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Notes

Dispersion Polymerizations of Methyl Methacrylate in Supercritical Carbon Dioxide with a Novel Ester End-Capped Perfluoropolyether Stabilizer

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Introduction

There is an increasing pressure to replace conventional solvents with more environmentally benign systems. For this reason, $scCO_2$ has been studied extensively as a polymerization medium because it is cheap and nontoxic. It also has an easily accessible critical point and tunable solvating properties.[1−3] However, $scCO_2$ is a poor solvent for most polymers. To utilize it as an alternative solvent for polymerization, an effective stabilizer is necessary to disperse the growing polymer chains in the reaction system. DeSimone et al. reported the first dispersion polymerization of methyl methacrylate in $scCO_2$ by using a highly $scCO_2$ soluble amorphous fluorinated polymer (poly(dihydroperfluorooctyl acrylate) pFOA) as a stabilizer.[4] Since then, a number of other stabilizer architectures based on block and graft copolymer fluorinated materials have been described.[5−10] A reactive macromonomer system has also been reported, based upon poly(dimethylsiloxane) monomethacrylate (PDMS) which acts a stabilizer while becoming incorporated in the growing polymer.[5,11,12] The drawback to the use of such materials is that they are necessarily incorporated into the final product.

We recently reported the use of a different system, a carboxylic acid-terminated perfluoropolyether, as stabilizer for the dispersion polymerization of methyl methacrylate in $scCO_2$.[13,14] This stabilizer was anchored to the growing polymer particles through a hydrogen bond between the terminal acid functionality of the stabilizer and the ester grouping of MMA, leading to a pseudo-graft copolymer. FTIR evidence confirmed the existence of a hydrogen bond. In this paper, we report the dispersion polymerization of MMA in $scCO_2$ in the presence of a well-defined ester end-capped perfluoropolyether, which was synthesized by the reaction of acid terminated perfluoropolyether with butanol. Surprisingly, although it has only a very short polymerphilic chain, this is sufficient to enable dispersion polymerization of MMA in $scCO_2$.

Experimental Section

Materials. The acid-terminated perfluoropolyether (Krytox 157FSL, $M_n = 2500$, Dupont), nonfunctionalized perfluoropolyether (Fomblin Y25, $M_n = 3200$, Ausimont), methyl methacrylate (inhibited with 2 ppm of Topanol, ICI), 1-butanol (anhydrous, 99.8%, Aldrich), and high-purity carbon dioxide (SFC grade, BOC Gases) were used as received. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, 98%, Acros) was purified through recrystallization.

Synthesis of Ester End-Capped Perfluoropolyether. Acid-terminated perfluoropolyether (7 g) was added into a molar excess of 1-butanol (1 g) in a 25 mL round-bottomed flask and then sealed under nitrogen flow (acid-terminated perfluoropolyether to 1-butanol; molar ratio = 1:5). The reaction mixture was kept at a temperature 75 °C for 24 h. After reaction, excess 1-butanol was removed under vacuum at the same temperature. A transparent viscous liquid was obtained and characterized by NMR and FTIR.

The ^1H NMR spectra for both the acid-terminated perfluoropolyether and 1-butanol and the final perfluoropolyether ester product were obtained in $CDCl_3$ (Figure 1). The ^1H NMR spectrum of the starting reaction mixture revealed five peaks that are as follows: a, 3.5 (2H); e, 2.4 (1H); b, 1.5 (2H); c, 1.3 (2H); d, 0.9 (3H). Among them, the peak at 2.4 (e: 1H) is assigned to the OH group of 1-butanol. The proton signal for the COOH group of carboxylic acid-terminated perfluoropolyether does not appear in this spectrum, presumably because H-bonding and exchange processes broaden the peak. After 24 h reaction time and subsequent removal of the residual 1-butanol under vacuum, the peak at 2.4 (e, 1H) totally disappears in the ^1H NMR spectrum of the final product. Calculating the integration ratio confirmed that the final product was indeed the perfluoropolyether ester. Additional evidence for the reaction between carboxylic acid-terminated perfluoropolyether and 1-butanol is provided by FTIR spectroscopy (see Supporting Information). A thin film of the pure carboxylic acid-terminated perfluoropolyether shows a broad peak at 3139 cm^{-1} for the functional group −CO(OH) and another at 1773 cm^{-1} for the ν(CO). The FTIR spectrum of the butyl ester product is very different with no feature at 3139 cm^{-1} and a clear shift in the ν(CO) to 1783 cm^{-1}, which is indicative of ester formation.[15]

