

## Dispersion polymerization of methyl methacrylate with three types of comblike fluorinated stabilizers in supercritical carbon dioxide

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**ABSTRACT:** Dispersion polymerizations of methyl methacrylate in supercritical carbon dioxide were conducted with three types of comblike fluorinate polymer stabilizers: poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PHDFDMA), poly(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate) (PTDFOMA), and poly(2,2,3,3,3-pentafluoropropyl methacrylate) (PPFPMA). The effect of the polymerization pressure was not significant on the mean diameters of the poly(methyl methacrylate) (PMMA) particles from 20 to 40 MPa. However, the coefficients of variation of the particle diameters produced at 20 MPa ( $\sqrt{1/(N-1) \sum_{i=1}^N (d_i - \bar{d})^2} / \bar{d}$ , where  $\bar{d}$  is the number-basis mean particle diameter), where the heterogeneous phase was found before polymerization, were larger than those produced at 30 and 40 MPa, where the homogeneous phase was found. The mean size of the PMMA obtained with PTDFOMA and PPFPMA strongly depended on the stabilizer concentration compared with that obtained with PHDFDMA. Moreover, the mean size decreased as the carbon dioxide-philic side chain length increased. As shown by the results of this study, the best stabilizer among the three types of stabilizers for producing PMMA particles was PHDFDMA. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43813.

**KEYWORDS:** radical polymerization; surfactants; synthesis and processing

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### INTRODUCTION

By comparison with organic solvents, supercritical carbon dioxide (scCO<sub>2</sub>) has many excellent properties; it is nontoxic, inexpensive, nonflammable, and relatively environmentally benign. Therefore, scCO<sub>2</sub> has been used as an extraction and reaction solvent in a variety of industrial fields.<sup>1–4</sup> In polymer processing, scCO<sub>2</sub> is often used as a foaming agent in the production of polymer foam, and it is also used as a reaction solvent for the syntheses of perfluoro polymers. Moreover, scCO<sub>2</sub> has been considered for use as a medium in the dispersion polymerization of microsized vinyl polymer particles such as poly(methyl methacrylate) (PMMA) and polystyrene. With the exception of amorphous fluorinated or siloxane-based polymers, high-molecular-weight polymers do not dissolve in scCO<sub>2</sub>,<sup>1,2,4,5</sup> whereas monomers often dissolve well in scCO<sub>2</sub>. Therefore, appropriate stabilizers are normally needed to expedite dispersion polymerization in scCO<sub>2</sub>. Many studies over the past 2 decades have focused on dispersion polymerization since the first report was presented by DeSimone *et al.*<sup>6</sup> These studies have included the effects of the monomer and stabilizer

concentrations and the polymerization pressures on the morphologies of the particles. Increases in the monomer concentration have led to increases in the particle diameter.<sup>7–10</sup> In an opposite fashion, the particle size often decreases with increases in the concentration of the stabilizers.<sup>9–16</sup> As for the polymerization dependency on pressure, the results of the particle morphology have varied according to the research group.<sup>7,9,17,18</sup>

The architecture of the stabilizer and the stabilizer concentration also has crucial effects on the morphology of the polymer particles and the molecular weight. The stabilizer generally consists of monomer-philic or particle polymer-philic anchor groups and carbon dioxide (CO<sub>2</sub>)-soluble groups such as fluorine or siloxane groups. The size and balance of the anchor group and the CO<sub>2</sub>-soluble group (called the *anchor-soluble balance*) are important factors in dispersion polymerization.<sup>1,14,19,20</sup> The amount of stabilizer that is used, particularly of fluorinated stabilizers, should be reduced with a molecular design that is appropriate for the stabilizers because they are generally expensive and toxic, as are their fluorinated monomers.

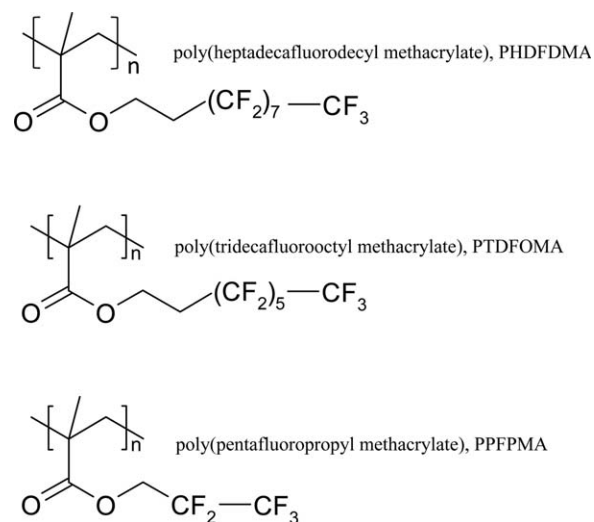
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The structure and function of the anchor group can be mainly categorized as one of two types from the viewpoint of how it contacts the particles. One is an inactive polymer-philic portion that stabilizes polymer particles via adsorption on the surface, and the other involves active end groups such as methyl methacrylate (MMA) that react with monomers and hold the particles. To elucidate the dispersion polymerization with polymer-type stabilizers, Yuvaraj *et al.*<sup>10</sup> investigated the effect of the ratio of the anchor portion to the CO<sub>2</sub>-soluble portion of stabilizers with a nonfluorous random copolymer stabilizer that was composed of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate and 2-dimethylaminoethyl methacrylate (poly{3-[tris(trimethylsilyloxy)silyl] propyl methacrylate-co-2-dimethylaminoethyl methacrylate}). The 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate/2-dimethylaminoethyl methacrylate ratios were set at 89/11, 71/29, and 47/53 w/w in the stabilizers, and the ratio 71/29 w/w showed the best results. Moreover, Kim *et al.*<sup>21</sup> studied the effects of the backbone structure of a comblike fluorinated stabilizer using polyheptadecafluorodecylacrylate, poly{oxy[(2-perfluorooctylethylene)thiomethyl]ethylene}, and poly(*p*-[(perfluorooctylethylene)thio]methylstyrene) and showed that the dispersibility was influenced by the polarity of the backbone on the basis of dispersion polymerizations with three types of monomers. Moreover, Lepilleur and Beckman<sup>11</sup> investigated the effects of the backbone, CO<sub>2</sub>-soluble graft sizes, and graft density on the graft polymer-type stabilizer of poly(methyl methacrylate-co-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide). The results of the polymerization of MMA show that a long backbone was necessary but not sufficient. Namely, a sufficient amount of CO<sub>2</sub>-soluble chains was also important for the stabilizer to be dissolved in scCO<sub>2</sub>.

