Dispersion Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide Using a Fluorinated Graft Maleic Anhydride Copolymer Stabilizer

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Introduction. In recent years supercritical carbon dioxide ($scCO_2$) has generated much interest in the polymer synthesis and polymer materials processing communities as an attractive alternative solvent.[1−4] CO_2 is inexpensive, nontoxic, nonflammable, and readily available in high purity from a variety of sources. Since CO_2 is an ambient gas, polymers can be isolated from the reaction mixture by a simple depressurization, resulting in a dry polymer product. This eliminates the necessity for energy-intensive drying procedures often required in polymer manufacture to remove residual solvent from the final polymer materials. Because of the poor solubility of most polymers and the high solubility of most vinyl monomers in $scCO_2$,[2] precipitation and dispersion polymerizations are commonly used to prepare polymers in this medium.[1−5] Usually, dispersion polymerizations lead to polymer products of higher molecular weight, in greater yield and with better particle morphology compared to a surfactant free precipitation polymerization.[2] To successfully accomplish a dispersion polymerization, specially designed stabilizers have to be used, which should have both a CO_2-philic and polymer-philic portion to allow them to stabilize the reaction system. Typical stabilizers reported so far have been fluorinated[3,4] and siloxane[5,6] based homopolymers (e.g., poly(1,1-dihydroperfluorooctyl acrylate) (poly(FOA))[3] and poly(dimethylsiloxane) (PDMS) macromonomers[7]), block or graft copolymers,[8−10] and reactive macromonomers.[7] In some cases the polymer itself plays a role as a stabilizer with no need for additional stabilizers.[11] Successful dispersion polymerizations of a wide variety of monomers have been conducted in $scCO_2$. Monomers reported include styrene,[12] methyl methacrylate (MMA),[3,8,13−16] glycidyl methacrylate,[7] 2-(dimethylamino) ethyl methacrylate,[17] ethyl methacrylate,[18] vinyl acetate,[19] vinylpyrrolidone,[20] and acrylonitrile.[21]

Poly(vinylidene fluoride) (PVDF) possesses excellent thermal, chemical, and weather stability and is used primarily for pipes, valves, coatings, and films as well as being an acceptable biomaterial.[22] The conventional methods for PVDF preparation are by aqueous suspension and emulsion polymerizations, which both generate a large quantity of wastewater and can require a substantial quantity of energy to dry the polymer.[23] A continuous polymerization of VDF in $scCO_2$ has been reported[24−26] as well as the dispersion polymerization of VDF using a range of VDF-based copolymers as stabilizers.[10] However, no distinctive, spherical particles were obtained. We have reported elsewhere that commercially available PDMS monomethacrylate (PDMS-ma) has a clear effect on the polymerization of VDF in $scCO_2$, leading to high molecular weight product with a broad molecular weight distribution (MWD), and primary particles (200−500 nm) that coagulate to form larger uniform coarse particles (200−500 μm).[27]

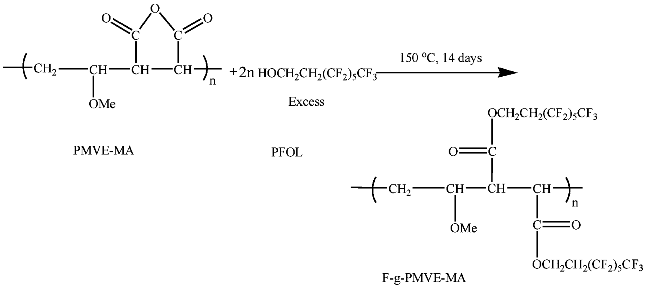

Figure 1. Synthesis of fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) (F-*g*-PMVE-MA).

In this paper, we report the development of a very effective steric stabilizer, a fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) (F-*g*-PMVE-MA) (Figure 1) for the dispersion polymerization of VDF in $scCO_2$.

Experimental Section. a. Materials. The initiator for VDF polymerization, diethyl peroxydicarbonate (DEPDC), was synthesized according to published methods.[28] The final product solution was approximately 10 wt % DEPDC in 1,1,1,3,3-pentafluorobutane and was stored at −15 °C. VDF monomer was donated by Solvay Research, Belgium, and used without further purification. Carbon dioxide (SFC grade) was purchased from BOC and used without further purification.

