Novel Graft Stabilizers for the Free Radical Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide

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ABSTRACT: This paper reports the free radical polymerization of methyl methacrylate (MMA) in supercritical carbon dioxide ($scCO_2$) using novel graft copolymer stabilizers. The stabilizers are formed by the thermal ring-opening reaction of poly(methyl vinyl ether-*alt*-maleic anhydride) with 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol (**1**) or 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol (**2**). These stabilizers are effective at low concentrations (0.1−2 wt % with respect to MMA) for the dispersion polymerization of MMA leading to high yields of poly(methyl methacrylate) (PMMA) with reasonable molecular weights, narrow molecular weight distribution, and narrow particle size distribution. The increase of graft chain length by only two carbon units has a substantial effect on the stabilizers' activity.

Introduction

The use of supercritical carbon dioxide ($scCO_2$) as a polymerization medium has increased rapidly over the past 5 years.[1] Carbon dioxide offers a number of advantages over conventional solvents as it is environmentally benign and relatively inexpensive, has tunable physical properties (density and dielectric constant), and leaves no solvent residues, leading to highly pure materials.[2] The polymerization of acrylates is industrially important, and there has been extensive research into the use of $scCO_2$ as a reaction medium. Poly(methyl methacrylate) [PMMA] is insoluble[3] in $scCO_2$, and the addition of a stabilizer is required to form a stable dispersion. The first reported polymerization of methyl methacrylate in $scCO_2$ utilized poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)] homopolymer as the steric stabilizer.[4] Other fluorinated and siloxane polymers and copolymers have also been identified as effective stabilizers for free radical dispersion polymerization[4−9] in $scCO_2$. In addition, poly(dimethylsiloxane) [PDMS] macromonomers have been used extensively in the polymerization of MMA.[10−14] Very recently, a commercially available perfluoropolyether that acts as a monofunctional pseudo-graft stabilizer has also been shown to be very effective.[15]

Another approach is the use of graft copolymers as stabilizers. Again, these require that one section is CO_2-"philic" (usually fluorinated or siloxane based) and the other section is CO_2-"phobic".[16,17] Careful control of the stabilizer properties has again been shown to greatly affect steric stabilizing properties, and the optimum balance must be achieved for effective dispersion.[16]

In this paper, we report preliminary results on the use of alternating maleic anhydride copolymers as stabilizers for polymerization of MMA in $scCO_2$. The stabilizers were prepared by thermal ring-opening reaction with a perfluoro alcohol to form a graft copolymer. The effect of varying the stabilizer concentration on the polymerization has been investigated for two different lengths of fluorinated grafts.

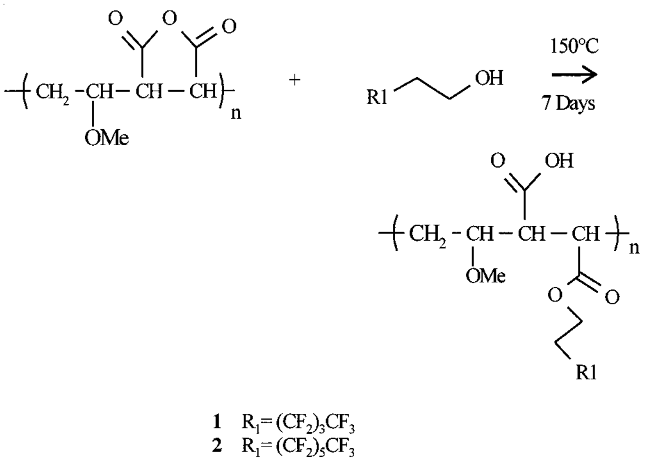

Figure 1. Synthesis of poly(methyl vinyl ether-*alt*-maleic anhydride)-derived stabilizers. Elemental analysis confirms that only the half ester product is formed.

