

Non-bioaccumulative, environmentally preferable stabilizer architectures for the dispersion polymerization of MMA in supercritical CO₂

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Abstract To overcome the environmental concerns associated with long-chain perfluorinated compounds, in this report, non-bioaccumulative, environmentally friendly stabilizer architectures based on short-chain fluorinated polymers have been designed for the dispersion polymerization of methyl methacrylate (MMA) in supercritical CO₂. Random copolymers composed of 2-(diisopropylamino)ethyl methacrylate (DPAEMA) and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (FBMA) or 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate were prepared with various comonomer ratios and utilized as stabilizers. It was found that the copolymers effectively stabilized PMMA latexes in CO₂, leading to the formation of free-flowing, spherical PMMA particles. With increase in the concentration of the stabilizer poly(FBMA-*co*-DPAEMA) from 2% to 6% (*w/w* with respect to MMA), the particles diameter decreased from 3.02 to 1.0 μm.

Keywords Non-bioaccumulative · Short-chain fluorinated stabilizers · Supercritical CO₂ · Random copolymers · Dispersion polymerization · Poly (methyl methacrylate)

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Introduction

An intense research activity concentrated in the last decade has demonstrated that supercritical carbon dioxide (scCO₂) is an attractive alternative medium for polymerization. Especially, dispersion polymerization in scCO₂ has been well documented [1–3]. In general, the stabilizers used in CO₂ are mostly homopolymers and block and graft copolymers based on fluorinated monomers or siloxanes. To overcome the problems such as poor solubility in organic solvents and the synthetic difficulties associated with block and graft copolymers, recently, we have demonstrated the use of random copolymers as successful stabilizers [4–6].

Recently, the concern over perfluorinated compounds have emerged globally since they are identified as environmentally persistent bioconcentrates [7]. In particular, perfluorooctyl sulfonates and perfluorooctanoic acids (PFOA; also called as ‘C8’ compounds) are the major widespread bioaccumulatives detected in the wildlife and humans from various geographic locations [8–10]. The environment contamination of PFOA is believed to be from the gradual degradation of products derived from fluorinated telomers, fluorinated alcohols, and other polyfluoroalkyl substances used in commercial products as surfactants, stain- and grease-resistant coatings, etc. [11]. The widespread occurrence, biopersistence, and unexpected toxicity of PFOA have raised worldwide environmental concern. Last year, the US environmental protective agency (EPA) classified the PFOA as a “likely” carcinogen in humans and thus the materials that may degrade to generate PFOA are being severely restricted by EPA and related agencies worldwide [7, 12].

Unfortunately, most of the successful fluorinated stabilizers used in scCO_2 are based on polymers derived from perfluorooctyl acrylates (FOA) or methacrylates (FOMA) [1–3], which are potential materials that can degrade in the environment to form the biopersistent perfluorooctyl alcohols. This is a serious setback for the implementation of CO_2 -based polymerizations in industrial as well as in biomedical applications [13]. Interestingly, however, recent systematic studies presented by Dams have shown that carboxylic and sulfonic acids containing a short chain of four or less perfluorinated carbon atoms do not bioaccumulate and, therefore, are not biopersistent [14]. Exploiting this property, DeSimone and co-workers have recently explored the use of short-chain-fluorinated polymers as non-bioaccumulative stain-resistant coating materials [15, 16]. More recently, commercial organizations have also introduced environmentally friendly fluorochemicals by replacing the previously used long-chain perfluorinated compounds in products like floor-wash and stain repellents [12].

Prompted by the ongoing research on replacing long-chain perfluorinated compounds with short-chain as “greener polymers”, in this study, we have designed new non-bioaccumulative stabilizer architectures based on semi-fluorinated random copolymers, which contain three or four perfluorinated carbon atoms. The random copolymers were investigated as efficient stabilizers for the dispersion polymerization of MMA in CO_2 .