Block copolymer stabilizers are also useful for dispersion polymerization. The influence of the species of the anchor parts on the particle morphology was investigated by Woods *et al.*,<sup>22</sup> and the stabilizers we used were perfluoropolyether (PFPE)-alcohol, PFPE-acetate, PFPE-methacrylate, and PFPE-*b*-PMMA. The most successful stabilizer was PFPE-*b*-PMMA, whereas PFPE-alcohol led to a low yield. The relationships between the anchor-soluble balance value and both the particle morphology and molecular weight have also been investigated, and other block copolymers have shown superior performance as stabilizers; these include poly(1,1-dihydroperfluorooctyl acrylate)-*b*-polystyrene,<sup>20</sup> polydimethylsiloxane-*b*-poly(methyl methacrylate-co-methacrylic acid),<sup>20</sup> poly(ethylene oxide)-*b*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate),<sup>23</sup> poly(ethylene glycol)-*b*-perfluoroalkyl diblock and perfluoroalkyl-*b*-poly(ethylene glycol)-*b*-perfluoroalkyl triblock copolymers,<sup>14</sup> and PMMA-*b*-poly(fluoroalkyl methacrylate).<sup>24</sup>

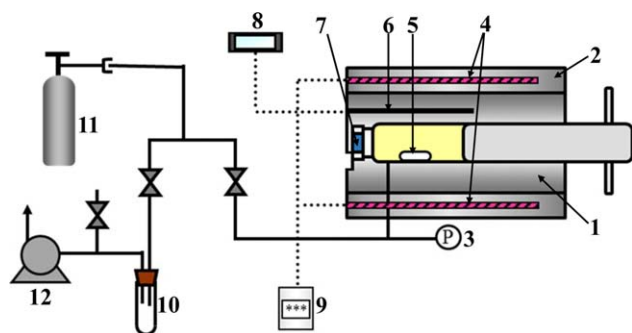
Reactive macromonomers also can be used as stabilizers in dispersion polymerizations in scCO<sub>2</sub>. Reactive macromonomers have a reactive anchor that reacts with the monomers during polymerization and a CO<sub>2</sub>-soluble portion, and the effect of the molecular structure on the particle morphologies is well documented.<sup>19,25-29</sup> For example, Giles *et al.*<sup>26</sup> examined the effect of the molecular weight of polydimethylsiloxane monomethacrylate macromonomers on the polymerization of MMA, and the results indicate that the use of a low-molecular-weight mac-



**Figure 1.** Chemical structures of the comblike fluorinated stabilizers.

romonomer could produce a high yield of PMMA with a high molecular weight. However, these stabilizers are the basis of reactive anchor parts, and they are incorporated into particles; this would induce a deterioration of the functionalities. Wang *et al.*<sup>30</sup> carried out the dispersion polymerization of MMA with an ester end-capped PFPE synthesized from acid-terminated PFPE and 1-butanol. Fine PMMA particles were obtained, although the anchor portion was short, and the level of the stabilizer residue in the produced particles was very low. The ability of the PFPE-acetate stabilizer to produce PMMA particles was also demonstrated by Woods *et al.*<sup>22</sup>

In this study, we focused on the effects of the CO<sub>2</sub>-philic perfluoro side chain length on the morphologies of the PMMA particles and their molecular weights for dispersion polymerization in scCO<sub>2</sub>. With respect to the influences of CO<sub>2</sub>-philic side chains, in addition to the research of Lepilleur and Beckman<sup>11</sup> described previously, Giles *et al.*<sup>31</sup> investigated PMMA production with homo graft polymer stabilizers with different side chain lengths: poly(methyl vinyl ether-*alt*-maleic anhydride) and poly(maleic anhydride-*alt*-1-octadecene) with 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol and 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol. In that study, the long CO<sub>2</sub>-philic side chain led to a better stabilizer performance. To systematically accumulate knowledge of the effect of the perfluoro side chain structure, in this study, three comblike stabilizers were prepared from the same backbone species and graft densities but with differences in the side chain lengths, as shown in Figure 1: poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PHDFDMA), poly(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate) (PTDFOMA), and poly(2,2,3,3,3-pentafluoropropyl methacrylate) (PPFOMA). First, the phase boundaries were measured for the CO<sub>2</sub>-stabilizer binary systems and CO<sub>2</sub>-stabilizer-MMA ternary systems. The dispersion polymerizations were then investigated at 70 °C with three types of stabilizers with different average molecular weights. The polymerization conditions had stabilizer/MMA ratios ranging from 0.11 to 0.81 w/w and pressures that ranged from 20 to 40 MPa.



**Figure 2.** Schematic diagram of the experimental apparatus for polymerization in  $sc\text{CO}_2$ : (1) high-pressure cell, (2) aluminum block, (3) pressure gauge, (4) cartridge heaters, (5) magnetic stirring bar, (6) thermocouple, (7) sapphire window, (8) temperature indicator, (9) temperature controller, (10) cold trap, (11)  $\text{CO}_2$  cylinder, and (12) vacuum pump. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