Experimental Section

Materials. Poly(methyl vinyl ether-*alt*-maleic anhydride) ($M_n = 79\,800$) and initiator 2,2′-azobis(isobutyronitrile) [AIBN] [BDH Ltd.], 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol and 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol [Fluorochem Ltd.], and methyl methacrylate [ICI; inhibited with 2 ppm of Topanol (a mixture of hindered amines)] were used as received unless stated otherwise. The stabilizers were synthesized as shown in Figure 1. In a typical synthesis, 0.75 g of poly(methyl vinyl ether-*alt*-maleic anhydride) and 5 g of 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol were weighed into a conventional glass pressure vessel and then sealed. The reaction mixture was then heated to 150 °C for 7 days to give a yellow solution. Excess alcohol was removed under reduced pressure to yield a yellow/orange solid in 60% yield. The solid was analyzed by infrared and NMR spectroscopies.

Polymerization. Polymerizations were performed in a 60 mL stainless steel autoclave (NWA GmbH) equipped with magnetic flea. High-purity carbon dioxide (BOC Gases, SFC grade) was initially passed through a drying column. In a typical polymerization, the autoclave was charged with reac-

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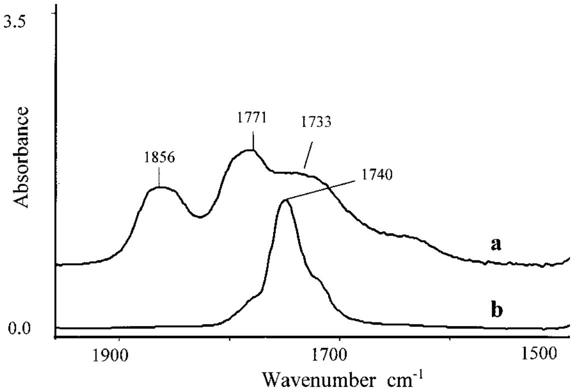

Figure 2. DRIFTS infrared spectra of solid samples: (a) starting material poly(methyl vinyl ether-*alt*-maleic anhydride) with at least three characteristic peaks at 1856, 1771, and 1733 cm^{-1}; (b) stabilizer **1** showing that the peaks at 1856 and 1771 cm^{-1} have completely disappeared, and a new feature now predominates at 1740 cm^{-1}.

tants and then pressurized to ca. 3000 psi with high grade N_2. This procedure was designed to leak test the equipment and to degas the reactants. Following careful release of the N_2, the autoclave was then filled with CO_2, stirred, and heated to the desired reaction temperature using a preheated thermocouple controlled aluminum block. The desired working pressure was attained with additional CO_2 as required. Polymerizations were carried out at ca. 3200 psi and 65 °C for a period of 4 h to provide a comparison with previously published polymerization studies. The yields of PMMA were determined gravimetrically.

Characterization. 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 refractive index detector. 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 SEM. Samples were mounted on an aluminum stub using an adhesive carbon tab and were gold-coated. The ^{13}C NMR data were collected using a Bruker 300 MHz spectrometer. Infrared data were collected on Perkin-Elmer system 2000 FTIR spectrometer equipped with a diffuse reflectance infrared spectroscopy (DRIFTS) attachment [Spectratech].

Results and Discussion

Diffuse reflectance infrared spectroscopy (DRIFTS) was used to obtain FTIR spectra from solid samples of the starting material and the product from the stabilizer synthesis (Figure 2). The FTIR spectrum of poly(vinyl ether-*alt*-maleic anhydride) revealed three characteristic peaks in the carbonyl region. Following thermally activated nucleophilic ring opening in the presence of fluorinated alcohol, the FTIR spectra of the solid samples were very different. The carbonyl region now shows only one distinct peak in a position typical of an ester. These data demonstrate that a majority of maleic anhydride units have undergone thermal ring-opening reaction with the fluorinated alcohol.

The NMR spectra for both the starting material and the ring-opened stabilizer products were obtained in a perfluorotoluene/$CDCl_3$ mixture. The ^1H NMR spectra were not informative; the broad features observed gave little structural data. However, the carbonyl region of ^{13}C NMR spectra (180−160 ppm) was particularly informative. The ^{13}C NMR spectrum of poly(methyl vinyl ether-*alt*-maleic anhydride) shows three broad, but distinct, resonances [173.2, 172.3, and 170.8 ppm].[18] Following the thermal ring-opening reaction in the presence of 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol, the ^{13}C NMR spectrum in the carbonyl region appears very different. Only two broad signals are now observed [173.6 and 172 ppm], and the signals corresponding to the starting material are no longer visible. The ^{13}C NMR spectrum of stabilizer **2** produced by the reaction of poly(vinyl methyl ether-*alt*-maleic anhydride) and 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol shows an almost identical change with two broad resonances appearing at 173.6 and 171.8 ppm. These spectra reinforce our interpretation of the DRIFTS infrared data, indicating that there is near-quantitative conversion of maleic anhydride groups to form the fully grafted ring-opened material.