The stabilizer F-*g*-PMVE-MA was synthesized as shown in Figure 1. Poly(methyl vinyl ether-*alt*-maleic anhydride) (PMVE-MA, M_n 79.8 kg/mol, Aldrich Chemical Co.) and 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol (PFOL, purity 97%, Lancaster Synthesis) were used as received. PMVE-MA and PFOL were weighed into a conventional glass pressure vessel and then sealed.[29] The reaction mixture was maintained at 150 °C for 14 days with stirring to give a yellow solution. After removal of the excess alcohol under vacuum, a brown solid product (F-*g*-PMVE-MA) was obtained.

b. Polymerization Apparatus and Procedure. Polymerizations were carried out in a 60 mL stainless steel autoclave[27] at 55 °C, with stirring at 300 rpm and an initial vessel pressure of 4000 psi (27.2 MPa). Other reaction conditions, including concentrations of the monomer, initiator, and stabilizer, are indicated in Table 1. The reactions were terminated when the pressure in the autoclave fell by 300 psi (2.04 MPa), the point at which the solid contents in autoclave approaches ca. 33 g/L. The carbon dioxide was vented slowly and the autoclave opened.

c. Characterization. Gel permeation chromatography (GPC) was performed at 80 °C using a K-501 HPLC pump with two PLgel 5 μm Mixed-C columns (300 × 7.5 mm, particle size 5 μm, with its linear calibration range of M_w 200−2 000 000 g/mol), 1 PLgel 5 μm guard column (50 × 7.5 mm, particle size 5 μm), and refractive index detector. *N*,*N*-Dimethylformamide (DMF) modified with 0.1 M LiBr was used as the solvent. DMF is a

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Table 1. Experimental Data for the Dispersion Polymerization of Vinylidene Fluoride (VDF) Using the Fluorinated Graft Poly(methyl vinyl ether-*alt*-maleic anhydride) (F-*g*-PMVE-MA) Stabilizer[a]

				GPC results		morphology	
entry	[M][b] (mol/L)	[S][c] (wt %)	monomer conversion (%)	M_w[d] (kg/mol)	PDI[e]	SEM images[f]	appearance[g]
1	2.6		13.5	49	1.5	agglomerated	fine powder
2	2.6	0.6	17.0	163	2.7	agglomerated	fine powder
3	2.6	2.0	14.1	84	1.9	agglomerated	fine powder
4[h]	2.6	0.6	5.0	180	2.8	agglomerated, some particles	fine powder
5	9.8		4.0	216	2.3	agglomerated	spongy solid
6	9.8	0.6	5.7	385	3.2	well-defined particles	fine powder
7	9.8	2.0	3.5	183	4.3	well-defined particles	fine powder
8[i]	9.8	0.6	4.0	243	2.5	particles	coarse powder
9[j]	9.8	0.6	14.1	350	3.7	agglomerated, some particles	fine powder
10[j]	9.8	5.0	14.2	130	3.9	well-defined particles	fine powder

[a] Reactions were carried out at 55 °C, initial pressure P_0 4000 psi, initiator concentration [I] 1.0 mmol/L, agitation at 300 rpm, solid contents of final product in the autoclave ~33 g/L. [b] Monomer concentration. [c] F-*g*-PMVE-MA concentration, percentage of weight/weight relative to VDF monomer. [d] Weight-average molecular weight. [e] Polydispersity. [f] Determined by scanning electron microscopy (SEM) analysis. [g] Visual observation. [h] Solid contents 8.3 g/L. [i] Poly(dimethylsiloxane) monomethacrylate macromonomer (PDMS-ma) was used as the stabilizer. [j] Solid contents 89 g/L.

polar solvent, and PVDF is a polar polymer. Therefore, there is a dipole interaction that occurs, causing artificial shoulders to appear on the high molecular weight end of the distribution. This interaction is eliminated by the addition of lithium bromide. The calibration was accomplished at 80 °C with narrow MWD standards of poly(methyl methacrylate) (PMMA) (Polymer Laboratories Ltd). The morphology of the PVDF product was determined using a Philips XL30 ESEM-FEG machine.

^{1}H NMR, ^{19}F NMR, and ^{13}C NMR were performed for F-*g*-PMVE-MA and the starting materials using a Bruker 300 MHz spectrometer. Infrared analysis for F-*g*-PMVE-MA and the starting material PMVE-MA was carried out using a Perkin-Elmer system 2000 FTIR spectrometer equipped with a diffuse reflectance infrared spectroscopy (DRIFTS) attachment (Spectratech).

