Fluorinated Graft Stabilizers for Polymerization in Supercritical Carbon Dioxide: The Effect of Stabilizer Architecture

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Received August 3, 2000; Revised Manuscript Received October 31, 2000

ABSTRACT: We describe the synthesis of new stabilizers for the free radical polymerization of methyl methacrylate in supercritical carbon dioxide. The stabilizers are based on commercially available copolymers containing maleic anhydride moieties. The maleic anhydride moieties undergo thermal ring opening in the presence of a fluorinated alcohol to form graft copolymers containing pendant fluorinated chains and carboxylic acid groups. We have investigated different polymer backbones to fabricate a range of materials that have been tested in $scCO_2$ for their effectiveness as stabilizers. FTIR analysis indicates that the mode of stabilization is through an interaction between the carbonyl group of monomer (methyl methacrylate) and the carboxylic acid group of the stabilizer. Our results confirm that the correct choice of stabilizer backbone and fluorinated chain length leads to effective stabilization and production of poly(methyl methacrylate) in high yield, with an acceptable molecular weight, and with spherical particle morphology even at very low stabilizer concentrations (ca. 0.1 wt % with respect to monomer). The balance between the length of the grafted chain and hydrocarbon content of the polymer backbone is found to be particularly important.

Introduction

Supercritical carbon dioxide ($scCO_2$) shows great potential as a replacement for conventional organic solvents.[1,2] It is environmentally benign, nonflammable, and nontoxic and possesses tuneable properties (i.e., density and dielectric constant).[3,4] Over the past decade, there has been renewed interest and extensive research into its use as a reaction medium for polymerization[5] and for polymer modification.[6]

The free radical polymerization of methyl methacrylate poses a particular problem: though the monomer is generally soluble, the product polymer is insoluble in $scCO_2$ at readily accessible experimental conditions.[7] For this reason, the most successful polymerization route is heterogeneous and a stabilizer is required. In 1994, DeSimone et al. utilized successfully poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)] homopolymer as a steric stabilizer.[8] Other fluorinated and siloxane polymers have also since been identified as effective stabilizers for free radical dispersion polymerizations in $scCO_2$.[5,9−12] An alternative approach is the use of block or graft copolymers as stabilizers. These require that one section is CO_2 "philic" (usually fluorinated or siloxane based) and the other section is CO_2 "phobic" (usually alkyl based). Careful control of the block size,[13] or the length of graft,[14] has been shown to greatly affect steric stabilizing properties and the optimum balance must be achieved for effective dispersion. Alternatively, stabilization can be achieved by copolymerization of a suitable macromonomer containing a suitable "CO_2-philic" moiety. Several studies have determined that poly(dimethylsiloxane) [PDMS] macromonomers are effective for the polymerization of MMA.[9,15,16] However, such macromonomers have the disadvantage of being incorporated into the final polymer product.

Recently, we reported the use of a single point anchoring stabilizer based upon a commercially available monofunctional polymer.[17,18] This comprises a CO_2-philic perfluoropolyether tail and a polymer-philic (carboxylic acid) headgroup. In a free radical dispersion polymerization, this stabilizer facilitates formation of PMMA in high yield and good molecular weight at very low loadings of stabilizer. The anchoring of the stabilizer to the growing polymer particles is through formation of a hydrogen bond between the carboxylic acid headgroup of the stabilizer and the ester group in methyl methacrylate.

This same anchoring interaction has been utilized in the development of graft stabilizers for polymerization of MMA in $scCO_2$. These can be synthesized from a commercially available copolymer of maleic anhydride simply by addition of a fluorinated alcohol through thermal ring opening of the maleic anhydride moieties in the copolymer backbone. The stabilizers produced were highly effective for polymerization of MMA in $scCO_2$.[19] In this paper, we extend those initial results to different backbone architectures and chain lengths and demonstrate their effect on stabilizer activity. We have developed new stabilizers with a substantially longer hydrocarbon backbone, and an analogous system with additional long pendant hydrocarbon groups as well as the fluorinated and carboxylic acid groups. The effect of these modifications upon the polymerization of MMA in $scCO_2$ is reported, and in particular, we investigate the effects of the stabilizer concentration upon yield, molecular weight, and morphology.