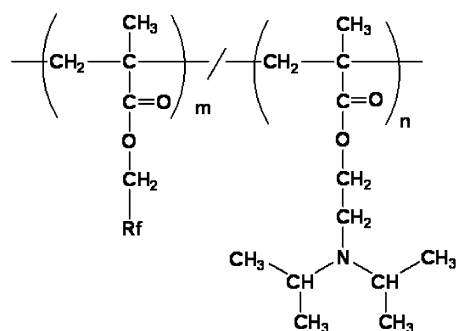
Experimental section

Materials

2,2,3,3,4,4,4-Heptafluorobutyl methacrylate (FBMA), 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (FPMA), and 2-(diisopropylamino)ethyl methacrylate (DPAEMA) were purchased from Aldrich and purified by passing the liquids through a neutral alumina column to remove the inhibitor. The 2,2'-azobisisobutyronitrile (AIBN, Aldrich) was purified by recrystallization in methanol. Research grade carbon dioxide with high purity (99.99%) was obtained from Daeyoung Co (Korea). The ratio of monomers incorporated in the copolymers were determined by ^1H NMR using JNM-ECP 4000 (JEOL) spectrometer with $\text{CDCl}_3/\text{CFCl}_3$ ($v/v = 1:1.35$) as the solvent. Microscopic images of PMMA particles were obtained from a Hitachi S-2400 scanning electron microscope (SEM).

Preparation of polymeric stabilizers

The random copolymers composed of FBMA and DPAEMA (poly(FBMA-*co*-DPAEMA)) with different monomer ratios were prepared by radical polymerization.



Poly(FBMA-*co*-DPAEMA) (C3) : Rf = $(\text{CF}_2)_2\text{CF}_3$

Poly(FPMA-*co*-DPAEMA) (C4) : Rf = $(\text{CF}_2)_3\text{CF}_2\text{H}$

Fig. 1 The chemical structure of non-bioaccumulative copolymeric stabilizers designed for the dispersion polymerization of MMA in scCO_2

Briefly, a 25-mL flask equipped with a stir bar was charged with 0.5 g of FBMA, 0.5 g of DPAEMA, and 0.01 g of AIBN. The flask was purged with argon and heated to 65 °C for 24 h. After polymerization, the reaction mixture was dissolved in the mixture of CFCl_3 and chloroform, and the solution was poured into hexane to precipitate the copolymer. The product was filtered and dried. Poly(FPMA-*co*-DPAEMA) was also prepared with the same procedure. For convenience, the copolymer with three perfluorinated carbons in the side chain, poly(FBMA-*co*-DPAEMA) was named as C3, and poly(FPMA-*co*-DPAEMA) with four fluorinated carbons was named as C4. The chemical structures of the copolymers are depicted in Fig. 1. The molecular weight of the copolymers was determined using a Agilent Technologies 1200 Series equipped with a set of three columns (10^4 , 10^3 , and 10^2 Å: HP PL gel 5 μ), with THF as an eluent. Polystyrene samples were used as standards to construct the calibration curve. The solubility of the copolymers in scCO_2 was determined by the cloud point method, as described previously [6].

Dispersion polymerization of MMA in scCO_2

The general procedure for the dispersion polymerization of MMA in scCO_2 using random copolymeric stabilizers has

Table 1 Properties of random copolymers

Copolymer	FBMA or FPMA feed ratio (w/w%)	FBMA or FPMA incorporated ratio ^a (w/w%)	M_n^b (kg/mol)	PDI ^b (M_w/M_n)
C3 (37:63)	40	37	16.9	1.77
C3 (46:54)	50	46	28.8	1.99
C3 (65:35)	60	65	48.7	2.34
C4 (71:29)	70	71	44.8	2.54

C3 Poly(FBMA-*co*-DPAEMA), C4 poly(FPMA-*co*-DPAEMA)

