

초임계 이산화탄소내에서 poly[perfluoroalkyl (meth)acrylate] 안정제를 이용한 PMMA 분산중합

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PMMA dispersion polymerization in supercritical CO₂ using poly[perfluoroalkyl (meth)acrylate] stabilizer

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INTRODUCTION

Dispersion polymerization in Supercritical carbon dioxide (scCO₂) is one of the best synthetic methods for the preparation of uniform and monodisperse particles in the micron range.¹ And of the reaction variables, surfactants as stabilizing agents have the key effects on controlling particle size and particle size distribution. But unfortunately, most common surfactants used in the conventional polymerization show negligible solubility in scCO₂. Only the siloxane and fluorinated polymer surfactants have been reported as successful stabilizers for the dispersion polymerization in scCO₂. And several research groups have prepared a series of block and grafted copolymers of siloxane and fluorinated polymers with PMMA, PS and etc. But few researches have been reported the relations between monomers and surfactants. And the steric stabilization mechanism of growing particles in scCO₂ has not been fully described. It is also thought that each monomer needs the specified type of surfactant and the optimal condition of temperature and pressure. Furthermore, it is required to study how the surfactants of different molecular weights and of different structural ratios of CO₂ philic parts and CO₂ phobic parts affect the particle formation in dispersion polymerization in scCO₂. Herein, we focused on the design of polymeric fluorosurfactants that can be utilized as effective steric stabilizers. We selected Heptadecafluorodecyl acrylate (HDFDA) and Heptadecafluorodecyl methacrylate (HDFDMA) because of its possible amphiphilic feature to both monomer and scCO₂. And we also selected commercially available poly[perfluoroalkyl (meth)acrylate] (TA-N, TM : Zonyl[®] DuPont). Since they have similar structure to HDFDA and HDFDMA. We prepared poly(HDFDA), poly(HDFDMA), poly(TA-N) and poly(TM) by homogeneous polymerization in scCO₂, which were tested in the dispersion polymerization of poly(methyl methacrylate).

EXPERIMENTAL

Materials

Heptadecafluorodecyl acrylate (HDFDA) [27905-45-9] and Heptadecafluorodecyl methacrylate (HDFDMA) [1996-88-9] were purchased from Aldrich. TA-N and TM were purchased from DuPont. Methyl methacrylate (MMA) of 99.5% pure was purchased from Junsei chemical. The inhibitor and dissolved oxygen in the monomers were removed by alumina column (Aldrich) and pure nitrogen, respectively. The initiator AIBN (Junsei chemical) of 98% pure was purified by recrystallization from methanol. Carbon dioxide of 99.99% pure was used in the polymerization.

Synthesis of Fluorosurfactants

Homogeneous polymerization of fluorosurfactants were carried out in a 30ml high-pressure view cell containing a miniature Teflon-coated magnetic stirring bar and fitted with two 5.0cm diameter by 1.9cm thick reinforced window [Fig. 1]. Known amounts of each monomer (HDFDA, HDFDMA, TA-N and TM) and AIBN were first introduced to the cell. The cell was then purged with CO₂ for 10 minutes to remove residual oxygen. The cell was pressurized with known amount of CO₂ at room temperature and then heated up to 75°C in the water bath with pressure increasing to around 300 bar. The reaction was conducted for 24 hours with continuous stirring and was monitored by pressure transducer (Honeywell) and thermocouple inside the cell. At the end of the polymerization the cell was cooled down to 5 °C and the CO₂ was slowly vented through two separation traps filled with methanol to solve unreacted monomer before releasing out into the air. The polymer product collected as a dry white powder was then washed by methanol several times to remove residual monomers. The resulting product was dried in vacuo at room temperature overnight.

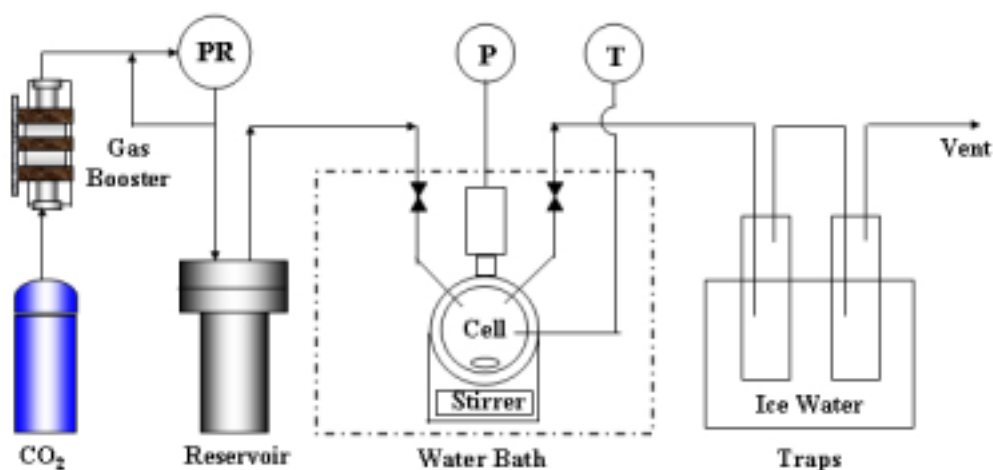


Figure 1 . Schematic diagram of the polymerization apparatus.

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

Dispersion Polymerization of Methyl methacrylate

Dispersion polymerization of MMA was carried out in the same cell. The AIBN and the previously synthesized fluorosurfactants were first introduced into the cell, which was then purged with CO₂. MMA was injected into the cell under CO₂ atmosphere. The cell was then charged with desired amounts of CO₂. The cell was gradually heated up to 70°C in the water bath with pressure increasing to 300bar. The reaction was also allowed to proceed for 24 hours and monitored in the same way. The polymer product was then treated in the previously described way.