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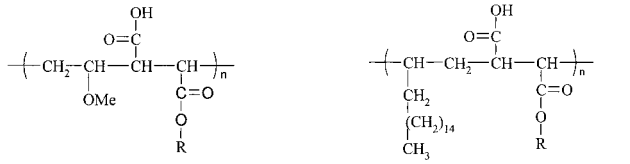
10.1021/ma001369b CCC: $20.00
Published on Web 12/08/2000



Based upon poly(methyl vinyl ether-alt-maleic anhydride)

Based upon poly(maleic anhydride-alt-1-octadecene)

Mn=79,000	Stabilizer
R= $-CH_2CH_2(CF_2)_3CF_3$	(1)
$-CH_2CH_2(CF_2)_5CF_3$	(2)

Mn=1,100,000	
R= $-CH_2CH_2(CF_2)_3CF_3$	(3)
$-CH_2CH_2(CF_2)_5CF_3$	(4)

Mn=30-50,000	Stabilizer
R= $-CH_2CH_2(CF_2)_3CF_3$	(5)
$-CH_2CH_2(CF_2)_5CF_3$	(6)

Figure 1. Stabilizer structures.

Experimental Section

Poly(methyl vinyl ether-*alt*-maleic anhydride) (M_n = 79 000 and 1 100 000) and poly(maleic anhydride-*alt*-1-octadecene) (M_n in the range 30 000−50 000) [Aldrich], 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] were used as received unless stated. In a typical synthesis,[19] 0.75 g 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, leading to a yellow solution. Excess alcohol was removed under reduced pressure to yield a yellow/orange solid in 60% yield. Each stabilizer was analyzed by infrared and NMR spectroscopy and also by elemental analysis.

Polymerization. Polymerizations were performed in a 60 mL stainless steel autoclave (NWA GmbH) equipped with a magnetic flea. High purity carbon dioxide (BOC Gases, SFC grade) was initially passed through a drying column and added to the autoclave through a Lee Scientific 501 syringe pump. In a typical polymerization, the autoclave was charged with reactants 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.

Visual observation of polymerization was performed in a 60 mL stainless steel autoclave (NWA GmbH) fitted with a sapphire window at one end. The polymerizations were carried under identical conditions to those in the more conventional 60 mL autoclave (described above).

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 and ^{19}F NMR data were collected using a Bruker 300 MHz spectrometer. Infrared data were collected on a Perkin-Elmer system 2000 FTIR spectrometer.

Results and Discussion

We have previously synthesized stabilizers based on a poly(methyl vinyl ether-*alt*-maleic anhydride) (M_n 79 800) which on thermal ring opening in the presence of a fluorinated alcohol forms a grafted copolymer.[19] The structures are shown in Figure 1: stabilizer **1** [1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol based] and stabilizer **2** [1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol based]. These stabilizers were characterized by a combination of FTIR and ^{13}C NMR spectroscopy to show that they are fully ring opened and therefore grafted quantitatively.