Dispersion Polymerization. Polymerizations were performed in a 60 mL stainless steel autoclave equipped with a magnetically coupled overhead stirrer. In a typical polymerization, the autoclave was charged with reactants (10 g of MMA, 0.1 g of AIBN, 0.1 g of Krytox butyl ester) and then pressurized to 3200 psi with high grade N_2. This procedure was designed to leak test the equipment and to degas the reaction system. Following careful release of the N_2, the autoclave was then filled with CO_2, stirred, and heated to the desired reaction temperature (65 °C) using a preheated thermocouple controlled aluminum block. Once the desired reaction temperature was reached, the desired working pressure (3500 psi) was attained with additional CO_2 as required. The stirring rate was kept at very low rate (20 rpm/min) throughout the reaction. The reaction was allowed to proceed for 4 h, after which the heating was stopped and the reaction system allowed to cool to room temperature (ca. 30 min). The pressure was then slowly released to atmospheric, and the polymeric product was recovered as a dry white powder which was then characterized (Table 1, entry 1).

Polymer Characterization. The monomer conversion was measured gravimetrically. Molecular weight data were obtained by gel permeation chromatography with two PLgel 5 μm Mixed-D columns (Polymer Laboratories, M_w range 200−

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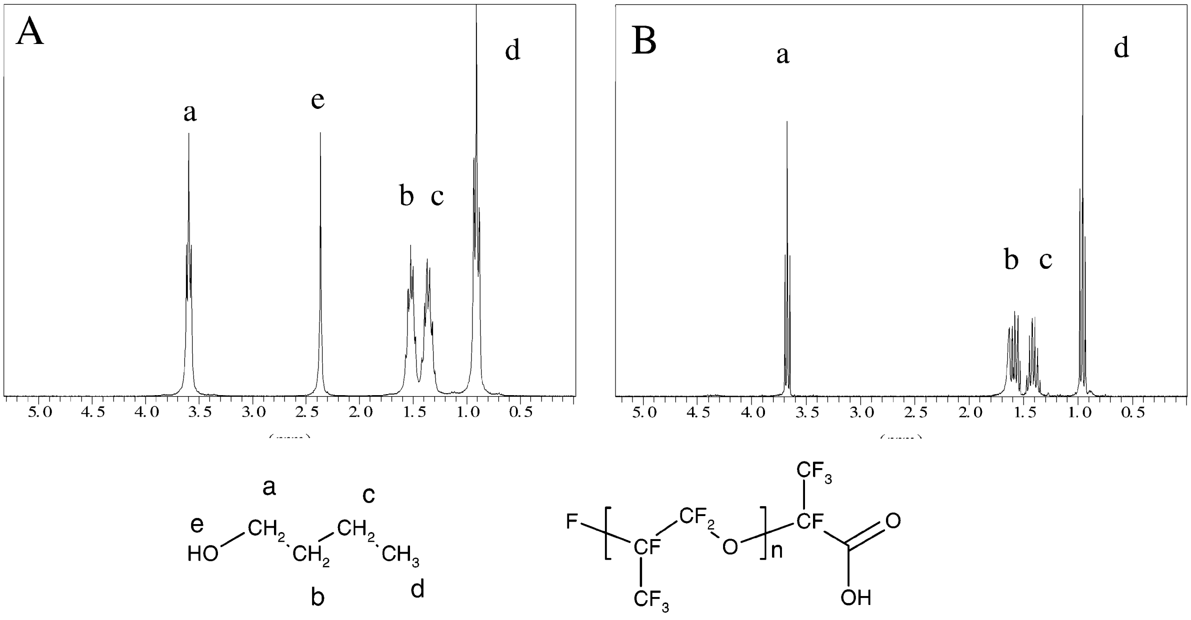

No detectable Hydrogen peak for -COOH group

Figure 1. ^{1}H NMR spectrum for (A) mixture of Krytox 157FSL and 1-butanol before the reaction and (B) the new butyl ester stabilizer synthesized through the reaction between Krytox 157FSL and 1-butanol.