Elemental analysis of the graft stabilizers confirms substantial incorporation of the fluorinated graft chains, but the results were complicated by small residues of the fluorinated alcohol, which proved difficult to remove completely from these solid materials. To overcome this difficulty and provide an accurate analytical analysis, we repeated the syntheses with a slightly different backbone polymer, poly(maleic anhydride-*alt*-octadecene). Under identical conditions, this backbone polymer yields viscous liquid products that show identical changes in the FTIR and NMR spectra. Excess alcohol was much more easily removed from these viscous liquids, and for these alternative systems the elemental analysis confirmed the quantitative reaction of all the maleic anhydride moieties. Polymerization studies using these alternative materials will be reported elsewhere.[19] Thus, we are confident that the fluorinated stabilizer materials **1** and **2** can reasonably be assumed to be fully grafted, and therefore a direct comparison can be made about their effectiveness as stabilizers for the polymerization of methyl methacrylate.

The solubility of the two stabilizers was observed in both pure $scCO_2$ and an MMA/$scCO_2$ mixture that corresponded to our reaction conditions. Using a miniature view cell,[20] a small sample of each stabilizer (corresponding to ca. 5 wt % with respect to MMA) was placed in the preheated cell, and CO_2 was added. We observed that both stabilizers were totally dissolved under the conditions of our polymerization experiments. Thus, we can be confident that all the reactants are in a single phase at the start of the polymerization.

Free Radical Polymerization of MMA Employing Stabilizer 1 (Perfluorohexanol Based). Initial studies were performed using 10 g of methyl methacrylate, 1% AIBN (by weight with respect to the monomer), and concentrations of stabilizer **1** ranging from 0 to 2%. When no stabilizer is present (Table 1, entry 1), polymerization of MMA leads to PMMA with a low molecular weight and a yield of only 50%, indicating that the polymerization is not stabilized. Similar results were obtained when the polymerization was performed with the addition of 1 wt % of the perfluorinated alcohol, thus indicating that the alcohols themselves show no activity as stabilizers.

By contrast, addition of 0.1 wt % stabilizer **1** produced PMMA in high yield and high molecular weights (Table 1, entry 2). The molecular weight distribution of the material (PDI = 3.1) is slightly broad. SEM images of the polymer indicate an aggregated material (Figure 3a) and strongly suggest that 0.1 wt % of the stabilizer is just insufficient to stabilize the dispersion.

The polymerization was repeated using 1% stabilizer **1** under similar reaction conditions (Table 1, entry 3).

Table 1. Reaction Conditions for the Polymerization of MMA Using Stabilizer 1[a]

entry	wt % AIBN[b]	wt % surfactant[b]	yield (%)	M_n[c]	PDI[b]	particle diameter[d] (μm)	PSD[e]	appearance[f]
1	1		52	25 400	4.06			oil and white solid
2	1	0.1	89	64 600	3.1			white powder
3	1	1	95	107 600	2.5	3.6	1.12	white powder
4	1	2	90	94 200	2.6	3.3		white powder

[a] Reactions were carried out at 3100−3400 psi at 65 °C for 4 h. [b] Percentage weight/weight relative to monomer. [c] Determined by gel permeation chromatography. [d] As determined by SEM. [e] Measured for a minimum of 100 particles. [f] Appearance of the material directly after venting.

Table 2. Reaction Conditions for the Polymerization of MMA Using Stabilizer 2[a]

entry	wt % AIBN[b]	wt % surfactant[b]	yield (%)	M_n[c]	PDI[c]	particle size[d] (μm)	PSD[e]	appearance[f]
1	1		55	37 000	3.1			oil/white solid
2	1	0.1	93	110 400	2.58	2.9	1.07	white powder
3	1	1	98	103 900	2.53	2.6	1.13	white powder
4	1	2	97	173 400	2.10	1.1		white powder

[a] Reactions were carried out at 3100−3400 psi at 65 °C for 4 h. [b] Percentage weight/weight relative to monomer. [c] Determined by gel permeation chromatography. [d] As determined by SEM. [e] Measured for a minimum of 100 particles. [f] Appearance of the material directly after venting.

