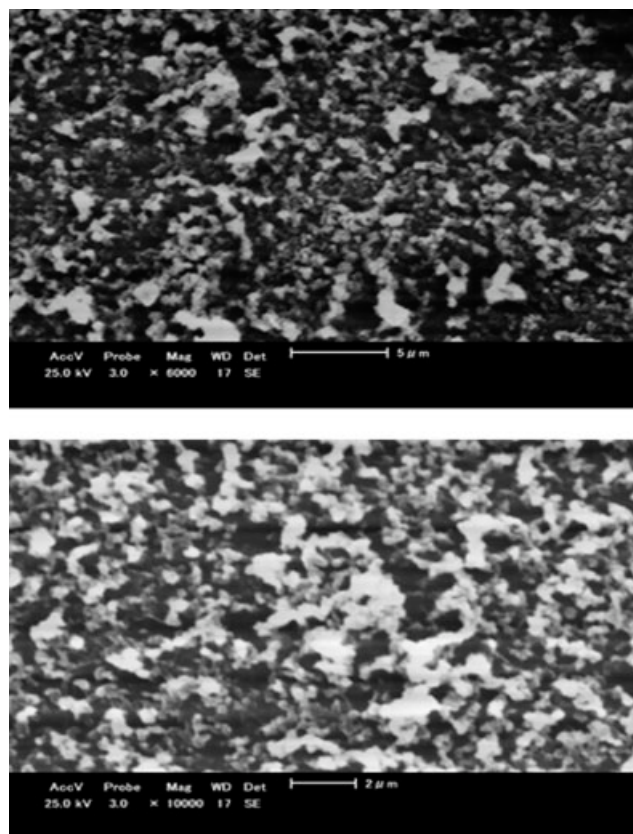

Figure 6 SEM photos for different monomer ratio. (a) MAA : 2-HEMA : ST = 5 : 1 : 0.2; (b) MAA : 2-HEMA : ST = 5 : 1 : 0.5.
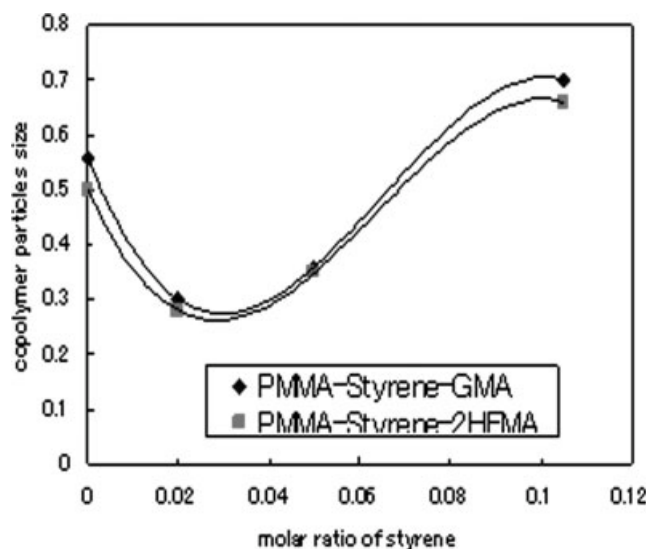
Figure 7 Effect of styrene concentration.

It can be concluded that the particle mean diameter of the (MAA-GMA-ST) copolymer increased with the temperature increase in the range of 338–368 K. The same trend also is found for the copolymer (MAA-2-HEMAA-ST). The dependence of particle size on the temperature may result from the change of $SC-CO_2$ density varying from 0.68 to 0.49 g/cm^3 with the temperature increase from 338 to 368 K at the 20 MPa pressure as shown in Table II. Thus, the monomers concentration will increase 40%, resulting in the bigger polymer particles production. Ethyl mercaptan was used as a chain transfer agent in the copolymerization to control the molecular weight, but there was no appreciable effect found on product molecular weight, molecular weight distribution, or particle size or morphology.
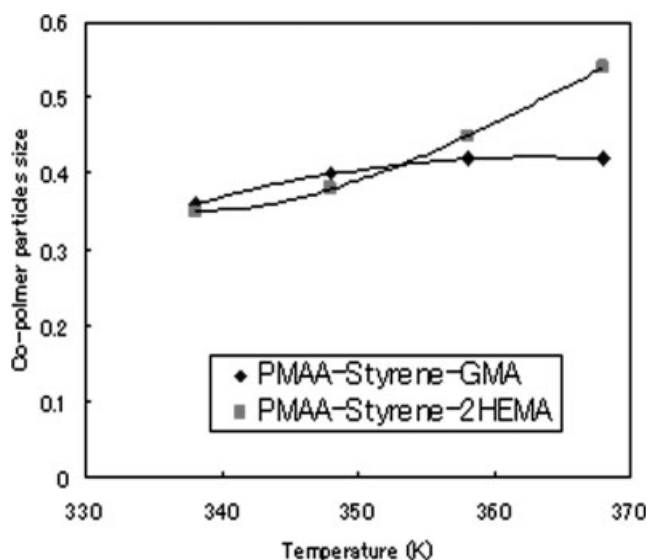
TABLE II
Density of SC-CO$_2$ During the Copolymerization^a

	P/MPa				
T/K	10	15	20	25	30
338	0.25	0.53	0.68	0.75	0.80
348	0.22	0.45	0.61	0.70	0.75
358	0.20	0.38	0.55	0.65	0.71
368	0.19	0.34	0.49	0.60	0.67

^{a} Values are densities given in g cm^{-3}.

