
열물성연구회 세미나

초임계 이산화 탄소 및 고분자합성을 위한 모노머의 상평형 연구

1. 초임계 용액 중합 및 초임계 분산중합

2003년 10월 13일

서울대학교 응용화학부 열물성연구실

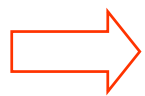
배 원, 김화용



Thermophysical Properties Lab.

Introduction

- Recently, **supercritical fluid** is considered as useful alternative of toxic or volatile organic solvents for **polymer synthesis and processing**.
- For **homogeneous radical polymerization** in **scCO₂**, polymer must be dissolved in monomer and CO₂ mixture.
- For **precipitation polymerization** in **scCO₂**, molecular weight and conversion are determined according to phase behavior of system.
- For **dispersion polymerization** in **scCO₂**, particle size and particle size distribution are affected by phase behavior of system.



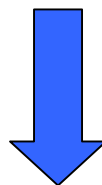
Therefore understanding and predicting the phase behavior of **polymer + monomer + CO₂ systems** are important.



Basic Characteristics of scCO₂

- No dipole moment
- Low dielectric constant

- Quadrupole moment
- Lewis acid



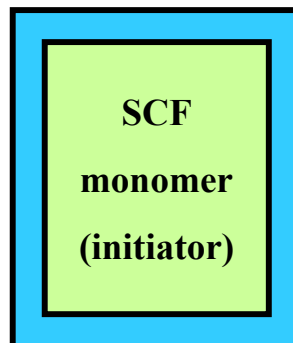
- Good solvent for non-polar molecules with low M.W.
- Poor solvent for non-polar polymers
- Good solvent for amorphous fluoropolymers and silicones



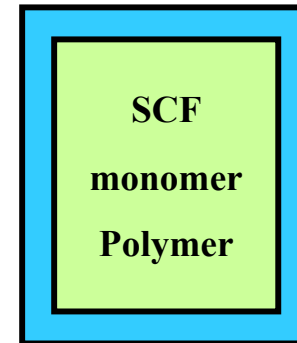
Polymer Synthesis using scCO₂

Homogeneous Polymerization

Initial State

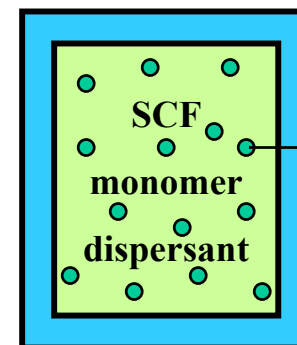
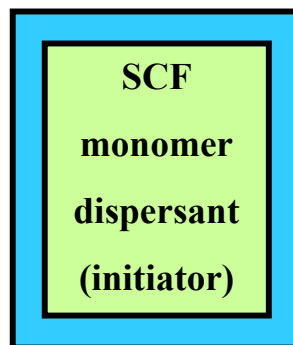


Final State



Dispersion Polymerization

Initial State

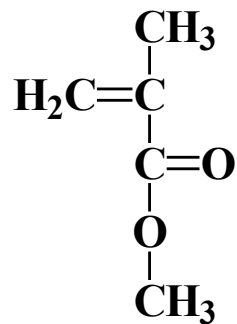


Polymer



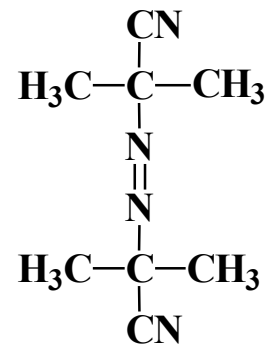
Materials

Monomer



Methyl methacrylate

Initiator

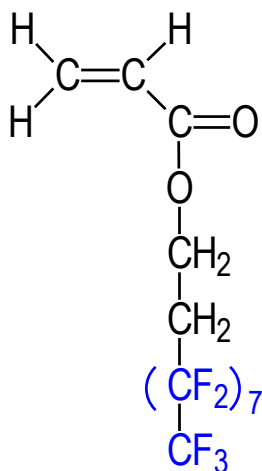


AIBN



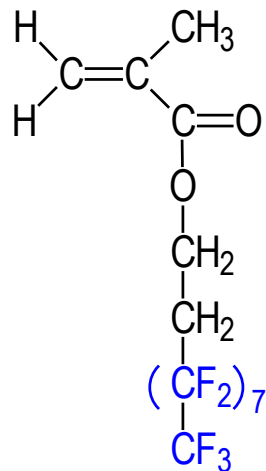
Materials (dispersant)

From Aldrich



HDFDA

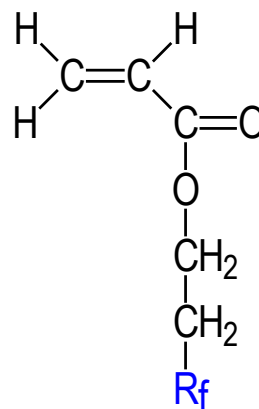
[27905-45-9]