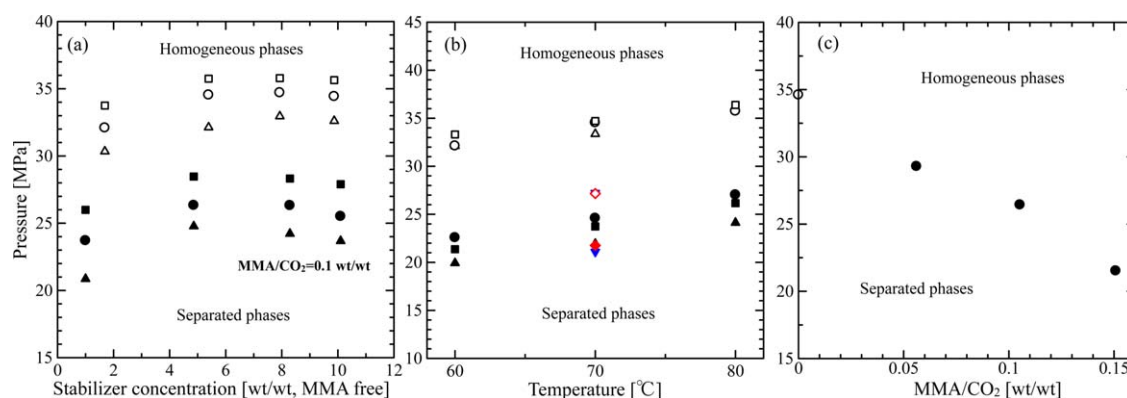
## EXPERIMENTAL

### Materials

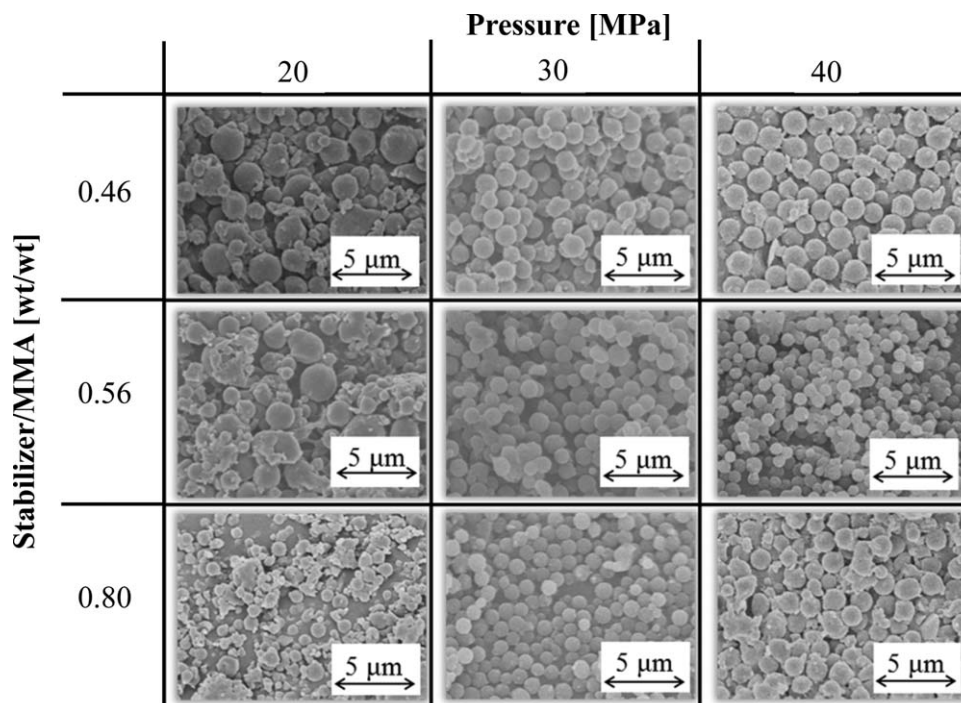
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate (>97%) used for the preparation of PHDFDMA was purchased from Sigma-Aldrich Co. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate (>95%) and 2,2,3,3,3-pentafluoropropyl methacrylate (>95%) were supplied by Daikin Industries, Ltd., and were also used as monomers for PTDFOMA and PPFOMA, respectively. Moreover, MMA (>99%) was purchased from Sigma-Aldrich Co. for the synthesis of PMMA particles. These monomers were purified via either a distillation or an inhibitor-remover preppacked column. As an initiator of polymerization, 2,2'-azodiisobutyronitrile (AIBN; >98.0%) was purchased from Tokyo Chemical Industry Co. and was used as received.  $\text{CO}_2$  with a purity of greater than 99.5 vol % was purchased from Chugoku Sanso Co. and used without further purification.

### Preparation and Characterization of the Stabilizers

All three stabilizers were synthesized by solution polymerization in benzene at  $70^\circ\text{C}$  for 24 h under a nitrogen atmosphere. After the polymerization, the synthesized stabilizers were purified, and solid masses of the stabilizers were obtained. The yields of the stabilizers synthesized are listed in Table S1 in the Supporting Information. The yields of most PHDFDMA (52–89%) were lower than those of PTDFOMA and PPFOMA (75–86%), although the definite reasons remain unclear. The molecular weight distribution and average molecular weight of the stabilizers could not be obtained via gel permeation chromatography (GPC) because limited solvents such as  $sc\text{CO}_2$  and CFCs (chlorofluorocarbons) could dissolve the polymers containing perfluoro groups. Only PPFOMA could be dissolved in tetrahydrofuran, but it was difficult to prepare appropriate conditions for GPC. Therefore, the zero-shear viscosities that were obtained via rotational rheometry (Paar Physica Co., UDS200) at  $130^\circ\text{C}$  were used as indices of the molecular weights. The ranges of the zero-shear viscosities for each stabilizer were as follows: from 17.1 to 235 Pa s for PHDFDMA, 295 to 416 Pa s for PTDFOMA, and 1860 to 13,500 Pa s for PPFOMA. The names of the stabilizers are expressed as a combination of the value of the zero-shear viscosity and the stabilizer species in the following section. The ranges of viscosities were quite different depending on the stabilizer species. These differences were caused not only by the molecular weight but also by the differences in the structures of the side chains. Therefore, the values of the zero-shear viscosities were used to evaluate the differences in the molecular weights within the same species of the stabilizers. Moreover, the Fourier transform infrared spectra of 124-PHDFDMA, 416-PTDFOMA, and 4760-PPFOMA obtained by the spectrometer (Thermo Scientific Co., Nicolet is5) are shown in Figure S1 in the Supporting Information. In every spectra, peaks were found that could be assigned to  $\text{CF}_2$  wagging,<sup>32</sup>  $\text{CF}_2$  asymmetric stretching,<sup>32</sup> and  $\text{C}=\text{O}$  stretching<sup>33</sup> vibration modes.



