Dispersion Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide with a Monofunctional Pseudo-Graft Stabilizer

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Introduction. The use of supercritical carbon dioxide ($scCO_2$) as a reaction medium has seen rapid growth in recent years, primarily driven by the need to develop environmentally acceptable alternatives to conventional organic solvents.[1,2] Polymerization studies began in the early 1960s with the preparation poly(isobutene) in liquid CO_2.[3] More recent work using $scCO_2$ began with a seminal paper by DeSimone describing homogeneous free radical polymerization of fluoropolymers,[4] and recently this field has been reviewed extensively.[5]

One major drawback in the use of $scCO_2$ as a solvent for polymerization is that while it is a good solvent for many monomer and initiator systems, it is a poor solvent for most hydrocarbon polymers.[6] Dispersion polymerization techniques[7] have now been developed by several groups, leading to improved molecular weights and yields, while also facilitating some control of polymer morphology. To perform these polymerizations, stabilizers were developed which are effective in $scCO_2$. The successful stabilizers for dispersion polymerization in $scCO_2$ have been block copolymers which incorporate either a siloxane [e.g., poly(dimethylsiloxane), PDMS] or a fluorinated [e.g., poly(fluorooctyl acrylate), PFOA] as the $scCO_2$ soluble segment: described as "CO_2-philic".[7] Such stabilizers have been shown to act effectively for polymerization of both methyl methacrylate and styrene[5,8,9,10] in which the polymer is insoluble in $scCO_2$ but the monomer is soluble. Others have shown that fluorinated graft copolymer systems are effective.[11] In each case, it is interaction of the stabilizer with the growing polymer particle through van der Waals' forces or dipolar interactions which leads to effective stabilization. However, synthesis of the most effective stabilizers can be complex, and may not be economically viable. An alternative strategy has been the use of commercially available siloxane-based macromonomers, which also work well[12] but result in incorporation of the siloxane into the polymer product by co-polymerization or chemical grafting.

An alternative strategy, in conventional solvents, has been the use monofunctional carboxylic acid stabilizers such as stearic and oleic acids as single-point anchoring stabilizers. In the presence of an additional basic comonomer (e.g., dimethylaminoethyl methacrylate) such stabilizers allowed preparation of dilute latexes of copolymers of methyl methacrylate (MMA) and dimethylaminoethyl methacrylate, but only at lower temperatures (20 °C).[13] In this example, the basic comonomer is required as an integral part of the growing PMMA polymer and acts as a hook for the monofunctional carboxylic acid stabilizer. Thus, the anchoring interaction is a hydrogen bond between the acid stabilizer and the additional basic comonomer in the growing PMMA polymer.

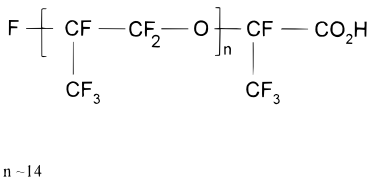

Figure 1. Krytox 157 FSL carboxylic acid terminated perfluoropolyether (M_n 2500 Da).

We have explored the use of similar single-point anchoring stabilizers in the free radical dispersion polymerization of MMA in supercritical carbon dioxide ($scCO_2$). Our aim has been to develop stabilizers in which an additional basic comonomer is not required. In this paper, we report the successful polymerization of MMA in $scCO_2$, in the presence of Krytox 157FSL, a commercially available carboxylic acid terminated perfluoropolyether (Figure 1). The key to our approach has been the use of infrared spectroscopy to demonstrate an interaction between the terminal acid group of the stabilizer with MMA, and hence with PMMA. Such an interaction dispenses with the need for addition of a basic comonomer and results in product PMMA in which there are no detectable stabilizer residues.