^a Determined by ^1H NMR

^b Obtained by GPC

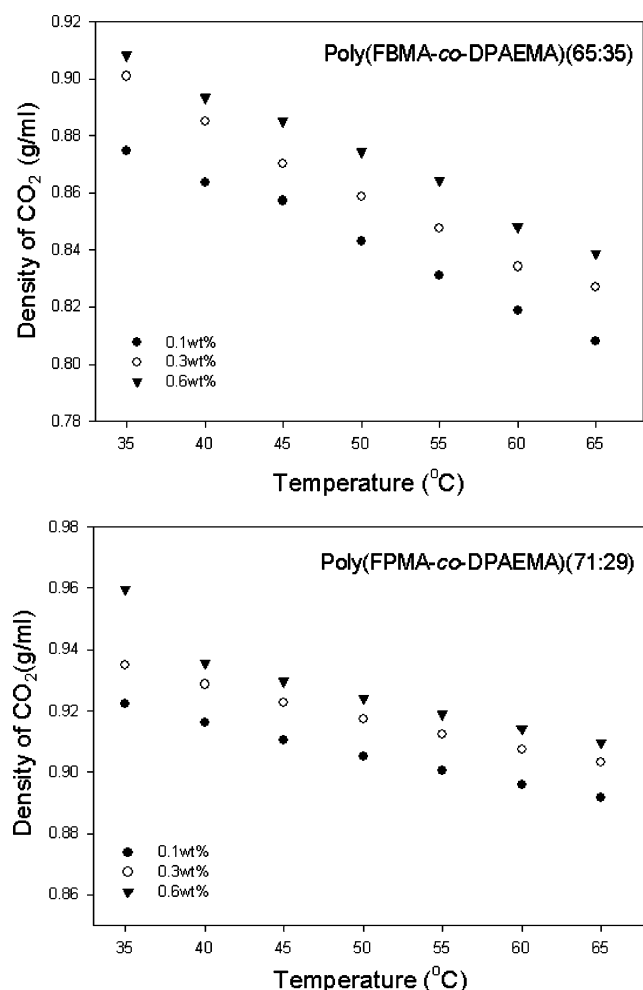


Fig. 2 Cloud point profiles of poly(FBMA-*co*-DPAEMA) (C3) (65:35) and poly(FPMA-*co*-DPAEMA) (C4) (71:29)

been reported previously [4–6]. In a typical polymerization, 1 g of MMA, 0.02 g of C3 or C4, 0.01 g of AIBN, and a Teflon-coated stir bar were placed in the stainless steel reactor. The reactor was pressurized by ISCO syringe pump (Model 260D) containing compressed CO₂ at a pressure of 70 bar, and the reaction mixture was heated to 65 °C in a water bath. Once this temperature was reached, the

remaining CO₂ was then added into the system at 345 bar (5000 psi). The reactor was sealed, and the polymerization was performed for 12 h. After polymerization, the reactor was cooled, and the unreacted MMA was extracted with liquid CO₂ at a flow rate of 20 mL/min. The remaining CO₂ was then slowly vented, and the polymer product was collected and weighed.

Results and discussion

The random copolymers were synthesized by free radical polymerization of FBMA or FPMA with DPAEMA in the presence of AIBN at 65 °C. Owing to the presence of DPAEMA units, the resultant copolymers were soluble in common organic solvents, which enabled ¹H NMR analysis of copolymers. The results of polymerizations are summarized in Table 1. As expected, the proportion of FPMA, FBMA, and DPAEMA incorporated in the copolymer is well in accordance with the feed ratio of monomers. To complement the use of copolymers as stabilizers, the phase behavior of the copolymer in CO₂ was investigated by the cloud point method [17]. Two copolymeric stabilizers having similar composition and molecular weight were selected for the experiment, and results were observed in the temperature range of 35–65 °C and pressure up to 500 bar. The cloud profiles of the stabilizers are shown in Fig. 2. While 0.1 wt.% (in CO₂) of C3 with 65 w/w% of FBMA content is soluble in scCO₂ at the density higher than 0.81 g/ml at 65 °C, the copolymer C4 (71:29) was found to be soluble above 0.89 g/ml at the same experimental condition. Though the C4 contains 71% FPMA (with an additional CF₂ group in compare to C3), the decrease in CO₂ solubility may be attributed to terminal CF₂H groups (see Fig. 1). The CF₂H groups are known to have poor interactions with CO₂ than CF₃ groups [18].