**Figure 3.** Phase boundary pressure for the  $\text{CO}_2$ -stabilizer binary and  $\text{CO}_2$ -stabilizer-MMA systems: (a) relationships between the stabilizer concentration and the phase boundary pressure for ( $\Delta, \circ, \square$ ) the  $\text{CO}_2$ -91.8-PHDFDMA system and ( $\blacktriangle, \bullet, \blacksquare$ ) the  $\text{CO}_2$ -91.8-PHDFDMA-MMA system (MMA/ $\text{CO}_2 = 0.1$  w/w) at 60, 70, and  $80^\circ\text{C}$ , respectively; (b) dependence of the temperature on the phase boundary pressure at a stabilizer concentration of approximately 5 wt % (MMA free) for ( $\Delta, \circ, \square$ ) the binary system and ( $\blacktriangle, \bullet, \blacksquare$ ) the ternary system (MMA/ $\text{CO}_2 = 0.1$  w/w) with 17.1-PHDFDMA, 88.0-PHDFDMA, and 235-PHDFDMA, respectively, as the stabilizers and for the ( $\nabla, \blacktriangledown$ ) binary and ( $\diamond, \blacklozenge$ ) ternary systems with 4760-PPFOMA and 416-PTDFOMA, respectively; and (c) effect of the MMA concentration on the phase boundary pressure for the  $\text{CO}_2$ -91.8-PHDFDMA-MMA system at the stabilizer concentration of 5 wt % (MMA free). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** SEM images of the PMMA particles produced with 124-PHDFDMA as a stabilizer at 70 °C. The stabilizer/MMA ratios and the pressures of polymerization ranged from 0.46 to 0.80 w/w and from 20 to 40 MPa, respectively.

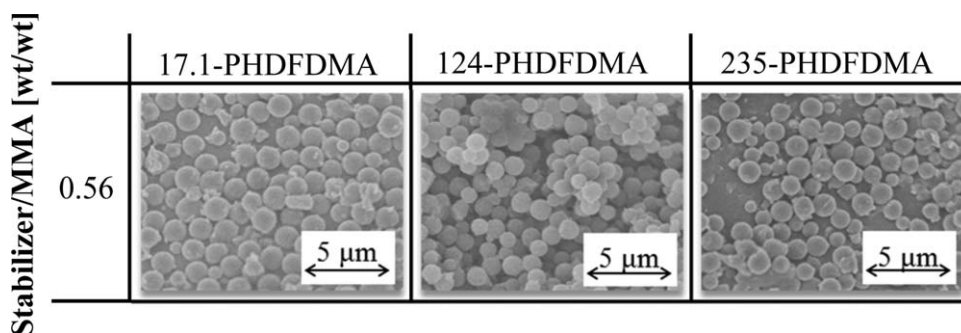
#### Phase Boundary Measurements

The phase behaviors of the CO<sub>2</sub>–stabilizer and the CO<sub>2</sub>–MMA–stabilizer systems were measured to establish the phase boundaries for each condition and system. An apparatus based on a synthetic method consisting of a variable-volume optical high-pressure cell with two sapphire windows and a CO<sub>2</sub> injection system was used to measure the phase separation pressure at a constant temperature and composition. Because the experimental apparatus was described in detail in previous studies,<sup>34</sup> a brief explanation of the apparatus, and the procedure is shown here. In the experiments, certain amounts of the stabilizer and MMA were introduced into the cell. The air in the cell was then purged with CO<sub>2</sub> at atmospheric pressure. The CO<sub>2</sub> in the sample cylinder was introduced into the cell via a freeze–thaw method. The cell was then heated to the experimental temperature with the mixture in the cell stirred by a Teflon-coated magnetic stirring bar. After the cell temperature reached the desired value, the pressure in the cell was raised until a transparent homogeneous phase appeared. The phase in the cell then became stable and transparent, the pressure in the cell gradually decreased, and the phase behavior was observed through the sapphire view windows. In this study, the phase boundary pressures where the transparent phase changed to a cloudy phase were determined by visual observation.

#### Dispersion Polymerization of MMA and Estimation of the Mean Particle Diameters

The apparatus used for the dispersion polymerization of the MMA is shown in Figure 2 and was based on a synthetic method that differed from that use for the apparatus used to measure the phase boundary pressure. The apparatus also mainly consisted of a variable-volume optical cell (30 mm in

diameter with a maximum volume of about 114 cm<sup>3</sup>) with a sapphire window, a CO<sub>2</sub> injection system, and a hand pump. The cell was surrounded by an aluminum block, which was heated by four 300-W cartridge heaters. The temperature was measured via a thermocouple connected to an indicator (Shimaden Co., SR94), and the uncertainty of the temperature measurement was estimated to within ±1 °C. A precision pressure gauge was used to measure the pressure (Huba Control Co., type 680, uncertainty of ±0.005 MPa). In this experiment, certain amounts of MMA, stabilizer, and AIBN were introduced into the cell at room temperature. The air in the cell was purged with atmospheric CO<sub>2</sub>. Then, CO<sub>2</sub> was introduced into the cell via the freeze–thaw method. To initiate polymerization, the temperature and pressure in the cell were raised to the polymerization conditions, 70 °C and 20, 30, or 40 MPa, via the cartridge heaters and a hand pump. The polymerization temperature was chosen on the basis of the temperature of the 10-h half-life for AIBN (65 °C) and the dispersion polymerization reported by Shin *et al.*<sup>35</sup> The polymerizations were carried out at cell volumes of approximately 20–24 cm<sup>3</sup> for all of the experiments. Slight variations in the volumes were caused by differences in the compositions of the mixtures for each of the individual polymerizations, although the pressures were constant (at 20, 30, and 40 MPa). The mixture in the cell was agitated via a Teflon-coated magnetic stirring bar at a constant speed of about 400 rpm during polymerization, which was conducted for 24 h in all of the experiments. The morphologies of the PMMA particles produced were observed with a scanning electron microscope (S-5200, Hitachi High-Technologies Co.), and the mean particle diameters and their coefficients of variation (CVs) were obtained by the analysis of more than 1000



**Figure 5.** SEM images of the PMMA particles produced with three different types of PHDFDMA with a stabilizer/MMA ratio of 0.56 w/w at 30 MPa and 70 °C.

particles. Moreover, the GPC system with a column (Shodex-804L) was used for the determination of the molecular weights of PMMA particles. Calibration with standard PMMA was used for the estimations of the molecular weights.