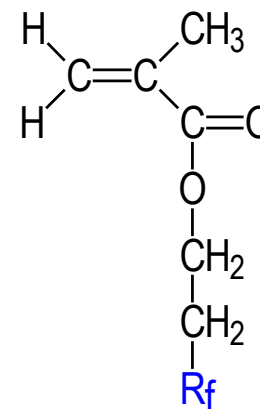
HDFDMA

[1996-88-9]

From DuPont



Zonyl TA-N



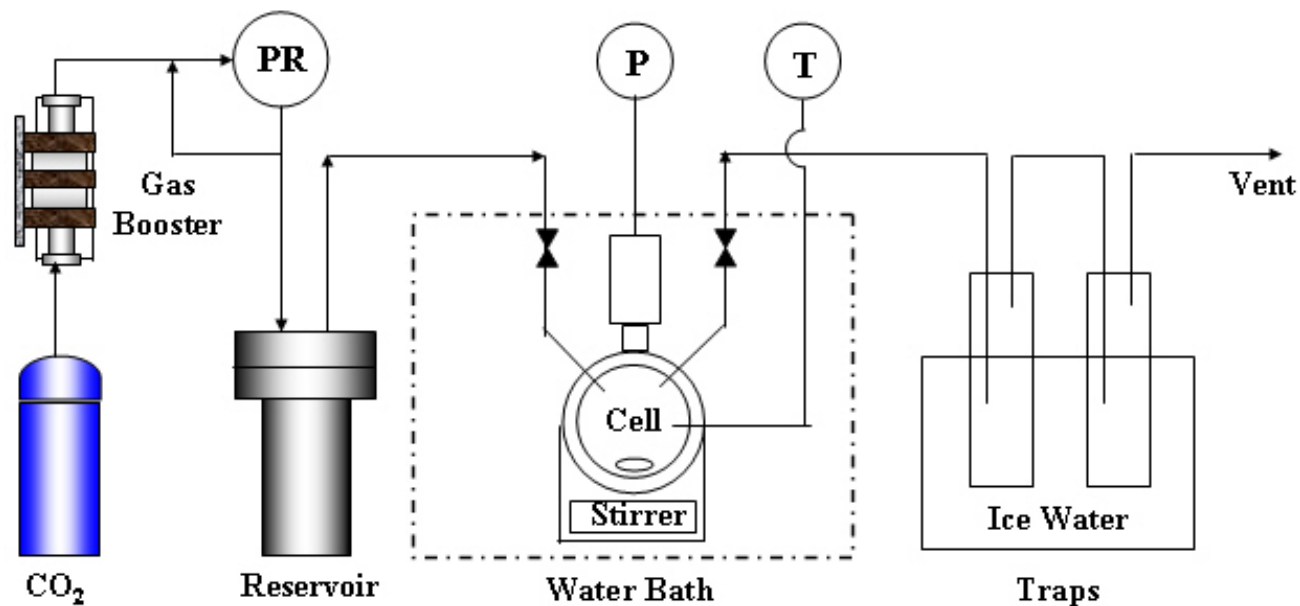
Zonyl TM

$R_f = \text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_x$

$x = 2\sim 4$



Experimental Apparatus



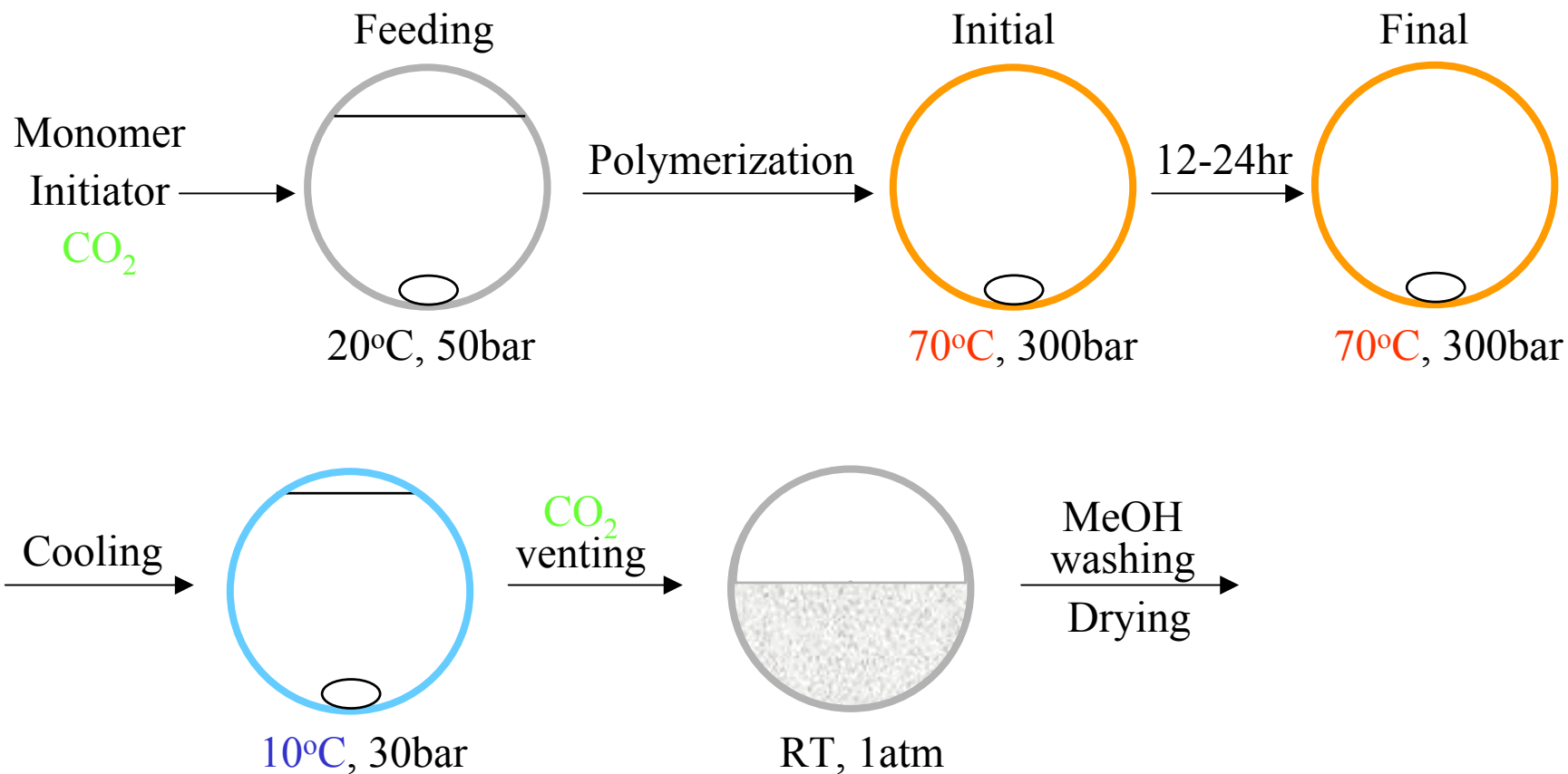