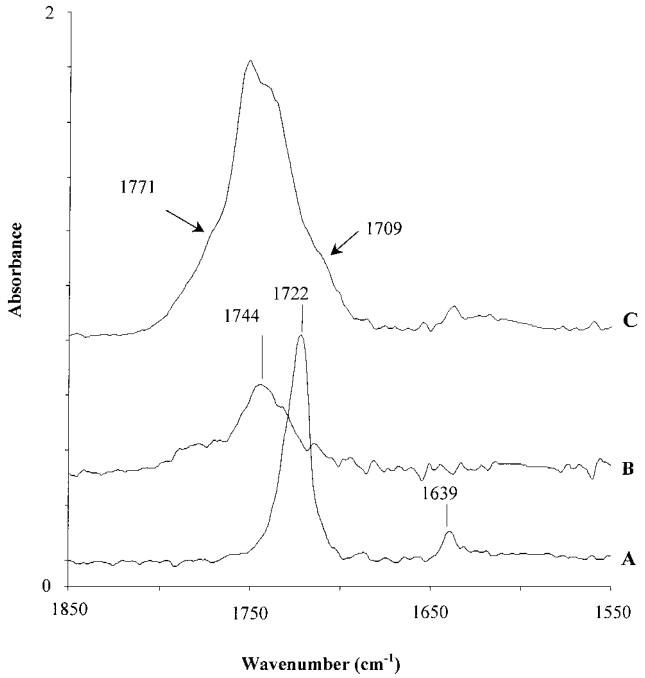


Figure 2. FTIR spectra in the carbonyl region for $scCO_2$ solutions (2500 psi and 65 °C) of (A) MMA, (B) stabilizer **1**, and (C) a mixture of MMA and stabilizer **1**. New bands in spectrum C (1771 and 1709 cm^{-1}) indicate a significant interaction between MMA and the stabilizer, most likely via a hydrogen-bonding mechanism.

The copolymer starting materials are insoluble in $scCO_2$ under the conditions used here, but the addition of the graft fluorinated groups from the alcohol leads to the solubilization of the stabilizers in $scCO_2$. In addition, the ring opening process also leads to formation of pendant carboxylic acid moieties (Figure 1). By analogy with our earlier studies on monofunctional perfluoropolyether stabilizers,[17,18] we believe that these groups may provide a method for anchoring of the stabilizer to PMMA via hydrogen bonding between carboxylic acid moieties and the ester of MMA. The key is to detect the presence of the hydrogen bond. FTIR spectroscopy is a sensitive probe of molecular interactions, and we have investigated the FTIR spectra of MMA, stabilizer **1**, and of a 50:50 mixture in $scCO_2$ using a small high-pressure FTIR cell described elsewhere.[20,21]

The FTIR spectrum for stabilizer **1** dissolved in $scCO_2$ shows a single ν(CO) feature in the carbonyl region corresponding to the presence of both the carboxylic acid and the ester carbonyl groups formed on ring opening (Figure 2). This spectrum is very similar to that obtained by FTIR DRIFTS spectroscopy of the solid surfactant,[19] and the width of the band clearly indicates the large number of such carbonyl groups and their many orientations. By contrast, the FTIR spectrum of MMA dissolved in $scCO_2$ shows a narrow carbonyl band at 1722 cm^{-1} and a much less intense band at 1639 cm^{-1} that corresponds to the ν(C═C) unsaturated moiety. When both MMA and stabilizer **1** are present, the FTIR spectrum is very different. New bands appear in the region of 1770 and 1710 cm^{-1} and clearly indicate that there is an interaction between MMA and the stabilizer.

Table 1. Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide Using Novel Grafted Stabilizers[a]

stabilizer	entry	% stabilizer[b]	yield (%)	M_n[c]	PDI[c]	particle size[d] (μm)	polymer morphology[d]	polymer appearance[e]
1	1	0.1	89	64 600	3.1		n/a	white granular solid
	2	2	90	94 200	2.6	3.3	discrete particles	fine white powder
2	3	0.1	93	110 400	2.6	2.9	discrete particles	fine white powder
	4	2	97	173 400	2.1	1.1	discrete particles	fine white powder
3	5	-	53	30 000	3.1	n/a	solid	oil and white solid
	6	0.1	86	63 000	2.6	n/a	aggregated particles	white granular solid
	7	1	95	67 000	2.2	4.5	discrete particles	fine white powder
	8	2	97	90 000	2.3	3.5	discrete particles	fine white powder
4	9	0.1	98	112 700	2.0	3.6	discrete particles	fine white powder
	10	1	97	135 400	2.1	2.6	discrete particles	fine white powder
	11	2	96	103 700	2.1	2.9	discrete particles	fine white powder
5	12	0.1	68	45 000	2.2	n/a	n/a	oil and white solid
	13	1	76	39 000	2.3	n/a	n/a	oil and white solid
	14	2	79	34 000	2.9	n/a	n/a	oil and white solid
	15	5	77	46 300	2.9	n/a	n/a	oil and white solid
6	16	0.1	96	99 700	2.4	4.5	discrete particles	fine white powder
	17	1	93	109 200	2.2	3.9	aggregated particles	fine white powder
	18	2	96	104 600	2.5	3.6	strings and particles	white granular solid
	19	5	93	96 000	2.3	n/a	solid	white chunks