## RESULTS AND DISCUSSION

### Phase Behaviors for the CO<sub>2</sub>–Stabilizer and CO<sub>2</sub>–Stabilizer–MMA Systems

The relationships between the stabilizer concentrations and the phase boundary pressures for the CO<sub>2</sub>–PHDFDMA binary and CO<sub>2</sub>–PHDFDMA–MMA ternary systems (MMA/CO<sub>2</sub> = 0.1 w/w) at temperatures ranging from 60 to 80 °C are shown in Figure 3(a). The phase boundary pressure increased with increases in the temperature; this was typical lower critical solution temperature behavior and is often observed in solvent–polymer systems. The addition of 0.1 w/w MMA against CO<sub>2</sub> drastically decreased the phase boundary pressure. This behavior approximated the data of the CO<sub>2</sub>–PHDFDMA system, as reported by Shin *et al.*<sup>36</sup> The phase boundary pressures of this study were slightly higher than the literature values, although the reason remained unclear.

Furthermore, the relationships between the temperature, molecular weight, and phase boundary pressure for the three types of stabilizers at a stabilizer concentration of 5 wt % are shown in Figure 3(b). A slight molecular weight (represented by the zero-shear viscosity) dependency of the phase boundary pressure was observed for the CO<sub>2</sub>–PHDFDMA–MMA systems, and the order of the phase boundary pressures at 70 °C was as follows: 91.8-PHDFDMA > 88.0-PHDFDMA > 235-PHDFDMA > 17.1-PHDFDMA, where the number indicates the zero-shear viscosity. This result also might have been caused by the effect of the polydispersity of the stabilizers' molecular weights and the values of the molecular weights.

The phase boundary pressures of both the binary and ternary systems, including 4760-PPFPMA and 416-PTDFOMA, are described in Figure 3(b). As for the CO<sub>2</sub>–4760-PPFPMA (5 wt %) binary system, the value of the phase boundary pressure was similar to that of the CO<sub>2</sub>–PPFPMA (3 wt %) systems reported by Yoon *et al.*<sup>37</sup> As shown in the figure, the phase boundaries for the binary systems, including 4760-PPFPMA and 416-PTDFOMA, were lower than that of PHDFDMA, although there was a smaller number of fluorinated groups in PPFPMA and PTDFOMA than that in PHDFDMA. The results of the

investigation into the effect of the addition of MMA on the CO<sub>2</sub>–91.8-PHDFDMA system at 70 °C and at a PHDFDMA concentration of 5 wt % (MMA free) are also shown in Figure 3(c). The phase boundary pressure was decreased as the concentration of MMA increased to at least an MMA/CO<sub>2</sub> weight ratio of about 0.15 w/w, and this behavior was considered to be based mainly on the entraining effect of MMA.

### Polymerization of MMA with PHDFDMA

The polymerization of MMA with PHDFDMA was carried out at 70 °C and at pressures that ranged from 20 to 40 MPa. Four types of PHDFDMA were used as stabilizers: 17.1-PHDFDMA, 124-PHDFDMA, 145-PHDFDMA, and 235-PHDFDMA. Figure 4 shows the scanning electron microscopy (SEM) images of PMMA particles that were obtained with 124-PHDFDMA at pressures ranging from 20 to 40 MPa and at stabilizer/MMA weight ratios ranging from 0.46 to 0.80 w/w. As shown in the figure, spherical particles were obtained at 30 and 40 MPa regardless of the value of the stabilizer/MMA weight ratio. On the other hand, nonspherical grains of stabilizers and PMMA were found along with spherical particles at 20 MPa. Furthermore, the distributions of the particle sizes at 20 MPa appeared to be larger than those at 30 and 40 MPa. The images of the PMMA particles obtained with 17.1-PHDFDMA, 124-PHDFDMA, and 235-PHDFDMA at a stabilizer/MMA weight ratio of 0.56 w/w and 30 MPa are shown in Figure 5 for the discussion of the effect of the molecular weight of the PHDFDMA. Spherical PMMA particles were also observed in the images, regardless of the molecular weight of PHDFDMA. On the basis of the analyses of the SEM images and the GPC studies, the particle diameters, their CV values, and the molecular weights are summarized in Table I. The effects of the polymerization pressure, stabilizer concentrations, and types of the stabilizers on the mean particle diameter and CV value are shown in Figure 6. As shown in Figure 6(a), the mean particle diameters that were number bases showed values between approximately 1 and 2 μm regardless of the pressure, PHDFDMA/MMA weight ratio, or molecular weight of PHDFDMA. The mean particle diameters decreased slightly with increasing pressure at a stabilizer/MMA ratio of 0.56 w/w for 124-PHDFDMA and at ratios of 0.57 and 0.80 for 145-PHDFDMA. Conversely, the mean particle diameters increased somewhat with increasing pressure at stabilizer/MMA ratios of 0.46 and 0.80 w/w for 124-PHDFDMA. The reason the different

**Table I.** Experimental Results for the Dispersion Polymerizations with PHDFDMA

Zero-shear viscosity at 130 °C (Pa s)	Stabilizer/MMA (w/w)	Pressure (MPa)	$\bar{d}$ ( $\mu\text{m}$ ) <sup>a</sup>	CV (%) <sup>b</sup>	Particle size distribution <sup>c</sup>	$M_w$ ( $10^4$ g/mol)	$M_w/M_n$	
17.1	0.55	30	1.68	14.2	1.05	12.8	1.8	
		30	1.43	20.7	1.10	8.9	2.0	
124	0.26	30	1.08	13.9	1.05	17.4	1.9	
		0.46	20	1.56	39.0	1.57	16.1	2.3
		30	1.64	16.2	1.07	7.9	2.0	
		40	1.85	16.7	1.08	9.4	1.7	
	0.56	20	1.73	33.8	1.36	14.0	3.3	
		30	1.38	14.3	1.06	13.1	1.8	
		30	1.21	15.1	1.08	10.3	2.5	
		40	1.06	15.6	1.07	10.5	1.8	
0.80	20	1.02	25.0	1.18	12.5	1.7		
	30	1.25	13.2	1.04	9.4	2.0		
	40	1.63	16.5	1.07	9.4	1.8		
	20	1.53	40.6	1.87	14.7	2.0		
	30	1.27	15.0	1.07	16.0	3.6		
	40	1.35	17.9	1.08	9.0	1.6		
235	0.55	30	1.55	16.9	1.07	14.6	1.5	
		30	1.52	12.7	1.04	13.8	1.7	

$M_n$ , number-average molecular weight,  $M_w$ , weight-average molecular weight.