Schematic diagram of the polymerization apparatus

P = pressure gauge, T = temperature gauge

PR = pressure regulator



Solution Polymerization of perfluoroalkyl (meth)acrylate



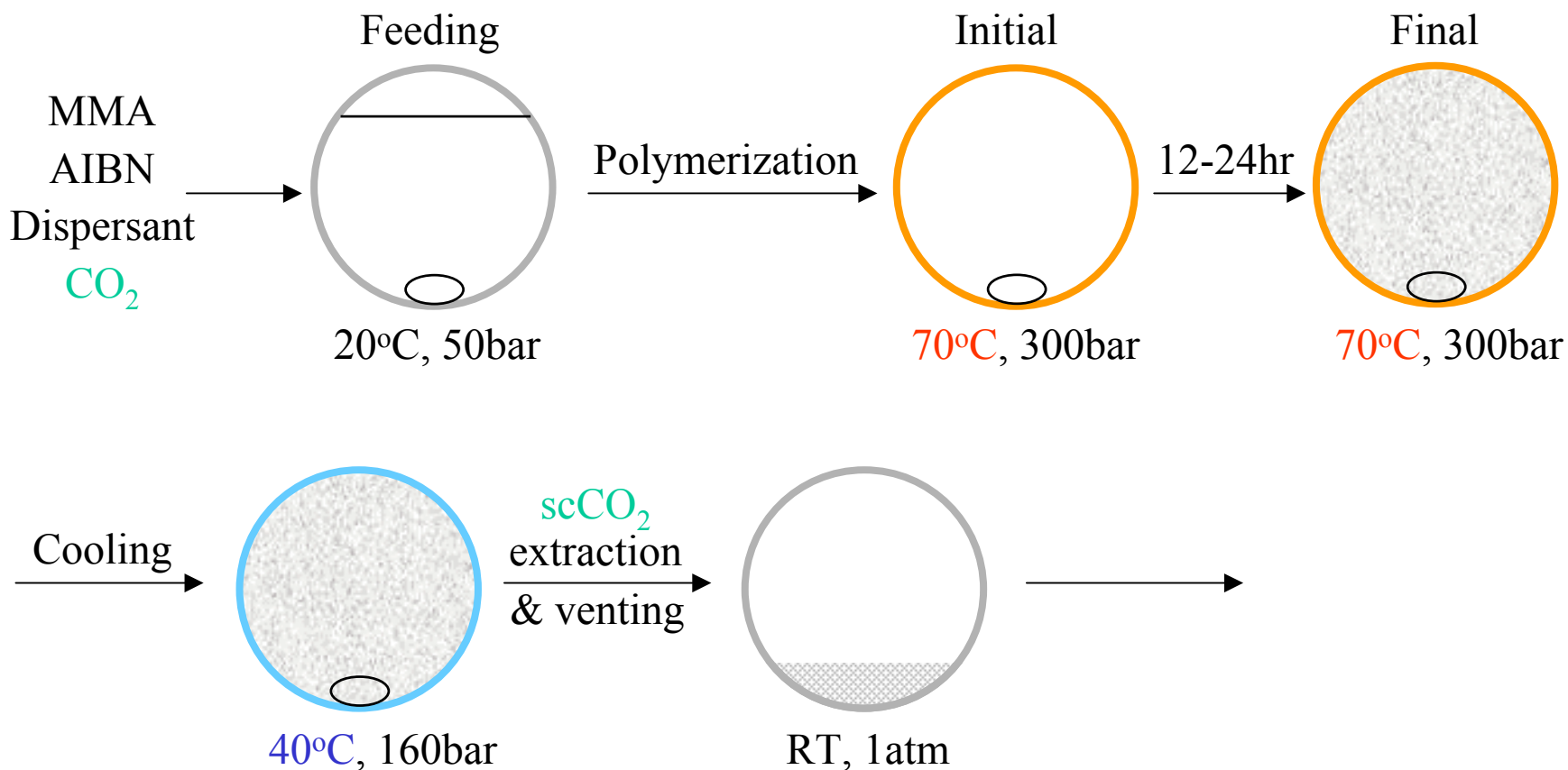
Solution Polymerization of perfluoroalkyl (meth)acrylate

