

# DISPERSION POLYMERIZATION OF POLY(METHYL METHACRYLATE) AND POLY(VINYL PYRROLIDONE) STABILIZED WITH POLY[PERFLUOROALKYL (METH)ACRYLATE] IN SUPERCRITICAL CARBON DIOXIDE

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In this study, homogeneous radical polymerization of perfluoro (meth)acrylate [ $\text{CH}_2=\text{C}(\text{H or CH}_3)\text{COO}(\text{CH}_2)_n\text{R}_f$ ,  $n=1$  or  $2$ ,  $\text{R}_f$ =perfluoroalkyl] using AIBN as the initiator in supercritical  $\text{CO}_2$  were carried out at  $T=343\text{K}$ ,  $P=300\text{-}320$  bar. And these fluoro-polymer were analyzed with  $^1\text{H-NMR}$ , FT-IR, GPC, etc. The resulting polymer was then used as a stabilizer for the free radical dispersion polymerization of PMMA [Poly (methyl methacrylate)] and PVP[Poly(vinyl pyrrolidone)] in supercritical  $\text{CO}_2$ . The dispersion polymerization was performed using AIBN as the initiator at  $T=343\text{K}$ ,  $P=200\text{-}340$  bar. PMMA and PVP were characterized by  $^1\text{H-NMR}$ , FT-IR, GPC, SEM, etc. From this study we could synthesis discrete spherical particles of PMMA, PVP in high yield and moderate molecular weight and relatively narrow size distribution.

## I. INTRODUCTION

Recently, Supercritical fluid technology has been used in a wide range of polymer industries including heterogeneous or homogeneous polymerization[1]. Specially in a variety of supercritical fluid, carbon dioxide ( $\text{CO}_2$ ) has been spotlighted and studied as alternative polymerization or polymer processing medium, since it has relatively mild critical conditions ( $T_c=304.25\text{K}$ ,  $P_c=73.8\text{bar}$ ). And it is also non-toxic, nonflammable, and inexpensive. As a solvent,  $\text{scCO}_2$  has no dipole moment and has low dielectric constant. But  $\text{scCO}_2$  has quadrupole moment, so  $\text{scCO}_2$  is a good solvent for non-polar molecules with low molecular weight and slightly polar molecules such as methanol, ethanol. However, in the case of polymer, the solubility of non-polar polymer including PMMA, PS etc in  $\text{scCO}_2$  is negligible. Only a few polymers such as amorphous fluoropolymer and polysiloxane are dissolved in  $\text{scCO}_2$ . Solubility of most polymers is quite low in  $\text{scCO}_2$ , but many polymers are plasticized and swollen in  $\text{scCO}_2$ . So many researches have been carried out about the heterogeneous polymerization in  $\text{scCO}_2$ .

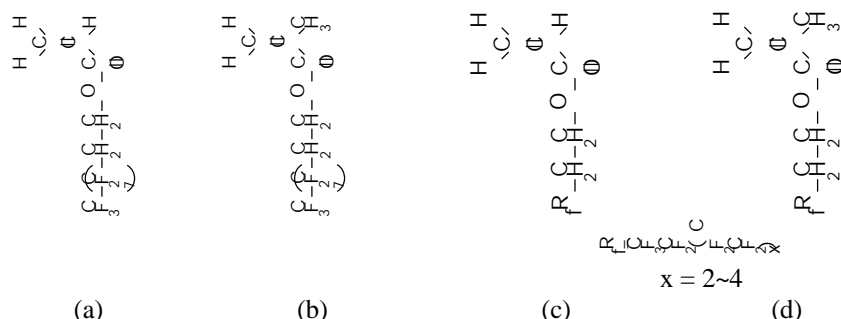
The first and pioneering research using supercritical fluid as polymerization medium was started by J. M. DeSimone group. They performed homogeneous free radical polymerization of 1,1-dihydroperfluorooctyl acrylate using  $\text{scCO}_2$  (supercritical carbon dioxide) as polymerization medium[2]. And they also reported heterogeneous dispersion polymerization of Poly[methyl methacrylate] in  $\text{scCO}_2$  phase using PFOA (poly[1,1-dihydroperfluorooctyl acrylate]) as a dispersion agent[3]. Thereafter several kinds of polymeric or oligomeric materials that could be used as dispersion agent to stabilize particles in  $\text{scCO}_2$  phase were studied. C. Lepilleur and E. J. Beckman[4] used block or graft