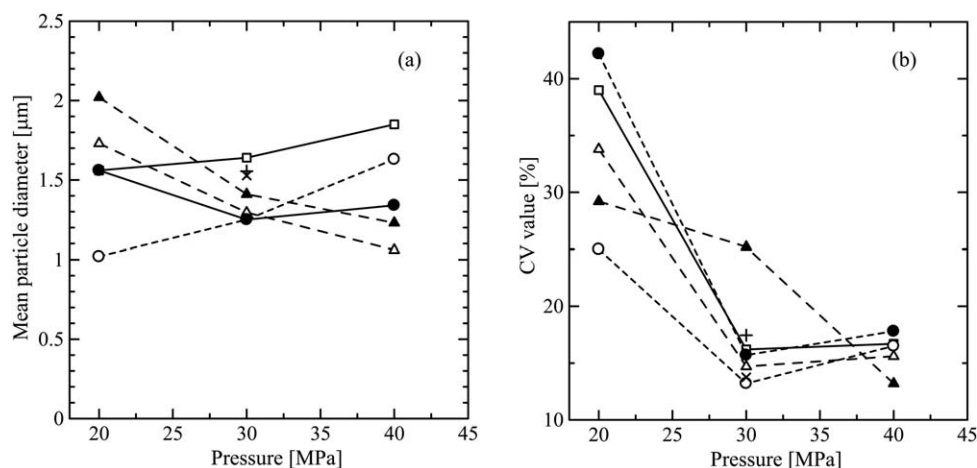
<sup>a</sup>Number-basis mean particle diameter.

<sup>b</sup> $\sqrt{1/(N-1) \sum_{i=1}^N (d_i - \bar{d})^2} / \bar{d}$ .

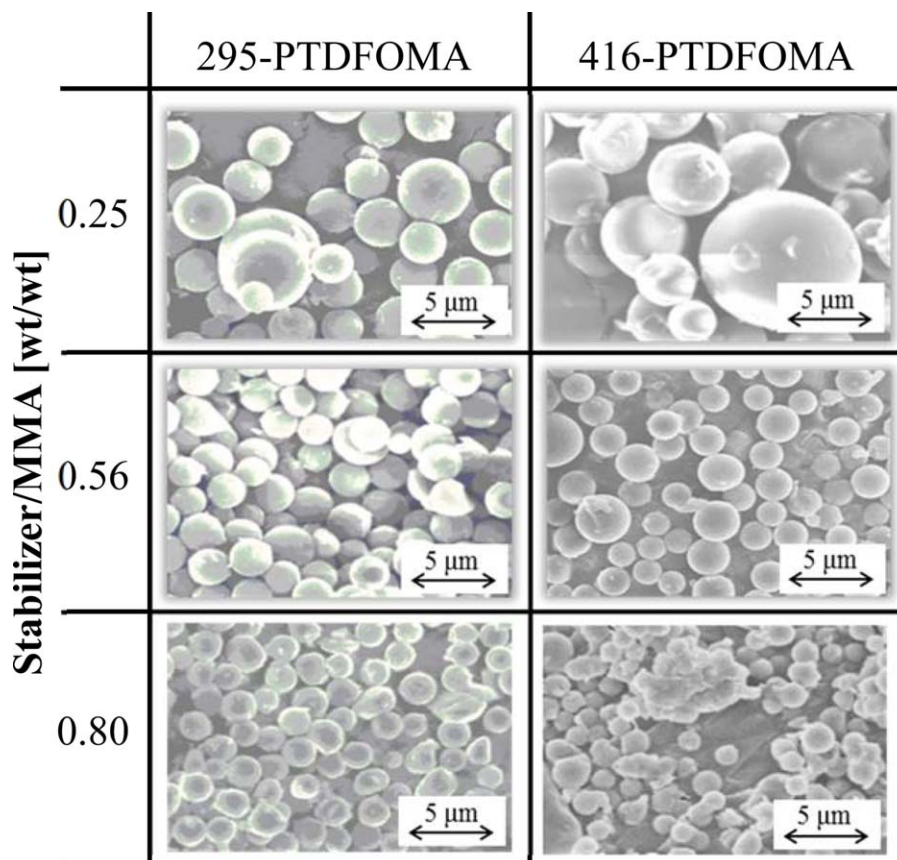
<sup>c</sup> $(\sum_{i=1}^N d_i^4 / \sum_{i=1}^N d_i^3) / (\sum_{i=1}^N d_i / N)$ .

pressure dependencies appeared could not be found, and previous works show that the pressure effect depends on the research groups, as described in the Introduction. However, the range of differences in the mean diameter was small, and therefore, the

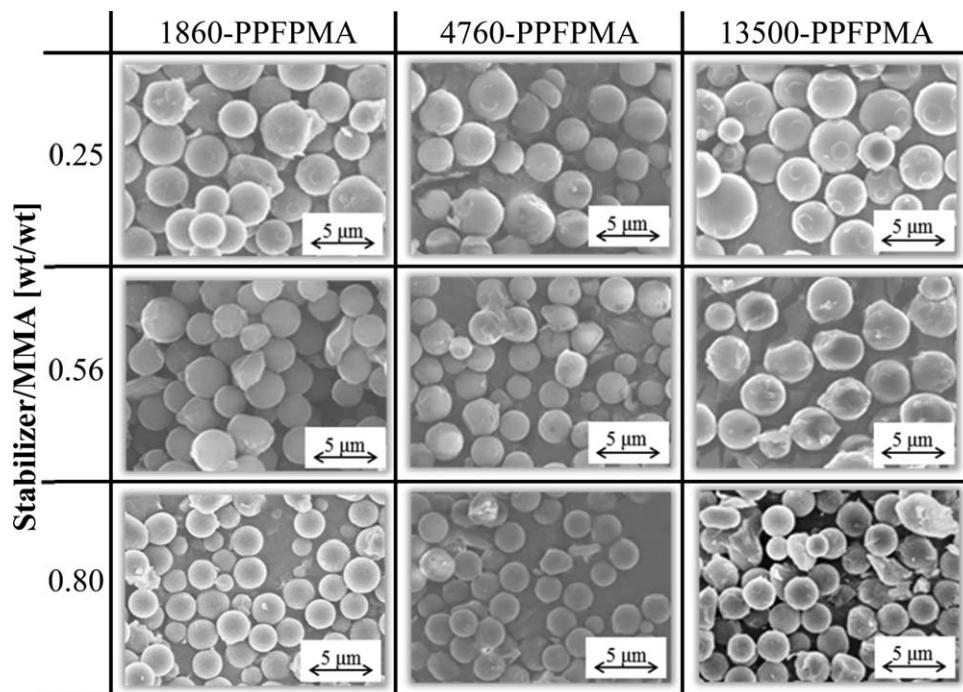
pressure dependency obtained in this study was considered to be insignificant, as was the case with the results obtained with poly(1,1-dihydroperfluorooctyl acrylate) as a stabilizer reported in the literature.<sup>7</sup> On the other hand, the CV values of the