Entry	Monomer	AIBN (wt%)	Recovery Ratio(%)	Yield(%)	Appearance
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

Monomer 4.0g at P=300±10bar, T=70.0±1.0°C for 24hrs with stirring



Dispersion Polymerization of PMMA in scCO₂



Dispersion Polymerization of PMMA in scCO₂

Entry	Dispersant (wt%)		M _w ¹⁾	PDI ¹⁾	Particle Size(μm) ²⁾	Appearance ³⁾
P1	None	0.0	75,000	3.27	NA	Aggregated Solid
P2	Poly(HDFDA) F-2	5.0	92,000	3.46	4-12	White Powder
P3		10.0	82,000	2.79	8-12	White Powder
P4		20.0	69,000	2.89	3-12	White Powder
P5	Poly(HDFDMA) F-5	5.0	109,000	3.22	10-12	White Powder
P6		10.0	94,000	3.23	4-6	White Powder
P7		20.0	111,000	2.89	3-5	White Powder
P8	Poly(TA-N) F-8	5.0	70,000	2.71	NA	Aggregated Solid
P9		10.0	77,000	2.89	10-20	White Powder
P10		20.0	95,000	2.81	10-15	White Powder
P11	Poly(TM) F-11	5.0	76,000	2.48	5-15	White Powder
P12		10.0	74,000	3.57	4-5	White Powder
P13		20.0	80,000	2.37	8-10	White Powder



Dispersion Polymerization of PMMA in scCO₂

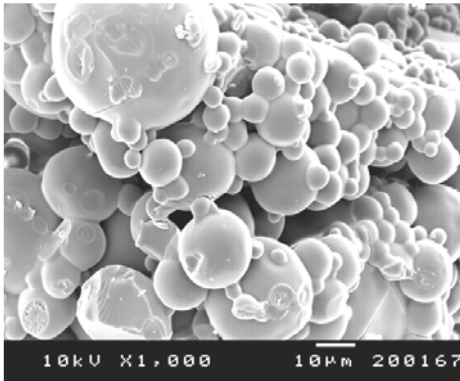
Entry	Dispersant (wt%)		AIBN (wt%)	M _w ¹⁾	Particle Size(μm) ²⁾	Appearance ³⁾	
P14	Poly(HDFDMA)	F5	10.0	0.1	144,000	5-7	White Powder
P15			10.0	0.5	100,000	5-7	White Powder
P16			10.0	1.0	53,000	4-8	White Powder
P17		F4	10.0	0.5	93,000	5-10	White Powder
P18		F5	10.0	0.5	100,000	5-7	White Powder
P19		F6	10.0	0.5	100,000	5-7	White Powder
P20	Poly(HDFDA)	F2	10.0	0.1	154,000	8-12	White Powder
P21			10.0	0.5	88,000	7-10	White Powder
P22			10.0	1.0	65,000	9-11	White Powder
P23		F1	10.0	0.5	94,000	9-11	White Powder
P24		F2	10.0	0.5	70,000	8-10	White Powder
P25		F3	10.0	0.5	95,000	3-8	White Powder