[a] Polymerizations were carried out at 3000−3400 psi at 65 °C for 4 h, 1 wt % AIBN with respect to MMA and 10 g of MMA. [b] wt % with respect to monomer. [c] As determined by GPC. [d] As determined by SEM. (error ca. ± 0.5 μm). [e] The polymer appearance directly after venting.

The interaction is analogous to that observed previously for carboxylic acid/MMA combinations,[17,18] and we believe this indicates the presence of a hydrogen-bonding anchoring interaction.

When used to stabilize the free radical polymerization of MMA in supercritical carbon dioxide, surfactant **1** formed discrete particles at a loading of 1 wt %.[19] But by contrast, stabilizer **2** [1*H*,1*H*,2*H*,2*H*-perfluorooctanol based] was highly active at only 0.1 wt % leading to acceptable molecular weight and discrete particles (1−2 μm) (see Table 1, entries 1−4). The length of the fluorinated graft was found to be extremely important in determining morphology. The longer the grafted chain, the lower the amount of stabilizer required to form discrete particles. A similar observation was reported by Beckman et al.[14] in the use of poly(methyl methacrylate-*co*-hydroxyethyl methacrylate-*g*-poly(perfluoropropyl oxide) as the surfactant, where the graft length, the degree of grafting, and backbone length were found to affect the polymer morphology. In this paper, we highlight the effect of changing the backbone length from M_n = 79 800 to M_n = 1 100 000 (stabilizers **3** and **4**; Figure 1) and also the effect of introducing additional long pendant hydrocarbon chains (stabilizers **5** and **6**; Figure 1).

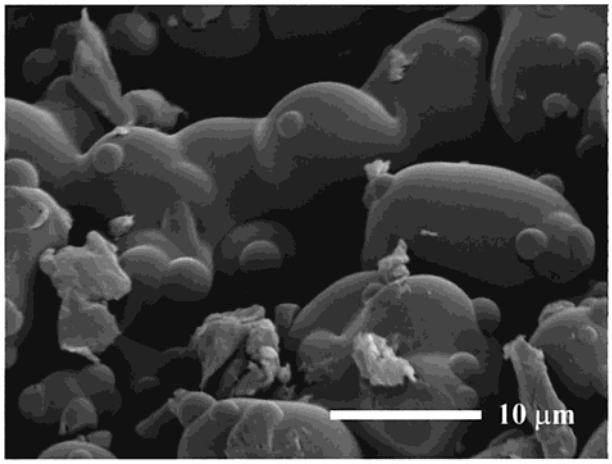
Synthesis and Characterization. The stabilizers were formed by the thermal ring opening of high molecular weight poly(methyl vinyl ether-*alt*-maleic anhydride) (M_n = 1 100 000) in the presence of 1*H*,1*H*, 2*H*,2*H*-perfluorohexanol (stabilizer **3**) or 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol (stabilizer **4**). The syntheses and analyses were very similar to those of stabilizers **1** and **2**.[19] The solid, orange/yellow colored crystalline products were analyzed using ^{13}C NMR, and the carbonyl region of the spectrum (160−180 ppm) is particularly informative. The ^{13}C NMR spectrum for the poly(methyl vinyl ether-*alt*-maleic anhydride) starting material shows three broad signals at 173.3, 172.0, and 170.0 ppm corresponding to the carbonyls in the maleic ring. On reaction with either of the perfluoro alcohols, the starting material peaks disappear and are replaced by two discrete but very broad resonances (at 174 and 172 ppm). The position and shape of these new resonances correspond to those observed for the lower molecular weight stabilizers **1** and **2**.[19] The copolymers also appear to have undergone quantitative conversion and therefore allow a direct comparison to be made between the different stabilizers.