**Figure 6.** Effects of the pressure, stabilizer concentration, and molecular weight of the stabilizer on the (a) mean particle sizes and (b) CV values with PHDFDMAs as the stabilizers: (□,△,○) 124-PHDFDMA with stabilizer/MMA ratios of 0.46, 0.56, and 0.80 w/w, respectively; (▲,●) 145-PHDFDMA with stabilizer/MMA ratios of 0.57 and 0.80 w/w, respectively; and (+,×) 17.1-PHDFDMA and 235-PHDFDMA, respectively, with a stabilizer/MMA ratio of 0.55 w/w.



**Figure 7.** SEM images of the PMMA particles produced with 295-PTDFOMA and 416-PTDFOMA at 30 MPa and 70 °C. The stabilizer/MMA ratios of the polymerizations ranged from 0.25 to 0.80 w/w. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** SEM images of the PMMA particles produced with three different types of PFPMA at 30 MPa and 70 °C. The stabilizer/MMA ratios of the polymerizations ranged from 0.25 to 0.80 w/w.

**Table II.** Experimental Results for the Dispersion Polymerizations with PTDFOMA at 30 MPa

Zero-shear viscosity at 130 °C (Pa s)	Stabilizer/MMA (w/w)	$\bar{d}$ ( $\mu\text{m}$ ) <sup>a</sup>	CV (%) <sup>b</sup>	Particle size distribution <sup>b</sup>	$M_w$ ( $10^4$ g/mol)	$M_w/M_n$
295	0.25	2.91	27.0	1.63	12.8	1.9
	0.55	2.41	14.1	1.06	12.1	2.2
	0.80	1.85	13.3	1.05	12.3	1.8
416	0.25	4.27	33.0	1.54	12.2	2.2
	0.57	2.24	22.1	1.16	13.5	2.1
	0.81	1.54	18.4	1.15	15.6	2.0

$M_n$ , number-average molecular weight,  $M_w$ , weight-average molecular weight.

<sup>a</sup>Number-basis mean particle diameter.

$$^b \sqrt{1/(N-1) \sum_{i=1}^N (d_i - \bar{d})^2} / \bar{d}.$$

$$^c (\sum_{i=1}^N d_i^4 / \sum_{i=1}^N d_i^3) / (\sum_{i=1}^N d_i / N).$$

particles produced at 20 MPa were much higher than those produced at either 30 or 40 MPa. The large CV values of the particles synthesized at 20 MPa could have been caused by a pressure that was below the phase boundary pressure for the CO<sub>2</sub>-PHDFDMA-MMA system, as shown in Figure 3. The polymerization would have begun in the phase behavior of the coexistence of the separated phases unlike at 30 and 40 MPa.

The weight-average molecular weight ( $M_w$ ) values of the PMMA particles ranged from  $6.6 \times 10^4$  to  $17.4 \times 10^4$  g/mol. Although the range of  $M_w$  values were broad, the effects of the molecular weight and concentration of the stabilizer and the polymerization pressure were not significant.

#### Polymerization with PTDFOMA and PFPMA and Effects of the Perfluoro Side Chain Length of the Stabilizer on the Morphologies of the PMMA Particles

The dispersion polymerization of MMA was also carried out with PTDFOMA and PFPMA to investigate the effect of the

perfluoro side chain length of the stabilizer on the morphologies of the PMMA particles. The PMMA particles in the SEM images shown in Figure 7 were synthesized at 30 MPa with stabilizer/MMA weight ratios ranging from 0.25 to 0.80 w/w with 295-PTDFOMA and 416-PTDFOMA. The particle size appeared to be more widely distributed and larger at a stabilizer/MMA weight ratio of 0.25 w/w for both stabilizers; this differed from the results obtained with PHDFDMA. Moreover, the SEM images of the PMMA particles produced at 30 MPa and with stabilizer/MMA weight ratios ranging from 0.25 to 0.80 w/w with three types of PFPMA are also shown in Figure 8. The images show that spherical particles were obtained even when we used stabilizers with a short fluorinated side chain length, and this also indicated a trend similar to those of the particle made with PTDFOMA, as shown in Figure 7. However, the agglomerated polymer masses were found along with the polymer particles after polymerization with PFPMA. The chemical structures of the agglomerate and particulate polymers were

**Table III.** Experimental Results for Dispersion Polymerizations with PFPMA at 30 MPa

Zero-shear viscosity at 130 °C (Pa s)	Stabilizer/MMA (w/w)	$\bar{d}$ ( $\mu\text{m}$ ) <sup>a</sup>	CV (%) <sup>b</sup>	Particle size distribution <sup>c</sup>	$M_w$ ( $10^4$ g/mol)	$M_w/M_n$
1860	0.25	3.36	22.2	1.17	8.4	2.7
	0.57	2.76	20.7	1.11	10.2	2.3
	0.80	2.31	20.3	1.09	12.0	2.0
4760	0.11	3.84	42.0	1.71	8.3	2.5
	0.25	3.20	25.8	1.23	8.4	1.8
	0.46	2.86	16.9	1.07	10.8	2.1
	0.56	2.49	16.7	1.07	9.9	1.8
	0.79	2.35	13.2	1.04	12.4	2.8
13,500	0.25	3.20	28.8	1.28	7.7	2.4
	0.55	3.10	21.5	1.11	12.1	2.6
	0.80	2.55	10.3	1.03	10.8	2.1