copolymer as dispersion agent, which have CO<sub>2</sub> phlic parts and CO<sub>2</sub> phobic parts in a polymeric molecule. M. Z. Yates *et al.*[5] proposed ambidextrous surfactants which can stabilize in both CO<sub>2</sub> and water phase with different mechanism. M. R. Giles *et al.*[6] used poly[dimethylsiloxane] monomethacrylate and P. Christian *et al.*[7] used carboxylic acid terminated perfluoroether as stabilizer.

In the industry dispersion polymerized particles are used as surface coatings for metal panels, chromatographic media for separating polymer molecules, spacers for liquid crystal display panels, anti-blocking and slip agents, electro photographic toners, pressure sensitive adhesives and cosmetic ingredients *etc*[8,9]. So in this paper we described poly[perfluoroalkyl (meth)acrylate] preparation by homogeneous free radical solution polymerization mechanism in scCO<sub>2</sub> and heterogeneous PMMA and PVP dispersion polymerization in scCO<sub>2</sub> using these fluorinated polymers.

## II. MATERIALS AND METHODS

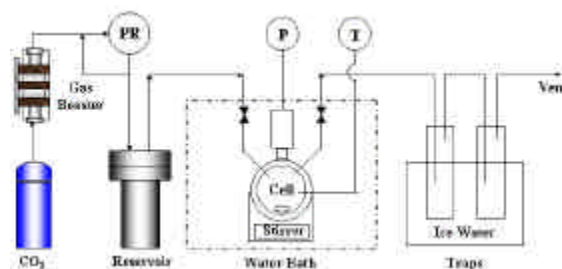
HDFDA(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate, min. 97%, CAS No. 27905-45-9) and HDFDMA(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate, min. 97%, CAS No. 1996-88-9) were purchased from Aldrich. Zonyl<sup>®</sup> Fluorosurfactants, TA-N(fluoroalkyl acrylate) and TM(fluoroalkyl methacrylate) were purchased from DuPont. AIBN(2,2-azobis(isobutyronitrile), min. 98%) and MMA(Methyl methacrylate, min. 99.5%) were purchased from Junsei Chemical. Carbon dioxide(min. 99.99%) was purchased from Korea Industrial Gases. The inhibitor in monomer was removed before use by alumina column and dissolved oxygen was removed through nitrogen purging. AIBN was purified by recrystallization from methanol.



**Figure 1. Chemical structure of perfluoroalkyl (meth)acrylate (a) HDFDA (b) HDFDMA (c) TA-N (d) TM**

Homogeneous radical solution polymerization of perfluoroalkyl (meth)acrylate (HDFDA, HDFDMA, TN-N, TM) and dispersion polymerization of PMMA and PVP were carried out in a 30mL SUS 316 reactor that has two windows at both-sides. From these windows we observed inner phase change. CO<sub>2</sub> was supplied with gas booster pump(Maxpro Technologies Inc. Model DLE 75-1). To minimize the fluctuation from pump and to maintain stable feeding, we used 300mL reservoir between pump and reactor. Pressure was measured with pressure transducer(Data Instruments Inc. Model AB/HP, accuracy  $\pm 0.25\%$ ) and indicator(Laurel Electronics Inc. L20010WM1). Temperature was measured with K(CA) type thermocouple(accuracy  $\pm 0.05K$ ) and indicator(Hanyoung Electronics Inc. Model DX-7). After polymerization was ended, CO<sub>2</sub> was vented through two glass traps. To prevent discharge of unreacted monomer to atmosphere during CO<sub>2</sub> separation, glass traps were filled with

methanol and cooled with ice water. PTFE coated magnetic stirring bar was used for agitation of reacting mixture.