Elemental analysis for the grafted polymers confirms that there is substantial incorporation of the fluorinated graft chains. However, the results were complicated by small residual amounts of the alcohol, which proved difficult to remove from these solid materials even after extensive treatment at reduced pressure. This same problem was also encountered with the synthesis of the lower molecular weight stabilizers **1** and **2**.[19]

By contrast, stabilizers **5** and **6** (Figure 1) formed by the thermal ring opening of poly(maleic anhydride-*alt*-1-octadecene) in the presence of 1*H*,1*H*, 2*H*,2*H*-perfluorohexan-1-ol or 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol were found to be waxy yellow/orange oils. Removal of residual fluorinated alcohol was facile under reduced pressure, and the elemental analyses confirmed that quantitative thermal ring opening of the maleic anhydride moieties had taken place. The materials were further characterized using ^{1}H NMR. By comparison of the resonances for $-OCH_2-$ from the fluoro alcohol (at 4.4 ppm) and $-CH_3$ from poly(maleic anhydride-*alt*-octadecene) (at 0.9 ppm), the degree of grafting can be calculated and both stabilizers **5** and **6** appear to be fully grafted.

All of the new stabilizers **3**−**6** were found to be highly soluble in $scCO_2$. Using a miniature view cell,[20,21] a sample of each stabilizer (corresponding to the amount present in a polymerization reaction; 5 wt % with respect to monomer) was placed in a preheated cell, and CO_2 added. All of stabilizers dissolved completely at conditions similar to those used for the polymerization reactions ($scCO_2$ at 2700 psi/65 °C).

The Effect of Changing Backbone Molecular Weight. Polymerizations Employing Stabilizer 3. Polymerization was carried out in the 60 mL autoclave using 10 g MMA (16% w/v with respect to CO_2), 1 wt % AIBN without any stabilizer. As expected, PMMA was produced in low yield and low molecular weight (Table 1, entry 5). In all our experimental procedures, this benchmark experiment was repeated to ensure that the autoclave was free from any residual stabilizer materials. On the addition of 0.1 wt % stabilizer **3**, there is a



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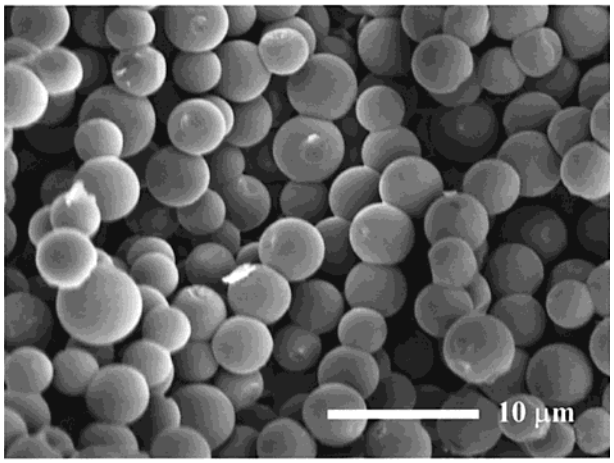

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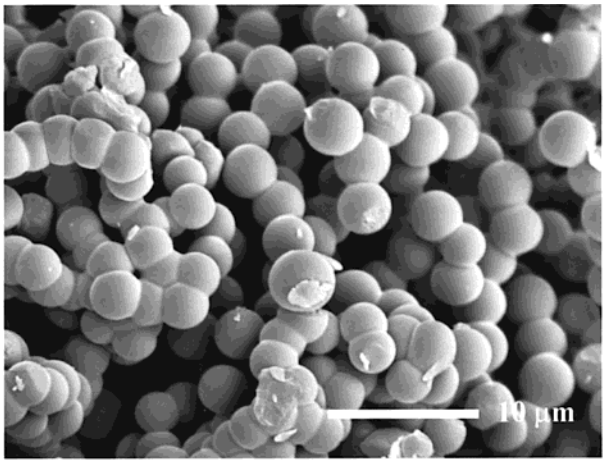
Figure 3. SEM images of PMMA produced using (a) 0.1 and (b) 1 wt % of stabilizer **3** (Table 1, entries 6 and 7).