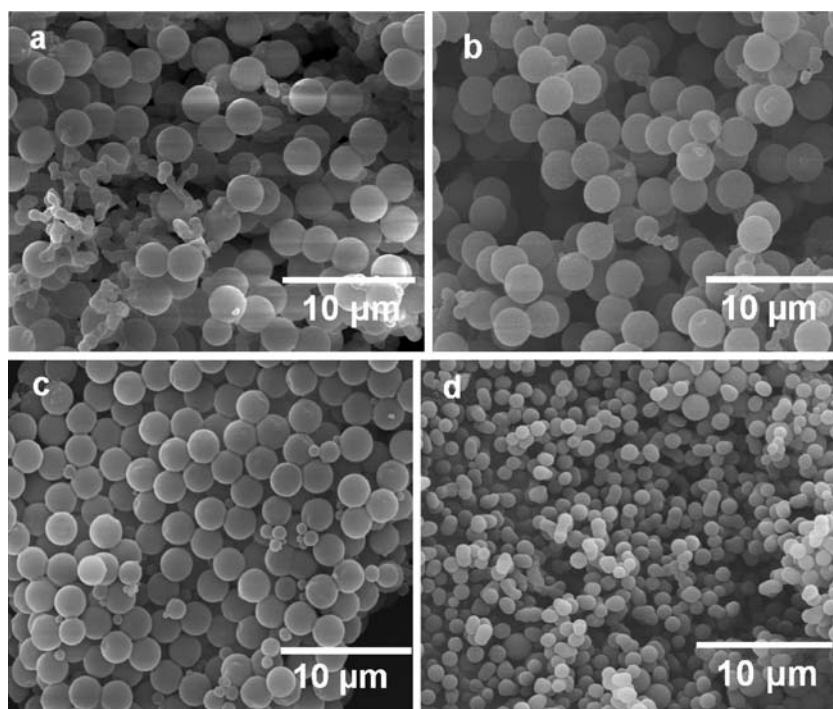
The dispersion polymerizations were carried out on 1 g (25 w/v% MMA in CO₂) scale using 1% AIBN and 2% copolymeric stabilizer (w/w with respect to MMA).

Table 2 Characterization of PMMA particles prepared in the presence of copolymer stabilizers

Stabilizer	Stabilizer concentration (w/w% to MMA)	Yield (%)	Particle size (μm)	PSD	Product morphology
C3 (37:63)	2	95	–		Clumpy solid
C3 (46:54)	2	95	2.73	1.02	Powder
C3 (65:35)	2	94	3.00	1.01	Powder
C3 (65:35)	4	93	2.33	1.08	Powder
C3 (65:35)	6	93	1.19	1.03	Powder
C4 (71:29)	2	94	–		Clumpy solid
C4 (71:29)	4	93	3.3		Clumpy solid

Reaction conditions: 25% MMA (w/v to CO₂), 1% AIBN (w/w to MMA), temperature at 65 °C, and pressure of 345 bar
C3 Poly(FBMA-*co*-DPAEMA), C4 poly(FPMA-*co*-DPAEMA), PSD particle size distribution

Fig. 3 Scanning electron micrographs of PMMA particles prepared with the copolymeric stabilizer **a** C3 (46:54) and **b**, **c**, and **d** C3 (65:35) with 2, 4, and 6 w/w% concentration (with respect to MMA), respectively. Reaction conditions: 25 w/v% MMA (with respect to CO₂), 1 w/w% AIBN (with respect to MMA), 65 °C, and 345 bar; C3 = poly(FBMA-*co*-DPAEMA)