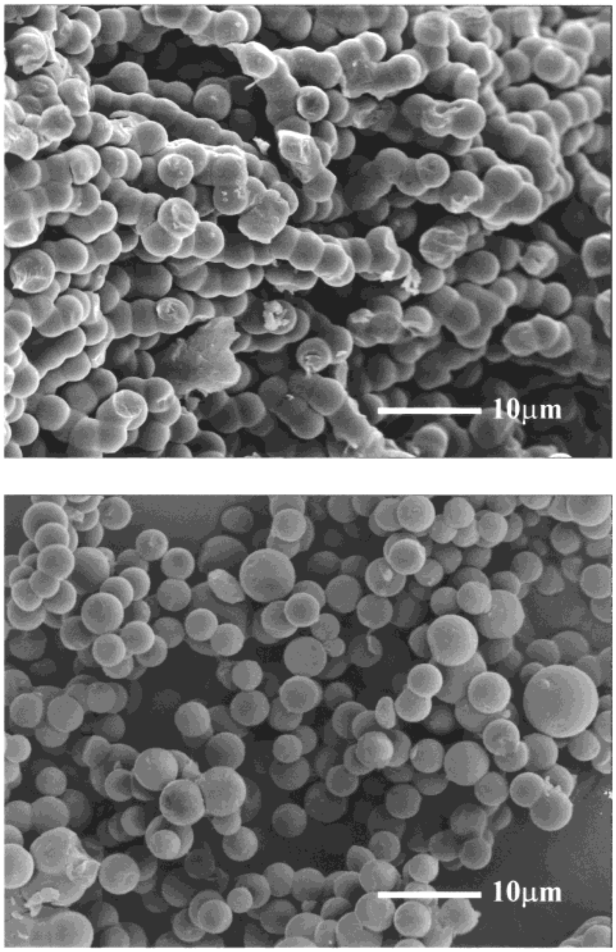

Figure 3. SEM images of PMMA produced using (a, top) 0.1 and (b, bottom) 1 wt % with respect to monomer of stabilizer **1**. Note that at 0.1% with respect to monomer there is insufficient stabilization to produce spherical particles

The molecular weight of the polymer is higher and the PDI is lower, indicating a more controlled polymerization. This is confirmed by the SEM image of the polymer, which shows spherical particles with an average diameter of 3.6 μm (Figure 3b). The particles appear to be slightly aggregated. A further increase in stabilizer concentration to 2 wt % appears to have little effect on the molecular weight or morphology of the resultant material (Table 1, entry 4).

The particles produced using stabilizer **1** show some aggregation at relatively high concentrations (2 wt %), although it is not possible to eliminate the possibility of some aggregation occurring during venting. However, the PMMA is produced in high yield and with acceptable molecular weight. This indicates that perhaps there is insufficient solubility of the stabilizer in the continuous phase, resulting in poor stabilization, or the interplay between the insolubility of the hydrocarbon backbone and the solubility of the fluorinated grafted groups was not sufficiently balanced for effective stabilization. The effect of “anchoring” and “buoy” groups has been studied extensively for the dispersion polymerization of MMA using a series of poly(methyl methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide) stabilizers.[16] These results demonstrated that a careful balance between anchor group size (backbone length) and amount of $scCO_2$ soluble (fluorinated) component is an important factor in achieving adequate stabilization. This earlier work developed and investigated stabilizers with very much shorter backbones (M_n 2500−8000), containing a few (2−16) very long grafts (M_n 2500−7000). By contrast, we have concentrated on much longer backbones (M_n 79 800) in which all possible sites contain a short graft. Thus, we reasoned that only a very small increase in the graft chain length may substantially alter the balance between anchoring and $scCO_2$ solubility. For this reason we substituted the perfluorohexanol-based graft with perfluorooctanol.