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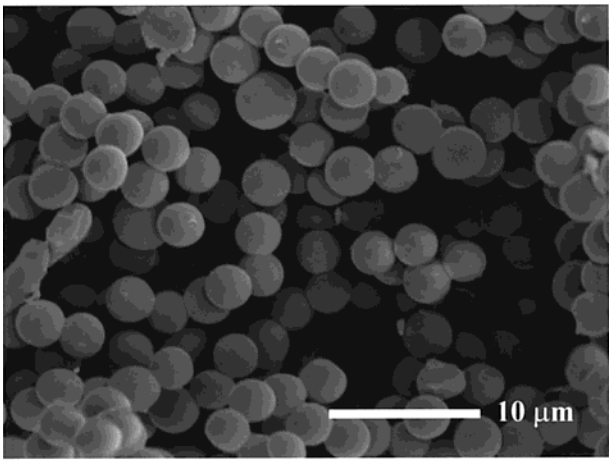

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Figure 4. SEM images of PMMA produced using (a) 0.1 and (b) 2 wt % of stabilizer **4** (Table 1, entries 9 and 11).

substantial increase in yield and a large increase in molecular weight (Table 1,entry 6). The SEM of the material shows that particles were formed initially, but these have become highly aggregated. Indeed, particles can be seen embedded in the bulk material (Figure 3). These data agree with the results published for stabilizer **1**[19] where an aggregated material was formed using 0.1 wt % stabilizer. (Table 1, entry 1)

On increasing the stabilizer concentration further up to 1 wt % and then 2 wt %, there is an increase in yield, a small improvement of molecular weights, and a negligible change of molecular weight distributions of the materials produced (Table 1, entries 7 and 8). The SEM images of the materials do however show that discrete particles are formed at these higher concentrations. The diameter of the particles decreases from 4.5 to 3.5 μm on increasing the stabilizer from 1 to 2 wt %. Such trends in particle size have been observed for a number of stabilizer systems in $scCO_2$ and in conventional solvents.[5,9,17] In addition, the results are also consistent with those for the lower molecular weight stabilizer **1** where the particle size is also observed to decrease with stabilizer loading.[19]

Polymerization Using Stabilizer 4. In the presence of only 0.1 wt % of stabilizer **4**, PMMA is produced in a very high yield (Table 1, entry 9). The material has a high molecular weight and improved molecular weight distribution. These differences between stabilizers **3** and **4** neatly mirror those observed between **1** and **2** and confirm that a small change in the fluorinated graft chain length has a substantial effect upon stabilizer activity. SEM images of the PMMA (Figure 4a) show that particles have been formed with a diameter of 3.6 μm. On further increasing the stabilizer concentration to 1 and 2 wt %, there is little change in yield, molecular weight, polydispersity (Table 1, entries 10, 11). In addition, the particle size remains constant over this range of stabilizer loadings (Figure 4b). These observations contradict the results seen with the others, particularly stabilizer **2**, where a decrease in particle size is clearly observed with increasing stabilizer concentration. Other workers have observed that there is a distinct decrease in particle size by increasing the concentration of an effective stabilizer[9,14] and examples have also been quoted where such behavior is not apparent.[13] Clearly, in the case of the novel graft copolymers described herein, the increase in backbone chain length from 79 000 to 1 100 000 has very little effect on the free radical dispersion polymerization except for an influence on the particle size at high loadings for stabilizers **2** and **4**.