Results and Discussion. a. Synthesis and Characterization of F-*g*-PMVE-MA Stabilizer. The stabilizer F-*g*-PMVE-MA was synthesized by a thermal ring-opening esterification reaction (Figure 1), leading to a fluorinated graft chain (CO_2-philic segment) and a hydrocarbon backbone (CO_2-phobic moiety). To obtain a high percentage of graft chain (formation of diester for every repeat unit of PMVE-MA), excess PFOL (mole ratio of PMVE-MA to PFOL is 1:5) was used. The mixture of PMVE-MA and PFOL formed a white slurry, indicating that PMVE-MA was not soluble in the PFOL. After 72 h, the mixture turned into a brown homogeneous solution, demonstrating that the F-*g*-PMVE-MA was soluble in the excess PFOL at elevated temperature. The reaction was continued for 14 days to obtain a fully grafted sample.

The FTIR spectrum (see Supporting Information) obtained using DRIFTS for the starting material PMVE-MA revealed three characteristic peaks in the carbonyl region.[29] Following nucleophilic ring-opening in the presence of fluorinated alcohol (PFOL), the carbonyl region revealed only one distinct peak in a position typical of an ester (1738 cm^{-1}). To determine the degree of grafting in the stabilizer, the ^{1}H NMR spectra (see Supporting Information) for both the starting material PFOL and the ring-opened stabilizer product F-*g*-PMVE-MA were obtained in an octafluorotoluene/$CDCl_3$ (50/50, v/v) mixture. The ^{1}H NMR spectrum (see Supporting Information) for the starting material PMVE-MA was obtained in deuterated acetone. The integration of the peak at 4.5 ppm for the $OC\mathbf{H}_2$ in the fluorinated graft chains is 100 (two protons). The total integration of peaks in the range of 4.0−3.0 ppm for $C\mathbf{H}$ (two protons) in the ring, $C\mathbf{H}$ (one proton) linked to $OC\mathbf{H}_3$ in the backbone, and $C\mathbf{H}_3$ (three protons) is 151 (a total of six protons). Therefore, the graft degree of F-*g*-PMVE-MA is

$$\text{graft degree} = \frac{100/2}{151/6} = 1.99$$

The molecular weight of F-*g*-PMVE-MA was estimated as ca. 400 kg/mol, based on the M_n of PMVE-MA (79.8 kg/mol) and the degree of grafting (1.99) for F-*g*-PMVE-MA.

If there is a partially grafted one-arm structure in F-*g*-PMVE-MA, carboxylic acid end groups should exist in the polymer chain. However, ^{13}C NMR analysis (see Supporting Information) of the product F-*g*-PMVE-MA failed to detect the presence of a carboxylic acid group in the polymer chain at 175 and 177 ppm, which are characteristic for carboxylic acid groups. Moreover, ^{19}F NMR (see Supporting Information) was also performed for F-*g*-PMVE-MA product and the starting material PFOL; typical broader peaks were observed for F-*g*-PMVE-MA copolymer. However, it is impossible to obtain the graft degree from the ^{19}F NMR spectrum of F-*g*-PMVE-MA because there are no other characteristic fluorine atoms in the product apart from the fluorinated graft chain.

The solubility of F-*g*-PMVE-MA in a mixture of VDF and CO_2 was examined in a 100 mL cylindrically shaped view cell. The stabilizer was found to be miscible in pure scCO_2, VDF, and a mixture of VDF/scCO_2 at the reaction conditions (5 wt % of F-*g*-PMVE-MA relative to VDF monomer, 55 °C, 4000 psi (27.2 MPa)).

b. Dispersion Polymerization of VDF in scCO_2 in the Presence of F-*g*-PMVE-MA. Observations in View Cell. The polymerizations of VDF in the presence and absence of F-*g*-PMVE-MA were observed in the view cell. The reactions started as a single phase. In the absence of stabilizers, the system became heterogeneous, and precipitated polymer particles were observed immediately after the injection of the initiator solution.[27] By contrast, in the presence of F-*g*-PMVE-MA, a stable milky emulsion formed after the initiator solution was charged, and after 30 min polymer particles were observed. This suggests that F-*g*-PMVE-MA acts as a stabilizer in the polymerization of VDF in scCO_2. F-*g*-PMVE-MA showed better stabilization than PDMS-ma; the latter kept the PVDF emulsion stable for ca. 15 min.[27]