MMA 2.0g at P=300±10bar, T=70.0±1.0°C for 24hrs with stirring

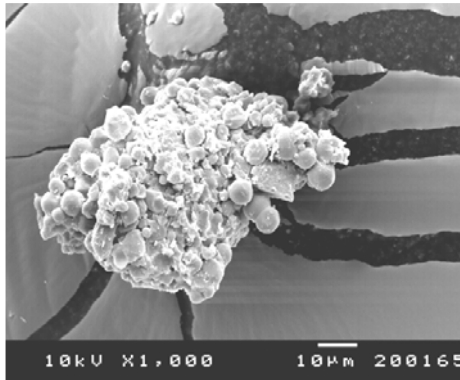
1) Determined by GPC, 2) Determined by SEM, 3) Observed after CO₂ venting



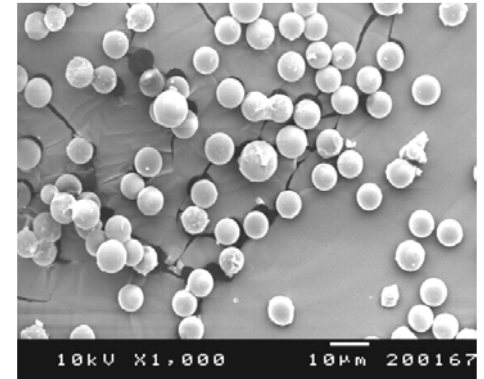
Result – Effect of dispersant and stirring



**Without dispersant
With stirring**



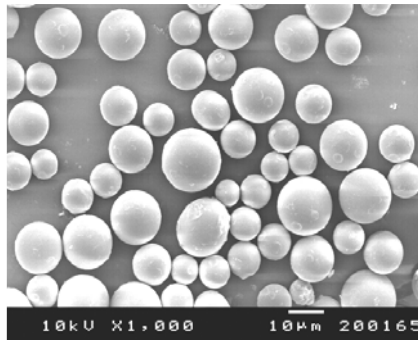
**With Poly(TM) ; F11
Without stirring**



**With Poly(TM) ; F11
With stirring**

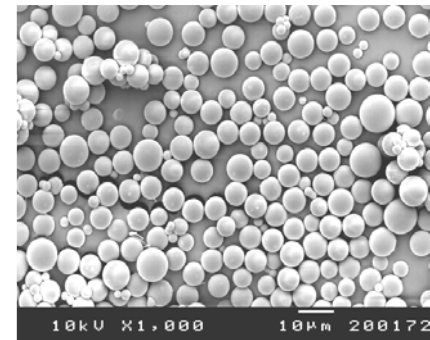
Result – Effect of dispersant kind

[P3]



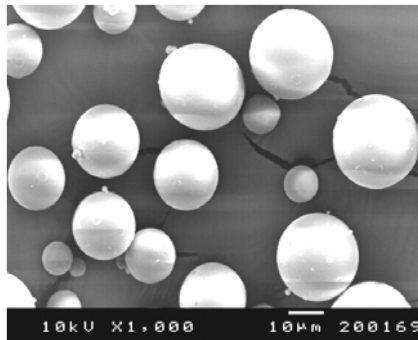
With **Poly(HDFDA)**; F2
10.0wt%

[P6]



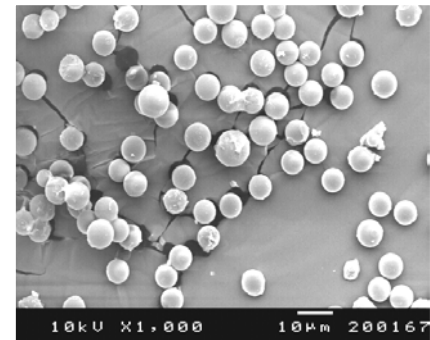
With **Poly(HDFDMA)**; F5
10.0wt%

[P9]



With **Poly(TA-N)**; F8
10.0wt%

[P12]

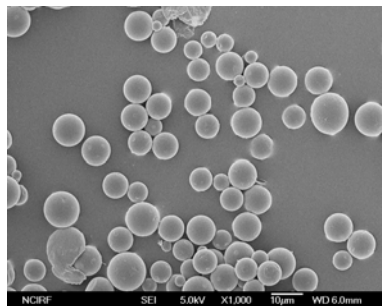


With **Poly(TM)**; F11
10.0wt%



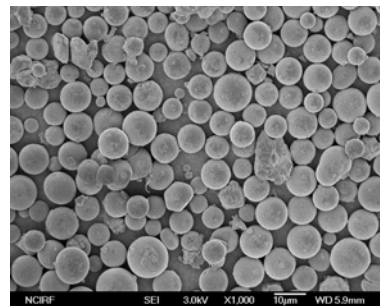
Result – Effect of dispersant amounts

5.0wt%



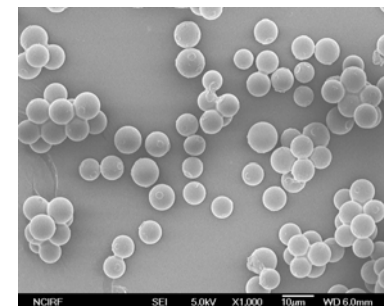
[P2]