Experimental Section. Polymerization reactions were performed in a 60 mL stainless steel autoclave (NWA GmbH) equipped with a magnetic stir bar, thermocouple (RS Components), and pressure transducer (RDP Electronics Ltd.). AIBN (BDH Ltd.) was recrystallized before use and assessed by ^1H NMR spectroscopy. Methyl methacrylate (ICI, inhibited with 3 ppm of troponone), Galden HT55 (nominal M_n 2000 Da) (Ausimont) and Krytox 157FSL (nominal M_n 2500 Da) (DuPont), were used as received. The autoclave was charged with monomer, initiator and stabilizer and sealed. A pressure of ca. 150 atm of nitrogen was added to confirm effective sealing of the autoclave. The nitrogen pressure was then slowly released, and liquid carbon dioxide (BOC Gases, High Purity SFC Grade) (dried over molecular sieve) added from a Lee Scientific 501 syringe pump. This solution was then stirred at room temperature until a constant pressure was reached. The cell was then placed in a preheated block and temperature and pressure allowed to rise to the required experimental conditions, typically 70 °C and 170 atm. The duration of the experiments was typically 4 h. After each polymerization reaction, the autoclave was carefully cleaned with a combination of conventional liquid solvents and $scCO_2$ extraction to ensure that no residues of fluorinated stabilizer remained. Yields of PMMA were determined gravimetrically.

Molecular weight data were obtained by gel permeation chromatography with chloroform as the solvent (Aldrich) at 30 °C using Polymer Laboratories Plgel 5 μm Mixed-D columns and a refractive index detector.

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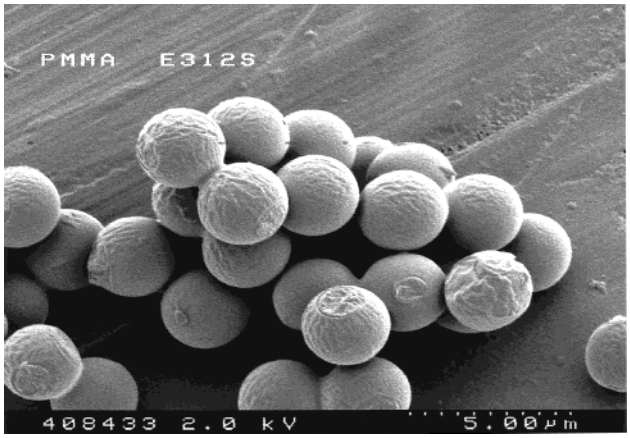

Figure 2. SEM images of PMMA particles prepared with Krytox 157FSL (1 wt % wrt MMA).

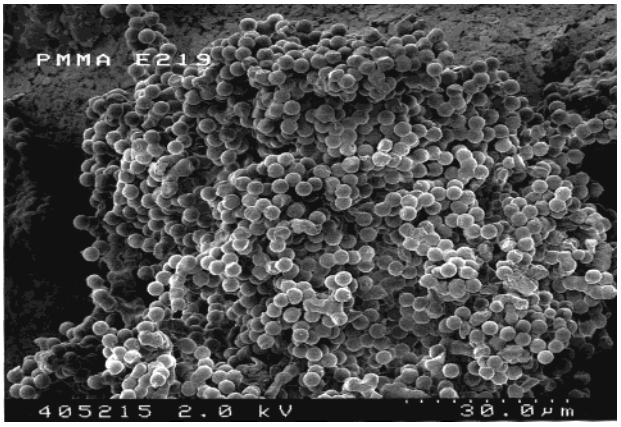

Figure 3. SEM images of PMMA particles prepared with Krytox 157FSL (0.1 wt % wrt MMA).

Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1.0 mL min^{-1}. Scanning electron microscopy (SEM) data were collected using a JEOL 6400 SEM. Samples were mounted on an aluminum stub using an adhesive carbon tab and were gold-coated. ^1H NMR data were collected using a Bruker 300 MHz spectrometer.

FT-IR data were collected with a Nicolet 730 spectrometer using OMNIC software. The samples were presented as thin liquid films of MMA, Krytox 157FSL and various mixtures on calcium fluoride disks and mounted in transmission mode in the FT-IR spectrometer.