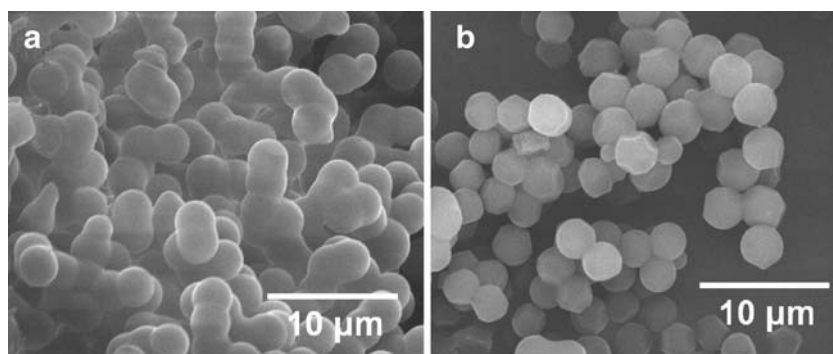


The polymerization temperature, pressure, and time were kept constant at 65 °C, 345 bar, and 12 h, respectively. Though the cloud point investigations showed that both C3 and C4 copolymers are insoluble in pure CO₂ at this concentration, all polymerizations were initially homogeneous due to the presence of MMA [4–6]. It may be noted that for a successful stabilization, stabilizers do not have to be completely soluble in the reaction medium throughout the polymerization but should be present in the nucleation stage of the polymerization, as observed previously [4–6, 19]. The copolymers of C3 with three different comonomer ratios were attempted in the polymerization as stabilizers. The concentration of the C3 stabilizer was controlled from 2 to 6 w/w% with respect to MMA. The results from the polymerization are summarized in Table 2. The polymerization conducted in the presence of the C3 with 37 w/w% of FBMA was not successful as PMMA was

obtained as a hard clumpy solid from the reactor. Morphological analysis of the PMMA by SEM revealed that spherical particles were produced in highly aggregated form. On the other hand, the polymerizations repeated with 2 wt.% concentrations of C3 having 46 w/w% of FBMA resulted in PMMA powder of slightly agglomerated morphology (see Fig. 3a). The copolymer with 65 w/w% of FBMA turned out to be the most successful in producing stable colloidal dispersions in CO₂. After venting the CO₂, PMMA was retrieved from the reactor as free-flowing powders. SEM micrographs confirmed that the PMMA was in the form of discrete spherical particles (see Fig. 3b).

It is generally known that the polymerization of MMA in CO₂ without stabilizer or in the presence of an inefficient stabilizer always results in low yields with nondescriptive morphology of PMMA [1–3]. However, the yield of

Fig. 4 Scanning electron micrographs of PMMA particles prepared with the copolymeric stabilizer poly(FPMA-*co*-DPAEMA) (C4) (71:29) with **a** 2 and **b** 4 w/w% (with respect to MMA) concentration. Reaction conditions: 25 w/v% MMA (with respect to CO₂), 1 w/w% AIBN (with respect to MMA), 65 °C, and 345 bar



PMMA was found to be largely insensitive to the C3 with different FBMA ratios. As can be seen from Table 2, in all cases, the polymerization resulted in 92–95% yield. Though the stabilizer C3 with 37 w/w% FBMA resulted in the form of clumpy solids, the high yield of PMMA obtained by the polymerization indicates that it had indeed stabilized the polymerization to some extent, possibly with the help of DPAEMA. In addition to the solubility provided by the fluoroalkyl groups, the stabilization effect of C3 can also be attributed to the physiochemical properties of its ‘polymer-philic’ component, DPAEMA. The *N*-methylated branches of DPAEMA and electron rich carbonyl group with basic nitrogen are believed to be the main factors, which allowed favorable interaction between the copolymer and CO₂ [4–6].

It is well known that the proper partitioning of the stabilizer at the growing polymer surface and a careful balance between the size of the anchor group (polymer-philic) and the size of the soluble component (CO₂-philic) are important factors for a stabilizer to be interfacially active in a successful stabilization [20]. Thus, the results obtained from this study suggest that 65 w/w% FBMA fraction is required for C3 stabilizer for producing a stable colloidal dispersion of PMMA in CO₂. Interestingly, the total fluorine content of C3 with 65% FBMA composition is relatively lower than that of a stabilizer with 34% FOMA content used in the previous study [4, 6].

In general, the concentration of stabilizer controls the morphology of materials produced in the dispersion polymerization. To investigate the effect of stabilizer concentration, the polymerizations were repeated with 4 and 6 w/w% of stabilizer. As shown in the Table 2, free-flowing powder of PMMA with high yield was obtained in both cases. SEM images confirmed that discrete PMMA particles were obtained from these polymerizations (see Fig. 3c and d). The average particle size was decreased from 3.02 to 1.0 µm when the stabilizer concentration was increased from 2 to 6 w/w%. This is a common phenomenon in the dispersion polymerization where an increase in the dispersant concentration generally produces smaller particles [1–3].