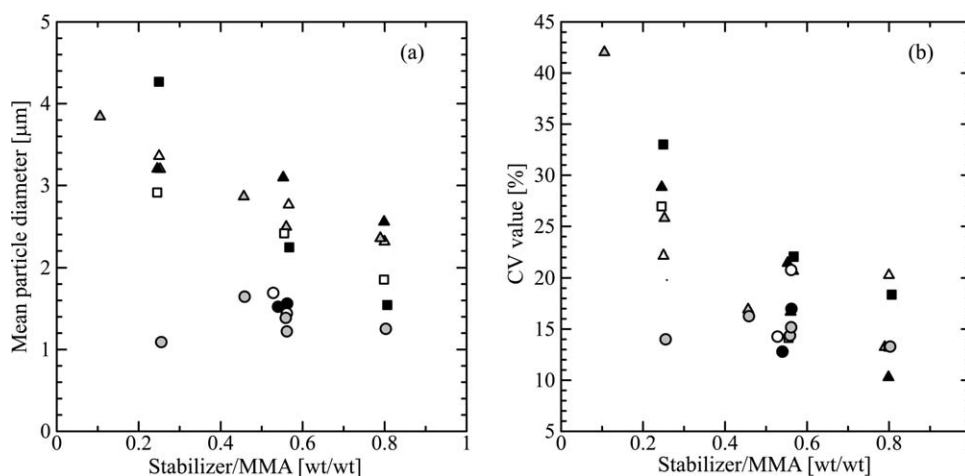
$M_n$ , number-average molecular weight,  $M_w$ , weight-average molecular weight.

<sup>a</sup>Number-basis mean particle diameter.

$$^b \sqrt{1/(N-1) \sum_{i=1}^N (d_i - \bar{d})^2} / \bar{d}.$$

$$^c (\sum_{i=1}^N d_i^4 / \sum_{i=1}^N d_i^3) / (\sum_{i=1}^N d_i / N).$$





**Figure 9.** Dependence of the stabilizer concentration on the (a) mean particle diameters and (b) CV values for the PMMA particles produced with different types of stabilizers at 30 MPa: (○) 17.1-PHDFDMA, (●) 124-PHDFDMA, (●) 235-PHDFDMA, (□) 295-PTDFOMA, (■) 416-PTDFOMA, (△) 1860-PPFPMA, (▲) 4760-PPFPMA, and (▲) 13,500-PPFPMA.

analyzed via Fourier transform infrared spectroscopy, and the agglomerates were identified as PPFMA rather than PMMA. As an example, the spectra of the agglomerates and particles synthesized with 4760-PPFPMA at a PPFMA/MMA ratio of 0.56 w/w and at 30 MPa are shown in Figure S2 in the Supporting Information along with the pure 4760-PPFPMA and pure PMMA synthesized in benzene without any stabilizer. The shapes of the spectra of the agglomerates were similar to that of pure PPFMA, but that of the polymer particles was similar to that of pure PMMA. A transparent phase was observed at 70 °C and 30 MPa in the phase boundary measurement of both the CO<sub>2</sub>-PPFPMA binary and CO<sub>2</sub>-PPFPMA-MMA ternary systems described previously. Therefore, the agglomerates might have formed during the depressurization process after polymerization because the short perfluoro side chains of PPFMA led to a weak repulsive force between the stabilizers. In this study, only the particle parts were evaluated.

For the PMMA particles produced with PTDFOMA and PPFMA, the dependencies of the stabilizer/MMA weight ratio on the mean particle diameter, the CV values, the  $M_w$ , and the polydispersity at 30 MPa are listed in Tables II and III. The values for  $M_w$  of the PMMA particles produced with PTDFOMA and PPFMA ranged from  $12.1 \times 10^4$  to  $15.6 \times 10^4$  g/mol and from  $7.7 \times 10^4$  to  $12.4 \times 10^4$  g/mol, respectively. The dependency of the stabilizer species and concentration on the molecular weights of the PMMA particles was not large and not systematic. The mean particle diameters of the PMMA that was produced and their CV values are shown in Figure 9 along with the results of the particles produced with PHDFDMA. As shown in the figure, both the mean particle diameter and CV values of the particles synthesized with both PTDFOMA and PPFMA showed a dependency on the stabilizer/MMA weight ratios compared with that obtained with PHDFDMA. The mean particle diameter was decreased as the perfluoro side chain length increased, although the molecular weight had no notable influence. The effect of the length of the grafted perfluoro chain obtained in this study corresponded to the results

reported by Giles *et al.*<sup>31</sup> However, the reason that an increase in the perfluoro chain length led to a decrease in the mean particle diameter remained unclear, although the longer CO<sub>2</sub>-philic perfluoro chain showed a higher steric effect in the dispersion polymerization. Also, the CV value of the particles produced with PTDFOMA and PPFMA were relatively larger than that obtained from PHDFDMA. Therefore, in this study, the best stabilizer for producing PMMA particles seemed to be PHDFDMA.

## CONCLUSIONS

In this study, the dispersion polymerization of MMA in scCO<sub>2</sub> was carried out with three types of fluorinate stabilizers with fluorinated side chains of differing lengths: PHDFDMA, PTDFOMA, and PPFMA. Spherical PMMA particles were obtained by all stabilizers. No significant differences were found for mean particle sizes at pressures ranging from 20 to 40 MPa, regardless of the concentration of PHDFDMA. On the other hand, the CV values of the particle diameters produced at 20 MPa where the heterogeneous phase was found for the scCO<sub>2</sub>-stabilizer-MMA mixture at the start of polymerization were significantly larger than those at 30 and 40 MPa where the homogeneous phase was obtained before polymerization started. The mean particle size of the PMMA obtained with PTDFOMA and PPFMA strongly depended on the stabilizer concentration compared with that obtained with PHDFDMA. Moreover, the mean particle size decreased as the CO<sub>2</sub>-philic side chain length increased. On the other hand, a systematic dependency of the particle molecular weight on the structure of the stabilizer was not found. The best stabilizer among the three types of stabilizers investigated in this study for producing PMMA particles was PHDFDMA.

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