The Effect of Introducing Pendant Alkyl Groups. Polymerization Employing Stabilizers 5 + 6. In the presence of a low concentration of stabilizer **5** (0.1 wt %), the polymerization of PMMA is not well stabilized. There is only a very modest yield and poor molecular weight (Table 1, entry 12). Indeed the results obtained

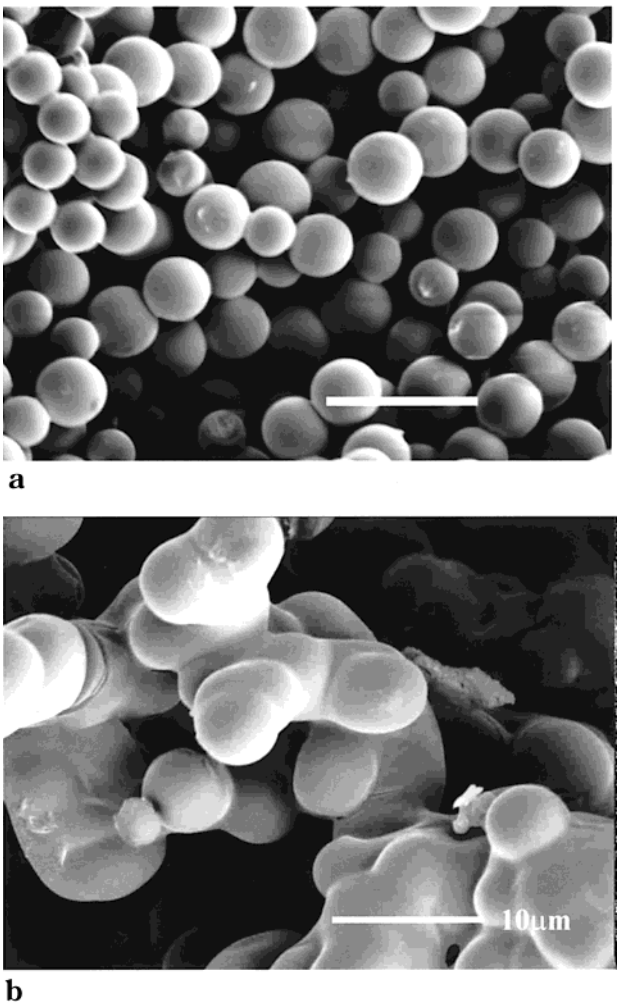

Figure 5. SEM images of PMMA produced using (a) 0.1 and (b) 5 wt % of stabilizer **6** (Table 1, entries 16 and 19).

are very similar to those obtained without any stabilizer present (Table 1, entry 5). On further increasing the stabilizer concentration to 1, 2, and 5 wt %, consecutively, there is a modest increase in yield but little change in molecular weight or polydispersity (Table 1, entries 13−15). A comparison between stabilizers **1**, poly(methyl vinyl ether-*alt*-maleic anhydride**)** and **5**, poly(maleic anhydride-*alt*-1-octadecene), indicates that the introduction of the additional pendant alkyl moieties substantially affects the stabilizer activity. The pendant alkyl groups alter the delicate balance in the stabilizer between the "CO_2-philicity" and "CO_2-phobicity". Beckman has previously shown with graft systems that if the stabilizer becomes too "CO_2-phobic", then it becomes ineffective, and this is the case for stabilizer **5** with the addition of pendant alkyl chains. To tip the balance back toward an effective stabilizer we synthesized the analogous stabilizer **6** in which longer 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol chains were added to the poly(maleic anhydride-*alt*-1-octadecene).

Polymerization in $scCO_2$ of MMA at 0.1 wt % of stabilizer **6** leads to production of PMMA in 96% yield and with acceptable molecular weight and PDI (Table 1, entry 16). The SEM images of the polymer show that discrete particles are formed with a diameter of 4.5 μm (Figure 5a). Clearly this stabilizer is much more effective than stabilizer **5**, and the correct balance of "CO_2-philic" and "CO_2 -phobic" behavior is restored. Increasing to 1 wt % stabilizer again leads to PMMA produced in high yield with a high molecular weight (Table 1, entry 17). The SEM of the material shows that slightly aggregated particles have been formed with a diameter of 3.9 μm. Intriguingly, further increases in stabilizer concentration lead to similar yields of PMMA with acceptable molecular weights, but a clear degradation in sample quality and particle morphology. Indeed, no particles are observed at 5 wt % (Table 1, entries 18, 19) (Figure 5b). Exhaustive repetition showed that the results were not artifacts; increasing stabilizer concentration leads to loss of morphology control.