**Figure 2. Schematic diagram of the polymerization apparatus**

(P = pressure gauge; T = temperature gauge; PR = pressure regulator)

Typical polymerization procedure for poly[perfluoroalkyl (meth)acrylate], PMMA and PVP were as follows. Monomer(4.00g) and AIBN(respectively 0.1wt%, 0.5wt%, 1.0wt% of monomer) were introduced to the reactor. Then the reactor was purged by CO<sub>2</sub> several times to remove residual air and charged with known amount of CO<sub>2</sub> at room temperature. Then reactor was heated up to 70.0 °C in the water bath. Polymerization was performed at 70.0±0.5 °C, 300-310 bar for 24hrs. After polymerization was completed, we cooled down the reactor below 10 °C. At that time pressure of the reactor was about 40bar and vapor/liquid phase separation occurred. CO<sub>2</sub> was vented from vapor phase. The polymer particles were washed with methanol to remove unreacted monomer. The resulting polymer was dried in vacuum at room temperature.

To characterize fluorinated polymer, <sup>1</sup>H-NMR(Bruker, 300MHz) and FT-IR(Jasco Model 200) were used. For <sup>1</sup>H-NMR spectroscopy each sample was dissolved in the 1:1 mixture of CDCl<sub>3</sub> and 1,1,2-trichlorofluoroethane(CFC-113). To characterize PMMA, <sup>1</sup>H-NMR, FT-IR, SEM(Jeol 5410LV), Particle size analyzer(Malvern, Mastersizer 2000) were used. Molecular weight of PMMA was measured by GPC(Waters, 600E controller) using THF as the solvent at 35 °C. RI detector(Waters, 410), three columns(Styragel<sup>®</sup> HT2, HT3, HT4) and narrow standard PMMA were used.

### III. RESULTS AND DISCUSSION

Table 1 shows the results of homogeneous radical polymerization of perfluoroalkyl meth(acrylate) in scCO<sub>2</sub>. As Shown in Table 1 poly(HDFDA), poly(HDFDMA), poly(TA-N) were synthesized as white fluffy solid. But poly(TM) was synthesized as white sticky solid or highly viscous liquid at room temperature. Recovery ratio was relatively very high. We think this was a result of CO<sub>2</sub> separation at low temperature(below 10 °C). At this low temperature, phase separation occurred and solubility of these polymers in vapor phase was negligible compared with that of liquid or supercritical phase. We vented CO<sub>2</sub> through vapor phase. On the whole, the yield of fluorinated polymer increased as initiator concentration increased. We think it was caused by the increase of polymerization rate.

**Table 1. Homogeneous polymerization of perfluoroalkyl (meth)acrylate in scCO<sub>2</sub>.**

Entry	Monomer	AIBN(wt%)	Recovery ratio(%) <sup>1)</sup>	Yield(%) <sup>2)</sup>	Appearance <sup>3)</sup>
F1	HDFDA	0.1	98.7	79.5	Fluffy solid
F2		0.5	96.1	84.9	Fluffy solid

F3		1.0	97.9	89.4	Fluffy solid
F4	HDFDMA	0.1	96.5	43.3	Fluffy solid
F5		0.5	98.2	75.3	Fluffy solid
F6		1.0	97.4	85.2	Fluffy solid
F7	TA-N	0.1	96.2	62.5	Fluffy solid
F8		0.5	98.6	85.6	Fluffy solid
F9		1.0	96.8	85.7	Fluffy solid
F10	TM	0.1	NA	NA	Sticky solid
F11		0.5	NA	NA	Sticky solid
F12		1.0	NA	NA	Sticky solid

1) Determined as the ratio of residual mass in the reactor after CO<sub>2</sub> separation to initially charged monomer mass

2) Determined as the ratio of residual mass after methanol washing to initially charged monomer mass

3) Observed after CO<sub>2</sub> venting

Table 2 shows the results of dispersion polymerization of PMMA in scCO<sub>2</sub>. Figure 3 shows SEM images of PMMA particles that were polymerized with different stabilizers. When no stabilizer was used, the resulting polymers[P1] were highly aggregated. In the case of poly(HDFDA), poly(TA-N), we observed aggregated particles at low stabilizer concentration (5wt% of monomer). On the whole particle size of PMMA was decreased as the stabilizer was increased. Specially, in the case of poly(HDFDMA) this tendency was distinct.