10.0wt%



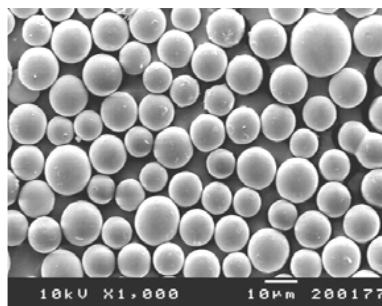
[P3]

20.0wt%

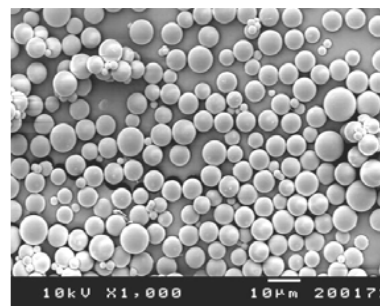


[P4]

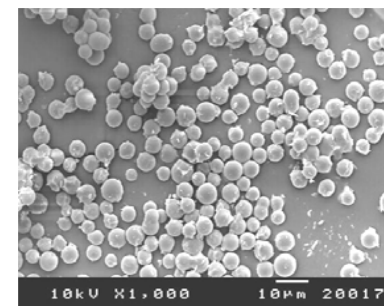
With
Poly(HDFDA)
; F2



[P5]



[P6]



[P7]

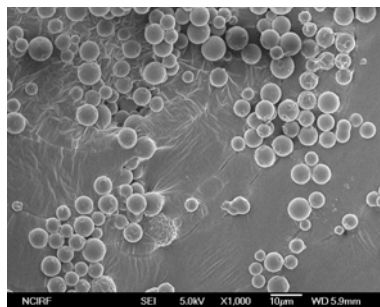
With
Poly(HDFDMA)
; F5



Result – Effect of AIBN amounts

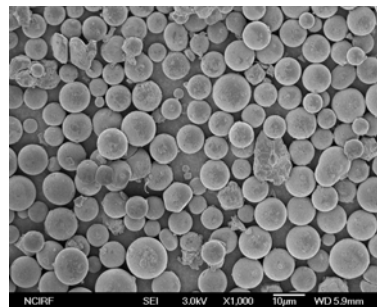
With
Poly(HDFDA)
; F2

AIBN **0.1wt%**



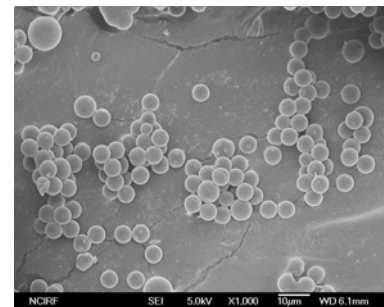
[P20] Mw=154,000

AIBN **0.5wt%**



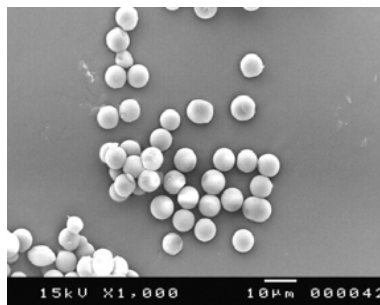
[P21] Mw=88,000

AIBN **1.0wt%**

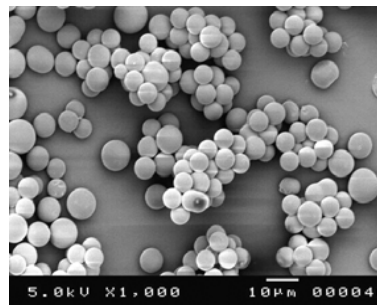


[P22] Mw=65,000

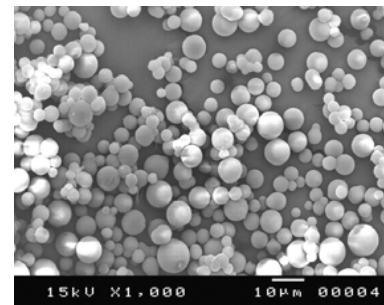
With
Poly(HDFDMA)
; F5



[P14] Mw=143,000



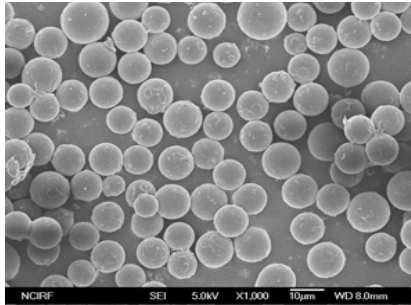
[P15] Mw=100,000



[P16] Mw=53,000

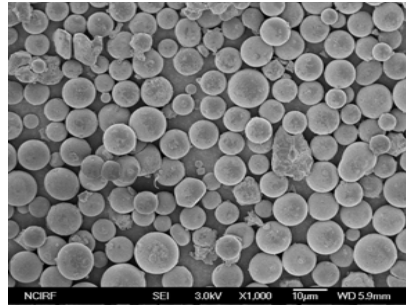


Result – Effect of MW of dispersant



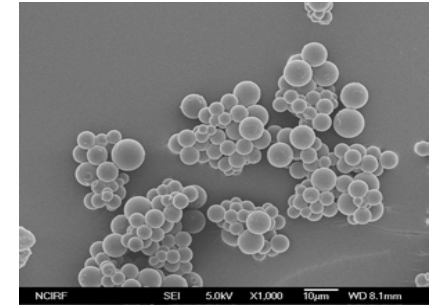
[P23]