Results. Dispersion polymerization reactions were conducted with 10 g of monomer at concentrations of 1 wt % Krytox (wrt monomer) and 1 wt % AIBN (wrt monomer) in the 60 mL autoclave. After depressurization, the reactions were found to have produced high yields (>95%) of PMMA powder with M_w 151 kD and polydispersity 2.5. SEM analysis of the material showed discrete particles of 2.5 μm in diameter with narrow particle size distribution of 1.1 (determined from 125 particles) (Figure 2). These are typical of the particles obtained from stabilized dispersion polymerization. In further experiments, much lower concentrations of Krytox were found to stabilize the dispersion polymerization of MMA. Concentrations of Krytox at 0.1 wt % resulted in high yields of white PMMA powder (93%) with M_w 112 kD and a polydispersity of 2.8. Analysis by SEM (Figure 3) again showed that the material consisted of particles, with diameter ~2.9 μm and narrow size distribution.

In both cases, ^1H NMR analysis of PMMA powder samples obtained directly from the autoclave showed minimal contamination by monomer (<0.9% w/w). Analysis by ^{19}F NMR indicated a detectable residue of Krytox of the order of less than 10% of the initial amount of stabilizer added to the polymerization reaction. However, on-line extraction with $scCO_2$ (300 atm, 50 °C for 3 h) removed this residual Krytox. Indeed, further ^{19}F NMR analysis showed that there was no longer a detectable residue.

Identical polymerization reactions with a very similar, but non-functionalized perfluoropolyether, Galden HT55 (Ausimont M_n 2000 D) were also attempted for comparison. In the absence of the functional headgroup, no stabilized polymerization was observed. Even at very high concentrations of Galden HT55, (20 wt %), no particles of PMMA were produced, and the yield and quality of polymer was poor (25% yield, M_w 58 kD; polydispersity 3.3). In the absence of any stabilizer, the yields of reaction were also very low (ca. 20%) and no particulate material appeared in the predominantly monomeric oil found in the autoclave after 4 h. Further experiments covering a range of different experimental conditions and concentrations will be reported elsewhere.[14]

Clearly the Krytox 157 FSL is acting as a stabilizer, and we propose that it forms a pseudo-graft copolymer with the PMMA during the polymerization. The combination of a CO_2-philic perfluoropolyether tail, and carboxylic headgroup ensures that the stabilizer partitions well between the polymer particle and the CO_2 phase. A hydrogen-bonding interaction between the Krytox acid headgroup and the carbonyl of the ester group on the backbone of the PMMA polymer chain appears to be the most likely interaction.

Evidence for such an interaction is provided by FT-IR spectroscopy. Thin films of mixtures of MMA with Krytox were analyzed by FT-IR spectroscopy (Figure 4). Pure MMA shows only two sharp bands, the carbonyl and vinyl stretching modes in the region 1850−1600 cm^{-1}, while pure Krytox shows only a carbonyl stretching mode in this region. However when mixed, new bands appear, indicating a strong interaction. The carbonyl and vinyl stretching modes of MMA shift down in wavenumber while, at the same time, the carbonyl mode of the acid headgroup of Krytox 157 FSL shifts up in wavenumber. Such spectroscopic shifts are indicative of a hydrogen bonding interaction.[15−17] At much higher concentrations (ca. 50:50 v/v), Krytox and MMA are no longer totally miscible, but the FT-IR spectrum of the Krytox-rich phase clearly shows the presence of the new bands.

If the Krytox is to act as a stabilizer, there must also be similar significant interactions with the growing polymer chains, and one might predict that samples of PMMA would interact with Krytox. PMMA dissolved only sparingly and very slowly in Krytox at room temperature. However on warming to 100 °C, dissolution was more rapid. No such interactions or solubility of PMMA are observed with the very similar nonfunctionalized perfluoropolyether Galden HT55, adding further weight to the argument for a specific functional end group interaction with PMMA.

The use of single-point anchoring monofunctional carboxylic acid stabilizers has been explored previously.