Finally, the stabilization efficiency of C4 was investigated with 71 w/w% FPMA fraction. Though the conversion was very high with 2 w/w% stabilizer concentration, the PMMA obtained was in the form of a clumpy solid (see Table 2). SEM micrographs confirmed that the PMMA particles were severely agglomerated (Fig. 4a). When the concentration of the stabilizer was increased from 2% to 4%, slightly agglomerated spherical particles with relatively narrow particle size distribution was obtained (Fig. 4b). Even though the C4 contains 71 w/w% FPMA content, its poor stabilization efficiency could be explained on the much lower solubility of C4 than C3 in polymerization

medium due to the semifluorinated pedant methyl groups, as described earlier in this report.

Conclusions

We have demonstrated the successful dispersion polymerization of MMA in scCO₂ with non-bioaccumulative short-chain fluorinated stabilizers. To overcome the environmental concerns associated with long-chain PFOMA based stabilizers, the newly designed copolymers (C3 and C4) were prepared with different comonomer ratios. The random copolymer, C3 with 65 w/w% of FBMA fraction, was found to be the most effective stabilizer in the dispersion polymerization of MMA leading to the formation of a free-flowing PMMA powder. Morphological analysis by SEM revealed that the PMMA obtained from these dispersion polymerizations were in the form of discrete spherical particles. Even though the particles were highly agglomerated from certain conditions, high yield (>93%) of PMMA was obtained irrespective of the concentration and composition of the copolymeric stabilizers. The combination of easy preparative method and most importantly, environmentally non-persistence nature of these stabilizers would be an advantage over the traditionally used FOMA and FOA based stabilizers, which release the toxic and bioaccumulative PFOAs in the environment.

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References

- Kendall JL, Canelas DA, Young JL, DeSimone JM (1999) Chem Rev 99:543
- DeSimone JM, Maury EE, Menceoglu YZ, McClain JB, Romack TJ, Combes JR (1991) Science 265:356
- Woods HM, Silva MMCG, Nouvel C, Shakesheff KM, Howdle SM (2004) J Mater Chem 14:1663
- Hwang HS, Gal YS, Johnston KP, Lim KT (2006) Macromol Rapid Commun 27:121
- Hwang HS, Lim KT (2006) Macromol Rapid Commun 27:722
- Yuvaraj H, Hwang HS, Woo MH, Park EJ, Ganapathy HS, Gal YS, Lim KT (2007) J Supercrit Fluids 42:359
- Renner R (2001) Environ Sci Technol 35:154
- Houde M, Martin JW, Letcher RJ, Solomon K, Muir DCG (2006) Environ Sci Technol 40:3463
- Dinglasan MJ, Ye Y, Edwards EA, Mabury SA (2004) Environ Sci Technol 38:2857
- Giesy JP, Kannan K (2001) Environ Sci Technol 35:1339
- Ellis DA, Martin JW, Silva AOD, Mabury SA, Hurley MD, Andersen MPS, Wallington TJ (2004) Environ Sci Technol 38:3316
- Renner R (2006) Environ Sci Technol 40:2083

13. Ganapathy HS, Hwang HS, Jeong YT, Lee WK, Lim KT (2007) *Euro Polym J* 43:11
14. Dams R (2004) In 14th European Symposium on Fluorine Chemistry, Poznan, Poland, paper C-O-07
15. Guo J, Resnick PR, Efimenko K, Genzer J, DeSimone JM (2007) *Ind Eng Chem Res* DOI [1021/ie0703179](https://doi.org/10.1021/ie0703179)
16. Guo J, Resnick PR, DeSimone JM (2006) Alternative Fluoropolymers to the Avoid Challenges Associated with Perfluorooctanoic acid (PFOA), 18th International Symposium on Fluorine Chemistry, Bremen, Germany; 232nd ACS National Meeting, San Francisco, CA
17. Lim KT, Hwang HS, Ryoo W, Johnston KP (2004) *Langmuir* 20:2466
18. Eastoe J, Dupont A, Steytler DC (2003) *Curr Opin Colloid Interface Sci* 8:267
19. Woods HM, Nouvel C, Licence P, Irvine DJ, Howdle SM (2005) *Macromolecules* 38:3271
20. Lepilleur C, Beckman EJ (1997) *Macromolecules* 30:745