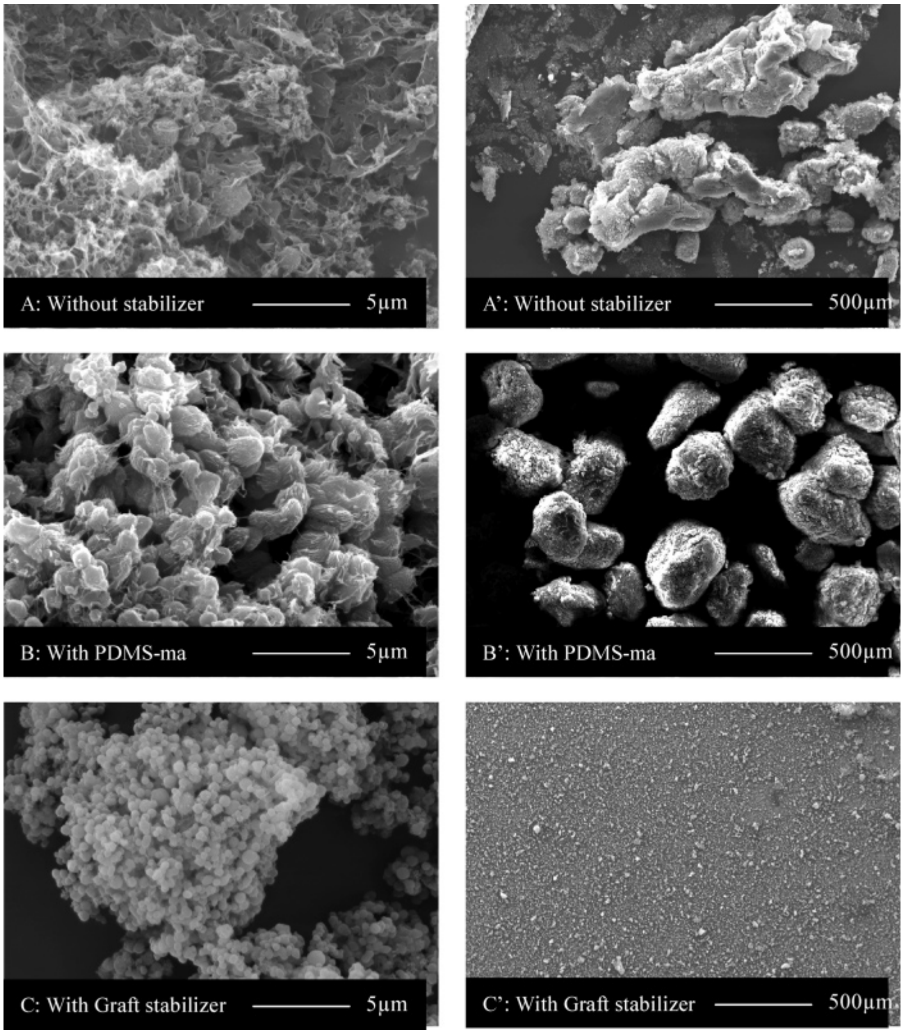

Figure 2. Effect of fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) (F-*g*-PMVE-MA) stabilizer on polymer morphology. Images A, B, and C were obtained at a high magnification (×4000). Images A′, B′, and C′ were obtained at a low magnification (×50) for three PVDF samples A, B, and C, respectively. These three samples were produced at the high monomer concentration (9.8 M) in $scCO_2$ with 0.6 wt % of poly(dimethylsiloxane) monomethylacrylate (B, B′, entry 8 in Table 1) or F-*g*-PMVE-MA (C, C′, entry 6 in Table 1) or without any stabilizers (A, A′, entry 5 in Table 1). A clear effect of stabilizer was observed.

c. Effect of F-*g*-PMVE-MA on Molecular Weight and Morphology of the Polymer. Monomer concentration is a key factor for VDF polymerization in $scCO_2$; it has strong effect on both molecular weight and the morphology of the PVDF product.[27] With increasing monomer concentration, the molecular weight of products increased (entries 1 and 5 in Table 1). A small amount of F-*g*-PMVE-MA stabilizer (0.6 wt % with respect to VDF monomer) led to high molecular weight PVDF at both low (entry 2 in Table 1) and high monomer concentration (entry 6 in Table 1). These products have much higher molecular weight compared to the products made without stabilizer present (entries 1 and 5 in Table 1). However, increasing the amount of F-*g*-PMVE-MA (2 wt %) did not increase the molecular weight (entries 3 and 7 in Table 1) as was demonstrated with PDMS-ma.[27] By contrast, the molecular weight decreased. This is likely a result of the chain transfer to F-*g*-PMVE-MA during the polymerization. This indicates that F-*g*-PMVE-MA acts as both stabilizer and chain transfer agent during VDF polymerizations.