With **low MW** of
Poly(HDFDA) ; F3



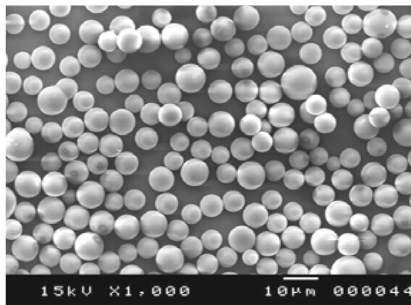
[P24]

With **medium MW** of
Poly(HDFDA) ; F2



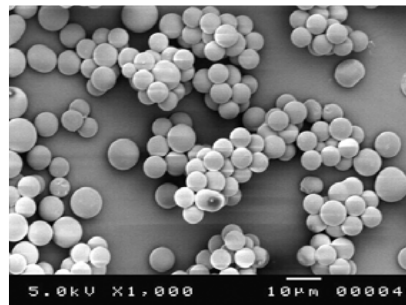
[P25]

With **high MW** of
Poly(HDFDA) ; F1



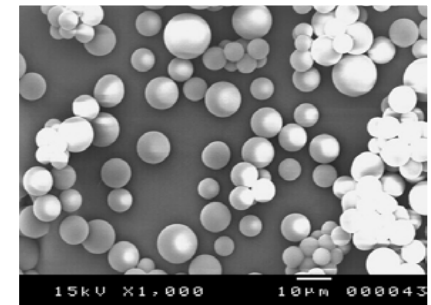
[P17]

With **low MW** of
Poly(HDFDMA) ; F6



[P18]