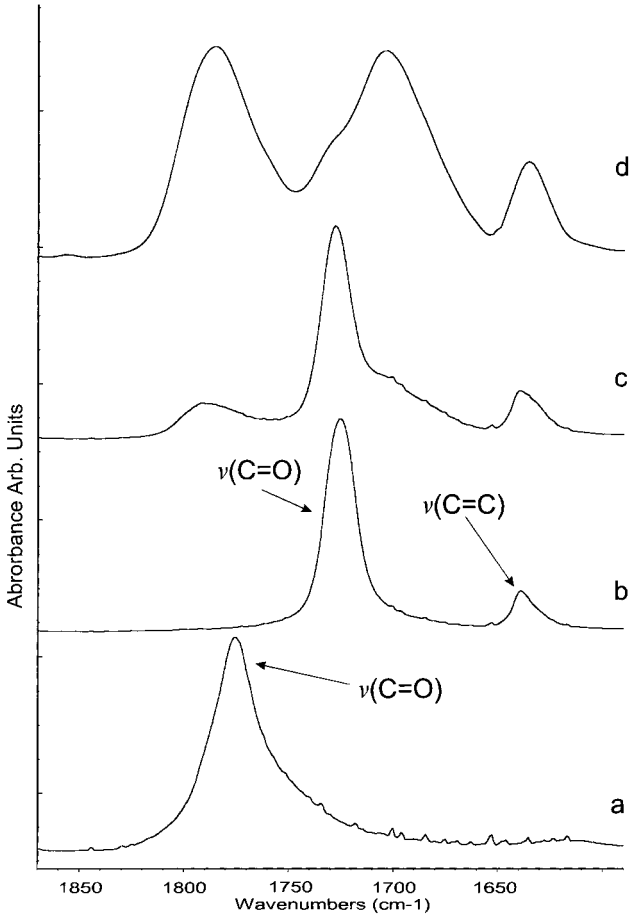

Figure 4. FT-IR spectra of thin films of (a) pure liquid Krytox [ν(C═O), 1775 cm^{-1}] and (b) MMA [ν(C═O), 1725 cm^{-1}; ν(C═C), 1639 cm^{-1}]. (c) FT-IR spectrum showing addition of Krytox 157 FSL (ca 5% v/v) causing new bands to appear in the spectrum of MMA [ν(C═O), 1705 cm^{-1}; ν(C═C), 1623 cm^{-1}]. In addition, a new carbonyl stretching mode appears at higher wavenumber for Krytox [ν(C═O), 1787 cm^{-1}]. (d) Spectrum at much higher concentrations (50:50 v/v), which more clearly reveals the substantial interaction between the carboxylic acid end group and MMA.

However, a basic comonomer was required to induce a stabilizing interaction. Moreover, the system worked only at low temperatures (ca 20 °C)[13] whereas free radical polymerizations are more normally performed at higher temperatures (ca. 70 °C). At these higher temperatures there is a substantial shift in equilibrium away from the acid base interaction.[13] Krytox 157 FSL circumvents both of these drawbacks. It interacts sufficiently with MMA to dispense with the need for a basic comonomer, and as a fluorinated carboxylic acid, it has sufficient acidity to work very effectively at more normal free radical initiation temperatures. Moreover for use of $scCO_2$, the fluorinated tail provides the "CO_2-philic" moiety required to achieve stabilization in this versatile and environmentally acceptable solvent.

Conclusions. Krytox 157FSL is an effective stabilizer for the free radical polymerization of methyl methacrylate in supercritical carbon dioxide. The interaction with PMMA is most likely via a hydrogen bond between the carbonyl of the methacrylate moiety and the terminal acid group of Krytox 157FSL. Control experiments with a nonfunctionalized perfluoropolyether demonstrate that a terminal acid functionality is required for stabilization of the polymerization reaction. The residual levels of Krytox in the PMMA product are very low, primarily because there are very few sites for chain transfer and hence little possibility of grafting to PMMA. Moreover, the Krytox is very easily removed from the PMMA product by supercritical fluid extraction which, on the commercial scale, may be performed in situ. Krytox 157FSL is an attractive stabilizer for dispersion polymerization in $scCO_2$ and brings closer the prospect of a commercially viable process.

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