**Table 2. Dispersion Polymerization of PMMA in scCO<sub>2</sub>**

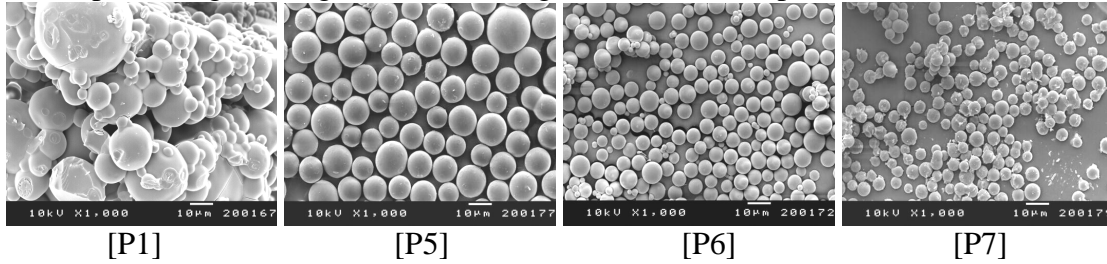
Entry	Stabilizer(wt%)		Mw <sup>1)</sup>	PDI <sup>1)</sup>	Particle size(μm) <sup>2)</sup>	Appearance <sup>3)</sup>	
P1	None		0.0	75,000	3.27	NA	Aggregated solid
P2	Poly(HDFDA) F-2	<b>5.0</b>	51,000	3.46	NA	Aggregated solid	
P3		<b>10.0</b>	82,000	2.79	8-12	White powder	
P4		<b>20.0</b>	69,000	2.89	3-12	White powder	
P5	Poly(HDFDMA) F-5	<b>5.0</b>	109,000	3.22	10-12	White powder	
P6		<b>10.0</b>	94,000	3.23	4-6	White powder	
P7		<b>20.0</b>	111,000	2.89	3-5	White powder	
P8	Poly(TA-N) F-8	<b>5.0</b>	70,000	2.71	NA	Aggregated solid	
P9		<b>10.0</b>	77,000	2.89	10-20	White powder	
P10		<b>20.0</b>	95,000	2.81	10-15	White powder	
P11	Poly(TM) F-11	<b>5.0</b>	76,000	2.48	5-15	White powder	
P12		<b>10.0</b>	74,000	3.57	4-5	White powder	
P13		<b>20.0</b>	79,000	2.37	8-10	White powder	

Entry	Dispersant(wt%)		AIBN (wt%)	Mw <sup>1)</sup>	PDI <sup>1)</sup>	Particle Size(μm) <sup>2)</sup>	Appearance <sup>3)</sup>	
P14	Poly(HDF DMA)	F5	10.0	<b>0.1</b>	144,000	3.47	5-7	White powder
P15			10.0	<b>0.5</b>	100,000	3.02	5-7	White powder
P16			10.0	<b>1.0</b>	53,000	3.14	4-8	White powder
P17		<b>F4</b>	10.0	0.5	93,066	2.73	5-10	White powder
P18		<b>F5</b>	10.0	0.5	100,000	3.02	5-7	White powder
P19		<b>F6</b>	10.0	0.5	100,000	3.13	5-7	White powder

1) Determined by GPC

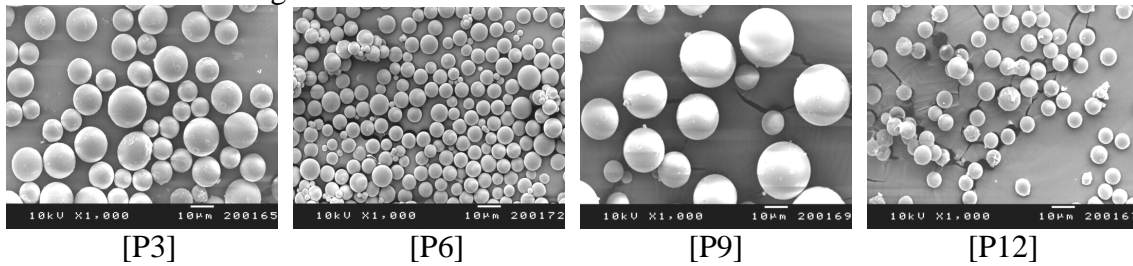
- 2) Determined by SEM
- 3) Observed after CO<sub>2</sub> venting

Weight average molecular weights of PMMA particles were 70,000~100,000 on the conditions of our polymerization experiments. But, it is not easy to find general trend in the average molecular weight. As shown in most results, average molecular weight increased in the case of good stabilization and decreased in the case of poor stabilization. But there are some unexpected high average molecular weights in the case of poor stabilization.