As described in the Experimental Section, the experiments were terminated when the pressure inside the autoclave fell by 300 psi. This was to keep the final product content in the autoclave constant at ca. 33 g/L. Observations in the view cell indicated that the autoclave was full of polymer above this point because of the very low apparent density of the polymer, which in turn leads to an ineffective agitation in the autoclave.[30] Monomer conversions for the experiments conducted at low monomer concentration (entries 1−3) were terminated at ca. 15 wt %; at high monomer concentrations (entries 5−8), the monomer conversions were terminated at ca. 5 wt %. To study the effect of monomer conversion on the molecular weight and morphology of the PVDF product, the polymerization (entry 4 in Table 1) was carried out at the same reaction conditions as the experiment entry 2 in Table 1 and then terminated at a monomer conversion ca. 5 wt %. The results indicate that the polymer obtained at low monomer conversion (5 wt %) has slightly higher molecular weight and better morphology than that obtained at high monomer conversion (15 wt %). The reduction of the monomer concentration as the polymerization proceeds could explain the decrease of the molecular weight with increasing monomer conversion. The slight loss of morphology at high monomer conversion might be due to the limitation of the stabilization. The results for entries 4 and 6 (carried out at different monomer concentrations, terminated at the same monomer conversion 5 wt %) indicate that a high monomer concentration leads to a higher molecular weight product with very well-defined particles (C in Figure 2). To further investigate the effect of monomer conversion on the molecular weight and morphology of PVDF product, an experiment (entry 9) using the same conditions as entry 6 was carried out but terminated at a higher monomer conversion, obtaining a higher solid content in the autoclave (89 g/L). The morphology of the product obtained was a mixture of particles and agglomerated material. This indicated that, with monomer conversion increasing, the stabilization of F-*g*-PMVE-MA was not sufficient to prevent primary particles from aggregating. This may be due to the increased surface area of polymer as polymerizations progress, leading to a shortage of F-*g*-PMVE-MA to stabilize the polymer. If this explanation is correct, then increasing stabilizer concentration should solve the problem. An experiment (entry 10) was carried out using 5 wt % F-*g*-PMVE-MA. Not surprisingly, a good morphology polymer was obtained at the monomer conversion of 14.2 wt %; i.e., the solid content in the autoclave is 89 g/L.

Comparative experiments (entries 5 and 8 in Table 1) in the absence and presence of PDMS-ma stabilizer were carried out under the same reaction conditions as for experiment entry 6. In the absence of stabilizer, no primary particles were observed (A in Figure 2), and the PVDF polymer was only obtained as a spongy solid (A′ in Figure 2). When using PDMS-ma as the stabilizer, the primary particles were aggregated and formed large particles (diameter ca. 200−500 μm) (B and B′ in Figure 2). By contrast, using the graft stabilizer F-*g*-PMVE-MA, the primary particles (diameter ca. 200−500 nm) were found to have a well-defined spherical morphology (C in Figure 2) and did not aggregate significantly (C′ in Figure 2).

Conclusions. A high molecular weight product with well-defined and uniform spherical particles (diameter at 200−500 nm) has been obtained for the first time by dispersion polymerization of VDF in $scCO_2$ using a fluorinated graft copolymer F-*g*-PMVE-MA as the stabilizer. Further results detailing our investigation into the effect of stabilizer architecture for this type of graft stabilizer, including the addition of fluorinated graft chains with different chain lengths, varying the degree of graft chain incorporation, and the use of a longer polymer backbone, will be reported shortly.

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Supporting Information Available: DRIFTS IR spectra of PMVE-MA and F-*g*-PMVE-MA, ^{1}H NMR spectra of F-*g*-PMVE-MA, PMVE-MA, and PFOL, ^{19}F NMR spectra of F-*g*-PMVE-MA and PFOL, ^{13}C NMR spectra of F-*g*-PMVE-MA, PMVE-MA, and PMVE-MA acid, and scheme of experimental setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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