Polymer Characterization

Yields were determined by Gravimetrically from the ratio of final mass of polymer washed by methanol to that of the unwashed. Molecular weight was characterized by GPC (600E controller, Waters) using THF as eluent. RI detector(410, waters), two columns(styragel HT3, HT4) and PMMA standard were used. Particle morphologies were analyzed and imaged with SEM (Jeol-5410LV).

RESULT AND DISCUSSION

The data for the homogeneous polymerization of fluorosurfactants in scCO₂ is summarized in [Table 1]. And these fluorosurfactants were evaluated for their effectiveness as stabilizers for the polymerization of methyl methacrylate in scCO₂ using AIBN as the initiator. The polymerizations were carried out with AIBN (0.5 wt%, based on the monomer) and various fluorosurfactants at 70°C, 300bar stirred by magnetic spin bar for 24hrs. For all of the reactions in which the fluorosurfactants were used as stabilizer, the resulting PMMA particles were left in the form of dry, white powder in the cell. ¹H NMR spectrum of the product polymer was identical to the typical spectrum of PMMA in the literature as expected [Figure 2]. Molecular weights and poly dispersity index (PDI) from the typical case of each reaction are shown in [Table 2]. Molecular weights were around 70,000~80,000.

Table 1. Homogeneous polymerization of fluorosurfactants in scCO₂^a

entry	monomer(g)	AIBN(wt%)	yield(%)
1	HDFDA	3.0	89
2	HDFDMA	3.0	67
3	TA-N	3.0	64
4	TM	3.0	70

^a Reaction conditions: P = 300 ±15bar, T = 70±0.5°C, reaction time = 24hrs

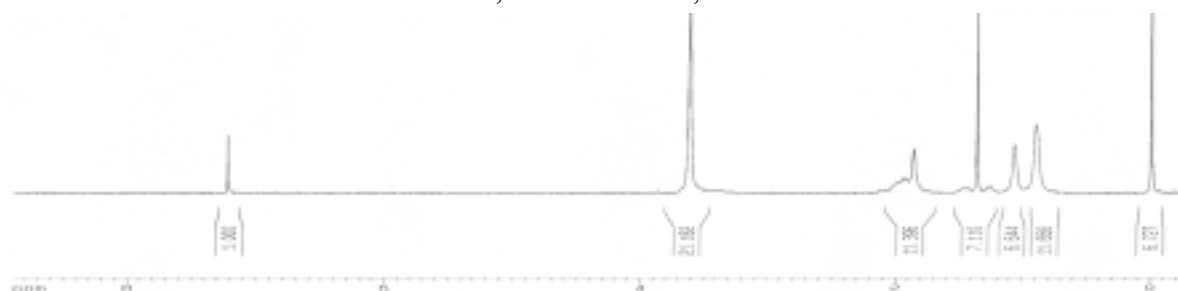


Figure 2. ¹H NMR spectrum of poly(methyl methacrylate) polymerized with poly (TA-N) as a stabilizing agent

Table 2. Dispersion polymerization of MMA with fluorosurfactants in scCO₂. a

entry	MMA(g)	AIBN(wt%)	Surfactant(wt%)	Mw(g/mol)	PDI
1	2.0	0.5	poly(HDFDA) 20	69,397	2.891
2	2.0	0.5	poly(TA-N) 10	76,896	2.888
3	2.0	0.5	poly(TM) 10	74,435	3.566

Through SEM micrographs [Figure 3], resulting polymer was observed as spherical particles in the diameter of 5~10 micrometer. The particles in [Figure 3(a)] are not monodisperse and some defects are found in the individual particle. However, successful stabilization prevented any aggregation of growing particles and resulted in the formation of spherical and uniform particles [Figure 3(b)].

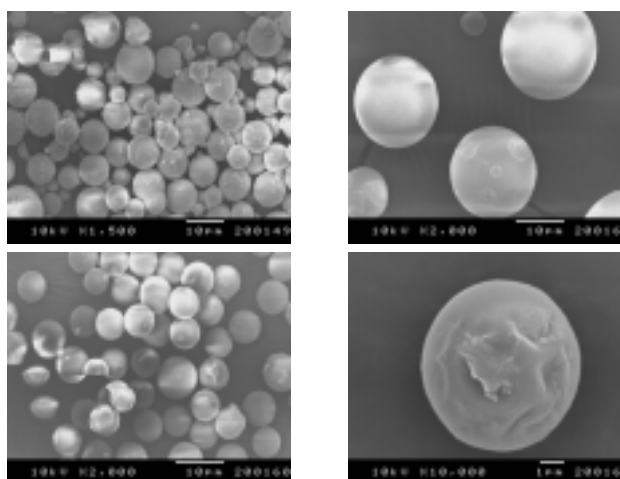


Figure 3. Scanning electron micrographs of PMMA particles polymerized with (a) poly(HDFDA), (b) poly(TA-N), (c)-(d) poly(TM) as a stabilizing agent

CONCLUSION

We prepared new polymeric fluorosurfactants in supercritical carbon dioxide with different yield according to the type of monomer. These fluorosurfactants were analyzed and evaluated for the dispersion polymerization of PMMA which showed good possibility as effective steric stabilizer. Successful stabilization prevented any aggregation of growing particles and resulted in the formation of spherical and uniform particles. And Further research is required to study how the molecular weights and the structural balance between CO₂ philic and CO₂ phobic part of the fluorosurfactants affect the particle formation by dispersion polymerization in scCO₂.

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