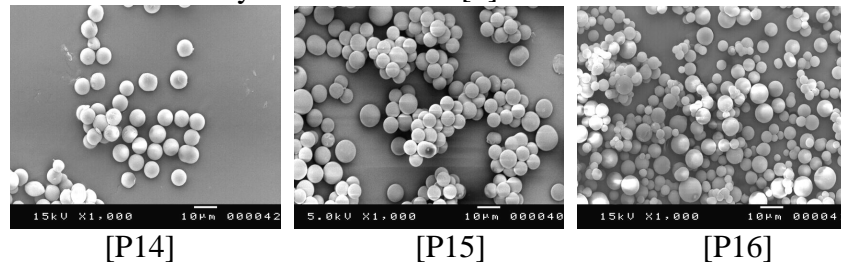
**Figure 3 – SEM images of PMMA particles – effect of dispersant amounts**

As shown in SEM images(Figure 3), the decreasing ratio of the PMMA particle size is not much high compared to the increasing concentration of the stabilizers. To figure out this unclear relationship, further experiments are needed with more various stabilizer concentration in the range of 5~10%.



**Figure 4. SEM images of PMMA particles – effect of dispersant types**

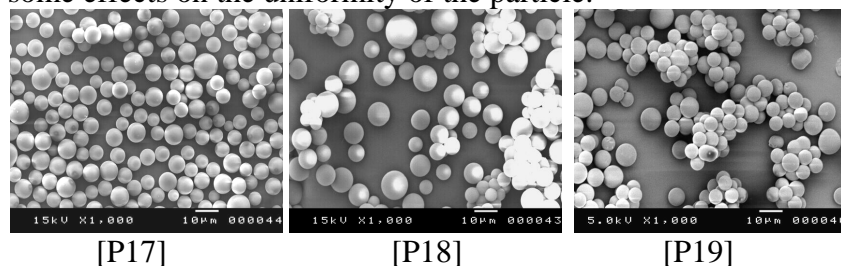
For the investigation of the effects of molecular weight of surfactant on the resulting particles, poly(HDFDMA) surfactant was selected. 10wt% of poly(HDFDMA) of three different molecular weights(low, medium, high) were used as a steric stabilizer in the dispersion polymerization of PMMA. SEM images of PMMA particles are shown in Figure 4. The results indicated that the use of lower molecular weight surfactant enabled the formation of more uniform PMMA particles. And the resulting particles polymerized using low MW surfactant showed smaller particle size, which is similar to the result of the previous study on the effect of MW of surfactant by DeSimone *et al*[3].



**Figure 5. SEM images of PMMA particles - effect of AIBN amounts**

Figure 6 shows the SEM images of the resulting PMMA particles. Each polymerization showed the molecular weight of [P17] 143,000 [P18] 100,000 [P19] 53,000. As expected, Increase of initiator concentration decreased the molecular weight of resulting PMMA particles. But all of the resulting particles showed the similar particle size of 4-8

micron. This means that the initiator concentration does not affect the resulting particle size, but does have some effects on the uniformity of the particle.



**Figure 6. SEM images of PMMA particles - effect of MW of dispersant**

## VI. CONCLUSION

We performed homogeneous polymerization of perfluoroalkyl (meth)acrylate, specially HDFDA, HDFDMA, TA-N, TM in  $scCO_2$ . Conventionally these polymers have been polymerized in hazardous, toxic solvents like CFC. But our results have shown that these polymers were easily polymerized with high yield and no solvent residue in  $scCO_2$ .

Also we investigated the stabilizing ability of these fluorinated polymers for dispersion polymerization of PMMA in  $scCO_2$ . In general, results have shown that particle size of PMMA decreased as the stabilizer concentration increased. In our polymerization conditions, poly(HDFDMA) was the most successful stabilizing agents for dispersion polymerization of PMMA in  $scCO_2$  to control particle size and particle size distribution.

However, further research is required to study how molecular weights and  $CO_2$  philic chain lengths of poly[perfluoroalkyl (meth)acrylate] affect the particle formation and particles stability in dispersion polymerization using  $scCO_2$ . We will try it as next step of our research.

## ACKNOWLEDGEMENTS

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