Table 1. Material Produced by the Polymerization of Methyl Methacrylate in scCO$_2$

entry	Krytox butyl ester (%)[a]	Fomblin Y25 (%)[a]	yield (%)	M_n[b]	M_w[b]	PDI[b]	sample description[c]
1	1.0		95	175 000	263 000	1.5	white fine powder
2	0.5		91	184 000	277 000	1.5	white fine powder
3		5	23	9 100	21 000	2.3	viscous liquid
4	0		29	17 000	45 900	2.7	viscous liquid

[a] With respect to monomer. [b] Measured using GPC relative to PMMA standards. [c] Appearance straight from autoclave.

400 000) and an evaporative light scattering detector (Polymer Laboratories) using chloroform as the solvent at 50 °C. Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 mL min^{-1}. Scanning electron microscopy (SEM) data were collected using a JEOL 6400. Samples were mounted on an aluminum stub using an adhesive carbon tab and were coated with gold. ^{1}H NMR data were collected on a Bruker 300 MHz spectrometer. Infrared data were collected on a Nicolet 730 using OMNIC software. The samples were prepared as thin liquid films on calcium fluoride disks and mounted in transmission mode in the FTIR spectrometer.

Results and Discussion

The solubility of the stabilizer was observed in both pure scCO$_2$ and an MMA/scCO$_2$ mixture that corresponded to our reaction conditions. Using a miniature view cell,[16−18] a small sample of the stabilizer (corresponding to ca. 5 wt % with respect to MMA) was placed in the preheated cell, and CO$_2$ was added. We observed that the stabilizer was totally dissolved under the conditions of our polymerization experiments. Thus, we are confident that all reactions were in a single phase at the start of the polymerization.

Dispersion polymerization reactions were conducted with 10 g of monomer at concentrations of 1 wt % stabilizer (with respect to monomer) and 1 wt % AIBN (with respect to monomer) in a 60 mL autoclave. After depressurization, the reactions were found to have produced high yields (95%) of PMMA powder with M_w 263 kDa and polydispersity 1.5 (entry 1 in Table 1). SEM analysis of the material showed discrete particles of 2.5 μm in diameter with narrow particle size distribution of 1.05 (Figure 2a). In further experiments, a lower concentration of stabilizer (0.5 wt %) was still able to effectively stabilize the polymerization of MMA in high yields (91%) with M_w 277 kDa and a polydispersity of 1.5 (entry 2 in Table 1). Analysis by SEM (Figure 2b) showed that the material consisted of particles although the final product was partially flocculated at this lower level. Analysis by ^{19}F NMR indicated no detectable residue of stabilizer in any of the PMMA product. Additional experiments were performed to collect and analyze the contents of scCO$_2$ as it vents from the autoclave. This was achieved by venting the scCO$_2$ into CHCl$_3$ to collect any dissolved material that was carried from the autoclave. These demonstrated that the major proportion of the perfluoropolyether material is removed from the autoclave at the end of the experiment. Thus, in these experiments an in-situ scCO$_2$ extraction is performed at the end of each reaction which removes the stabilizer. Clearly, some stabilizer must be left within the autoclave, and within the polymer product, but these residues are at a very low level.

Clearly, it is also necessary to eliminate the possibility that the perfluoropolyether ester is simply being hydrolyzed in situ back to the carboxylic acid and butanol, as the carboxylic acid is itself a highly effective stabilizer.[13,14] ScCO$_2$ can support a low concentration of water that could lead to conditions for acid hydrolysis by formation of carbonic acid.[19] To eliminate this possibility, we have exhaustively tested the stability of perfluoropolyether ester to hydrolysis in scCO$_2$. This was achieved by adding the ester to the autoclave along