Effect of copolymerization pressure on the particle morphology

The effect of the pressure on the particles morhpology was studied with the fixed monomers ratio of MMA : GMA : ST = 1 : 1 : 0.5 at a constant temperature of 338 K. The results are demonstrated in Figure 9, in which the copolymer particle size decreased with the increase of the copolymerization pressure. This may be explained as the increasing density of carbon dioxide with the increasing pressure, resulting in the lower monomer concentration in the copolymerization system. The data in Table II shows the $SC-CO_2$ density varied from 0.25 to 0.8 g^{-3}, as the pressure increased from 10 to 30 MPa at the temperature of 338 K. Thus, the monomers concentration will decrease more than three times. The effect of pressure on the particle size at a ratio of MMA : 2-HEMA : ST = 1 : 1 : 0.5 is also indicated in Figure 9 with a similar trend to the poly (GMA-MAA-ST). In general, the effects of copolymerization temperature and pressure in the process on the copolymer particle morphology were mainly through the monomer concentration which is dependent on the density of CO_2.
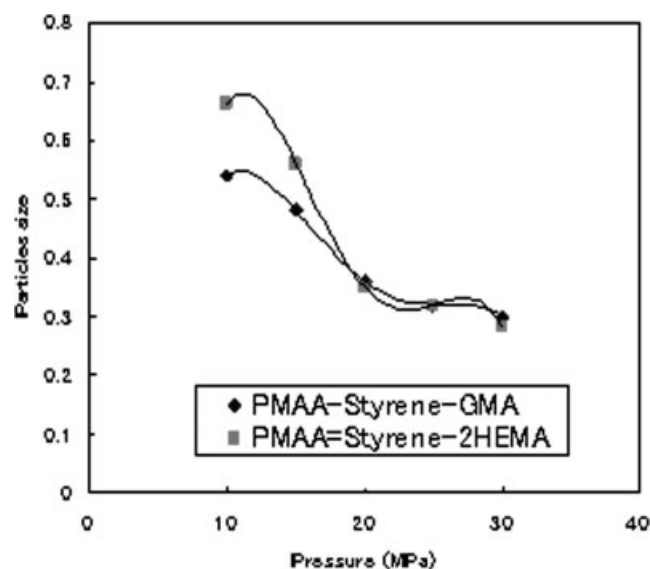

Figure 8 Effect of temperature.

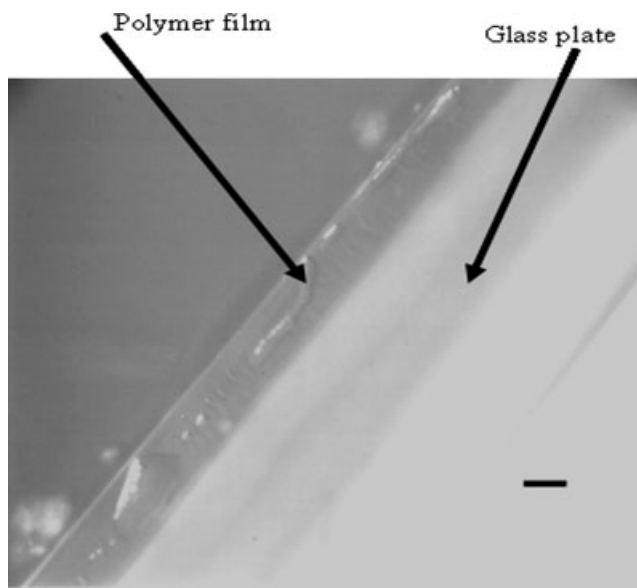**Figure 9** Effect of pressure.

Figure 10 Cross section of the film.

Powder coating by poly(GMA-MAA-ST) microparticles

The obtained polymer particles (poly(GMA-MAA-ST)) were applied as powder coatings. The polymer particles were baked at 423 K for 30 min on a glass plate and melted into a coherent coating film. An optical photograph of the cross section of the film shown in Figure 10 indicated that the coating had a uniform thickness (about 30 μm) and excellent coalescence, because the polymer microspheres were very small in the order of only several microns and spherical. There were no faults on the surface of the polymer film, because the polymeric microspheres did not contain any impurities such as residual solvent and/or surfactant. Compared with acrylic resin in the powder coating, the addition of ST enhanced the flexibility and impact resistance, and offered excellent thin film appearance, good chemical resistance, and hard film simultaneously.

CONCLUSIONS

Polymeric microspheres were synthesized by the precipitation copolymerization of GMA with MAA

or 2-HEMA containing ST in SC-CO$_2$ without fluorous surfactant. Scanning electron microscopy (SEM) showed that the products were spherical microparticles with the addition of MAA and/or 2-HEMA as the monomers. The mean diameter of the particles is from 0.2 to 2 μm. The factors, the copolymerization pressure, temperature, and initial GMA-MAA-ST and GMA-2-HEMA-ST ratio, affecting the particle size and morphology were studied in detail. These results demonstrated that copolymerization technique in SC-CO$_2$ can be used to form micron-sized powders for powder coating using environmentally benign CO$_2$ to replace millions of tons of organic solvents used every year in the industry. The addition of ST enhance the flexibility and impact resistance for acrylic powder coating, and offered excellent thin film appearance.

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