Free Radical Polymerization of MMA Employing Stabilizer 2 (Perfluorooctanol Based). The polymerization of methyl methacrylate using 1 wt % AIBN and 0.1 wt % of stabilizer **2** produced PMMA in very high yield and with high molecular weight (Table 2, entry 2). The SEM images of the resulting polymer material showed discrete particles even with this very low concentration of stabilizer (Figure 4a) although some particles did show a “string of pearls” morphology. Increasing the concentration of stabilizer **2** has little effect on yield, but the molecular weight and PDI are moderately improved (Table 2, entries 3 and 4). However, there is a substantial change in morphology, and increasing stabilizer concentration (from 0.1 to 2 wt %) clearly affects particle size (Table 2, entries 2−4). At 2

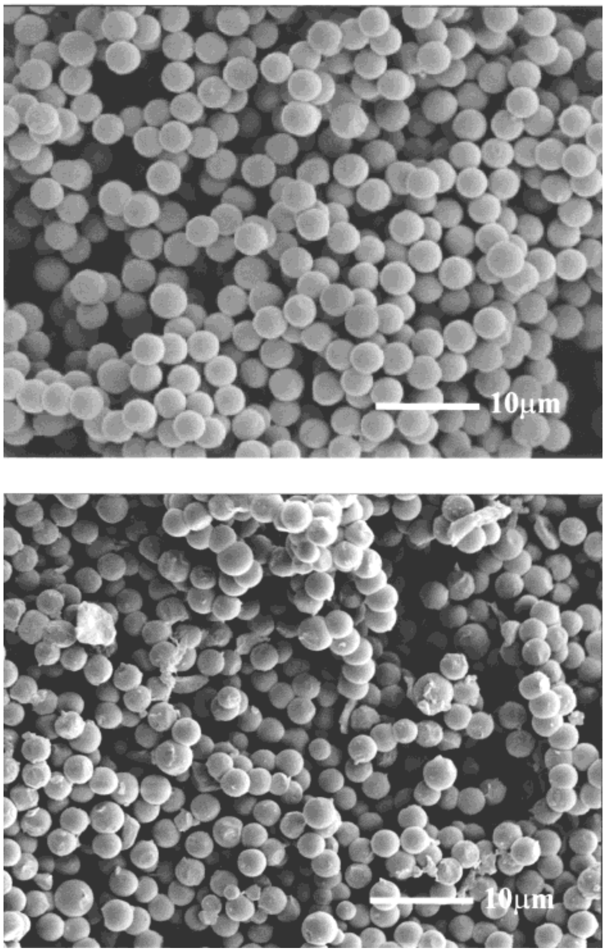

Figure 4. SEM images showing PMMA produced using (a, top) 0.1 and (b, bottom) 1 wt % with respect to monomer of stabilizer **2**. In contrast to stabilizer 1, spherical particles are now produced even at the very low concentration.

wt % the particles are significantly smaller than those obtained under identical conditions using stabilizer **1**.

The increased length of the fluorinated graft chain has clearly improved the effectiveness of the stabilizer and also lead to a *decrease* in the particle size. There is some agreement here with the earlier work of Beckman,[16] who also noted that for their largest backbone (M_n 8000) a trend of decrease in particle size to increased graft length is observed.

FTIR studies in $scCO_2$ indicate that the anchoring of this stabilizer is via hydrogen bonding between the carbonyl group of methyl methacrylate and carboxylic acid groups on the stabilizer **1** or **2**. It is this interaction that stabilizes the growing polymer chain and allows the formation of particles at low stabilizer concentrations. Similar results were obtained with an alternative stabilizer system containing carboxylic acid moieties.[15]

Conclusions

Stabilizers **1** and **2** are highly effective for dispersion polymerization of methyl methacrylate in supercritical carbon dioxide. Both stabilizers have been synthesized with near-quantitative incorporation of the fluorinated side chain to form fully grafted materials. Stabilizer **2** has a fluorinated graft that is only two carbon units longer but is found to be substantially more efficient as a stabilizer, working at lower concentration and producing smaller particles. Further results detailing our investigation into the addition of other graft chains, varying the level of graft chain incorporation, and use of longer and shorter polymer backbones will be reported shortly.[19]

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Supporting Information Available: The ^{13}C NMR spectra (carbonyl region) for (a) poly(methyl vinyl ether-*alt*-MA), (b) stabilizer **1**, and (c) stabilizer **2** in $CDCl_3$/perfluorotoluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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