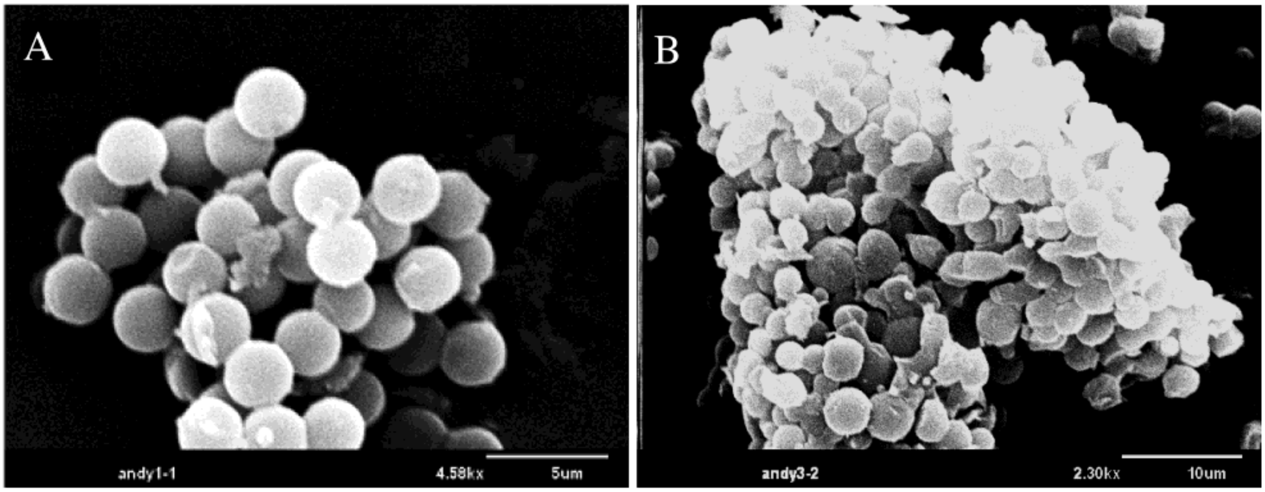

Figure 2. SEM images of PMMA prepared with the Krytox butyl ester: (A) 1 wt % with respect to MMA; (B) 0.5 wt % with respect to MMA.

with water (1% with respect to MMA) and $scCO_2$ (3500 psi, 65 °C) for a period of 4 h to match the conditions found in the polymerization reactions. Clearly, this level of water is substantially greater than one might normally find in $scCO_2$. After venting the contents and collecting the perfluoropolyether, FTIR data demonstrated no observable shift in the ν(CO) band, thus confirming that there was no evidence that hydrolysis of the ester to acid had occurred (see Supporting Information). This process was repeated on three separate occasions to confirm the stability of the ester under these conditions.

Steric stabilization usually involves an amphiphilic graft or block copolymer that is adsorbed as a layer on the surface of the growing polymer particle. This layer is partially solvated by the continuous phase and prevents the polymer particles from coalescing. Most steric stabilizers consist of two components—one soluble and one insoluble in the continuous phase. The insoluble component, or anchor group, associates with the dispersed polymer phase. The main criteria for the soluble component of the stabilizer are that it should be freely soluble in the continuous phase and also sufficiently bulky to promote steric stabilization. An effective stabilizer must have the correct balance of soluble and insoluble components (i.e., a good “anchor-to-soluble ratio”). It is clear that the perfluoropolyether ester stabilizer described in this work will interact with the polymer particles through a weak van der Waals interaction. This association is likely to be much weaker than that of the hydrogen bonding found in the Krytox acid and the covalent bonding present in the use of the PDMS−MMA macromonomer. However, the interaction is clearly capable of providing sufficient anchoring to ensure a stable dispersion in $scCO_2$. Additional proof that there must be an anchoring interaction comes from comparison with a very similar, but nonfunctionalized, perfluoropolyether, Fomblin Y25 (Ausimont). In this case in the absence of the functional headgroup, no stabilized polymerization was observed. Even at very high concentrations of Fomblin Y25 (5 wt %), no particles of PMMA were produced, and the yield and quality of polymer were poor (entry 3 in Table 1). This result is very similar to that obtained in the complete absence of any stabilizer (entry 4 in Table 1).

Conclusions

A novel and simple ester end-capped perfluoropolyether has been synthesized by the reaction of acid-terminated perfluoropolyether (Krytox 157FSL) with 1-butanol. It is an effective stabilizer for the free radical polymerization of methyl methacrylate in $scCO_2$. Control experiments with this stabilizer demonstrate that this very short polymer-philic chain is sufficient for the stabilization of the polymerization reaction. The residual levels of stabilizer in the PMMA product are very low, primarily because there is weak affinity between the PMMA polymer chain and the stabilizer.

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Supporting Information Available: FTIR spectra of thin films of perfluoropolyethers. This material is available free of charge via the Internet at http://pubs.acs.org.

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