With **medium MW** of
Poly(HDFDMA) ; F5

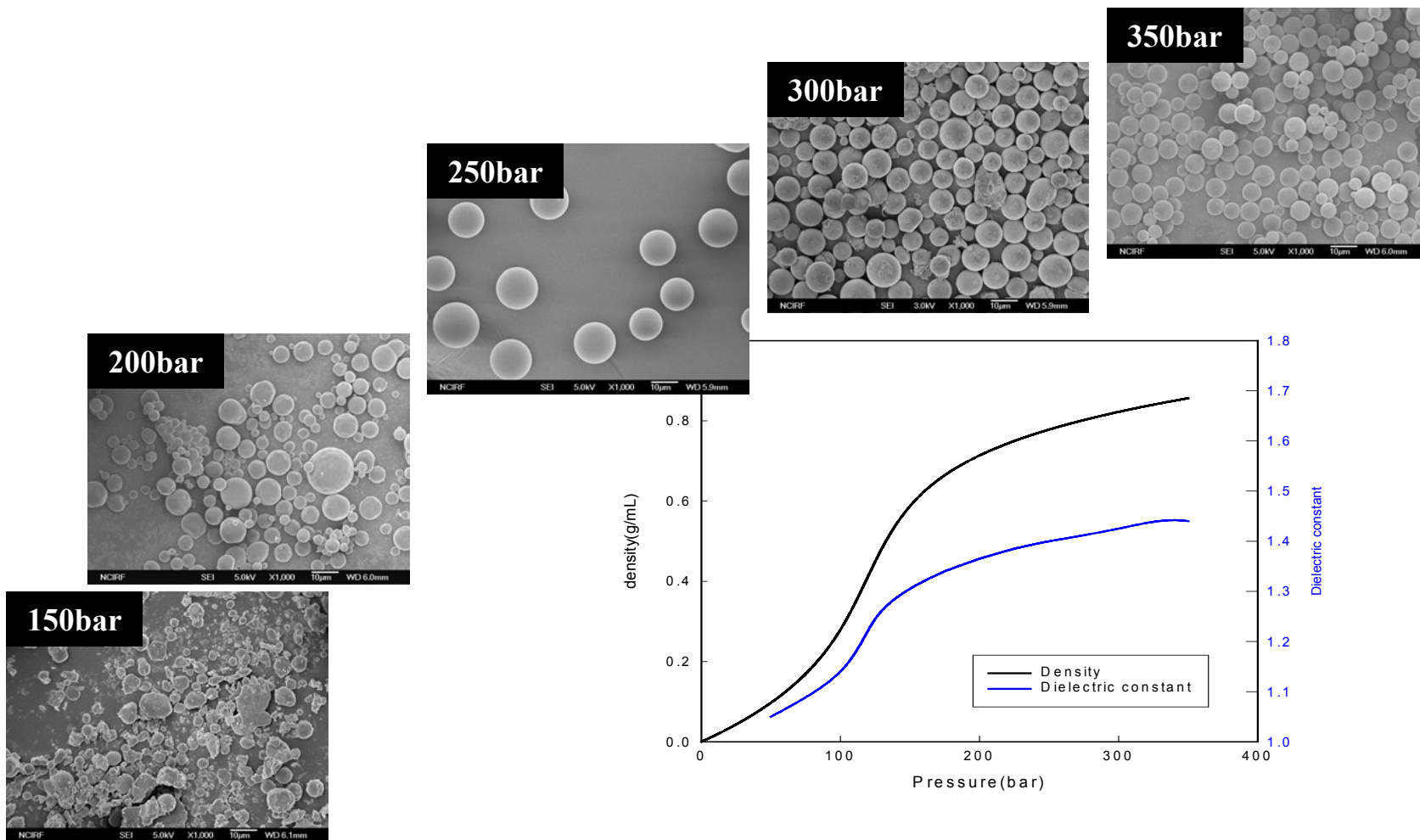


[P19]

With **high MW** of
Poly(HDFDMA) ; F4

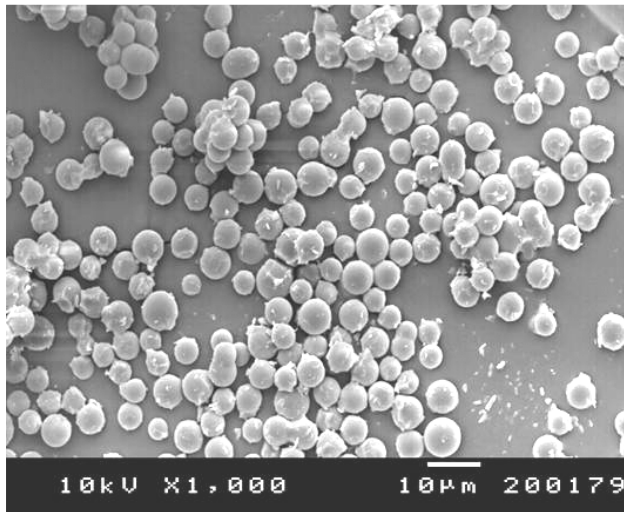


Result – Effect of Pressure with poly(HDFDA)



Result - Particle Size Distribution

SEM image

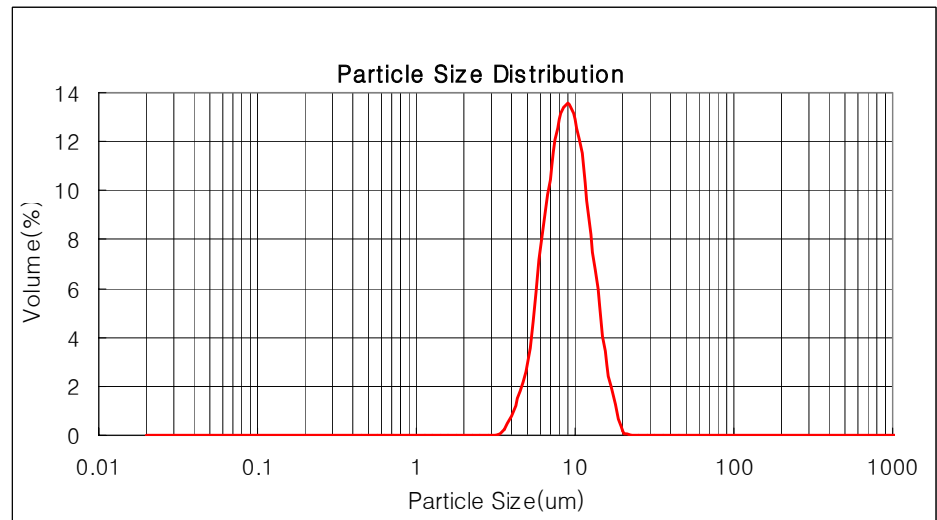


[P7]

With Poly(HDFDMA) ; F5

20.0wt%

By Malvern Mastersizer 2000



Surface Weighted Mean Diameter : 4.695µm

Volume Weighted Mean Diameter : 8.310µm



Conclusion

- We performed **homogeneous solution polymerization** of perfluoroalkyl (meth)acrylate in **scCO₂** and **dispersion polymerization** of PMMA and PVP using these fluorinated polymeric dispersants in **scCO₂**.
- We could control **MW** and **morphology** of PMMA and PVP with varying **polymerization conditions** and **dispersant kinds**.
- Further research is required to study how **CO₂ philic chain length** of poly[perfluoroalkyl (meth)acrylate] affects the **particle morphology** in dispersion polymerization using scCO₂.