To investigate further this phenomenon, we have carried out experiments in a view cell equipped with a sapphire window. These experiments allowed visual observation of the polymerization throughout the reaction. All reaction conditions were identical to those used in the more conventional autoclaves and described earlier. At a loading of 0.1 wt % of stabilizer **6** in MMA/$scCO_2$, a single clear phase is initially observed indicating that all components are dissolved. After just a few minutes, a milky white dispersion is formed, and the formation of PMMA is clearly observed. After around 2.5 h a small amount of fine white powder begins to settle out at the base of the window. After completion of reaction, a dry, fine, free-flowing white powder is poured from the view cell. Exactly the same procedure was repeated with 5 wt % of stabilizer **6** in MMA/$scCO_2$. Again, a single clear phase is initially observed, indicating that all components are fully dissolved, and after a few minutes a milky white dispersion is formed. After 2 h, a very distinct precipitation of PMMA has occurred, and large, solid chunks of PMMA can clearly be observed through the sapphire window. On completion of reaction, a rigid rod is required to dislodge the white solid from the inside of the view cell. Clearly, increasing the concentration of stabilizer results in a loss in the control of morphology using this particular stabilizer, even though PMMA is still produced in a high yield. Analysis of the two PMMA samples by GPC and SEM confirmed the materials to be identical to those produced earlier (Table 1, entries 18, 19) (Figure 5). In addition, NMR analysis (^{13}C and ^{19}F) reveals no significant indication of entrapment or grafting of the stabilizer into the PMMA. In other view cell experiments, stabilizer **6** proved to be completely soluble in $scCO_2$ at 65 °C and 3000 psi at loadings of 5 wt %; thus, we are confident that the inactivity at the higher stabilizer concentration is not caused by precipitation. Clearly, the additional pendant alkyl chains have an unusual effect on the stabilizer activity and further investigations are in progress.

Conclusions

We have demonstrated that for the grafted copolymers under study, the stabilizer activity is independent of the backbone chain length. Stabilizers **1** and **3** both display similar properties, with low stabilizer loadings producing aggregated materials but higher loadings leading to discrete particles. By contrast, stabilizers **2** and **4** produce discrete particles even at low concentrations. Change of the stabilizer chain length appears to have little effect upon stabilizer activity. Very similar observations were reported by DeSimone et al. for similar order of magnitude increase in the stabilizer molecular weight of the poly(FOA) system. By contrast, the addition of pendant hydrocarbon moieties has a substantial effect upon activity. The stabilizer formed

using poly(maleic anhydride-*alt*-1-octadecene) and 1*H*,1*H*,2*H*,2*H*-perfluorohexanol (stabilizer **5**) does not form particles even at a 5% loading. However, the analogous stabilizer **6** produced using a longer 1*H*,1*H*,2*H*,2*H*-perfluorooctan-1-ol graft forms discrete particles even at very low loadings. Intriguingly, when stabilizer **6** is used, the PMMA formed becomes aggregated at higher concentrations. The reason for this is unclear and is under investigation. A comparison between stabilizers **6** and **2** indicates an increase in particle size, and this may well show that the addition of the alkyl groups lowers the ability of **6** to anchor to the growing particles of PMMA.

In conclusion, the best choice of backbone and fluoro alcohol is poly(methyl vinyl ether-*alt*-maleic anhydride) with 1*H*,1*H*,2*H*,2*H*-perfluoro-octan-1-ol (stabilizer **2**) which produces discrete PMMA particles at very low concentrations.

Acknowledgment. We gratefully acknowledge the EPSRC for support (M.R.G.: GR/K76009). We also acknowledge the Royal Society for a University Research Fellowship (S.M.H.). We thank also Dr. K. H. Pickel (NWA GmbH) Mr. J. M. Whalley, and Mr. K. Stanley for their technical assistance and Miss S. E. Jones, Prof. M. Poliakoff, and Dr. M.W. George for their help and advice.

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MA001369B