Free Radical Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide Using a Pseudo-Graft Stabilizer: Effect of Monomer, Initiator, and Stabilizer Concentrations

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ABSTRACT: This paper describes the free radical polymerization of methyl methacrylate [MMA] in supercritical carbon dioxide [$scCO_2$] using a commercially available acid-terminated perfluoropolyether [Krytox 157FSL] as a polymerization stabilizer. We have investigated the effect of varying the concentrations of monomer, initiator, and stabilizer upon the molecular weight and morphology of the resultant poly(methyl methacrylate). The results obtained are compared to those observed for other stabilizers used for polymerization in $scCO_2$. Krytox 157 FSL is shown to be an effective stabilizer leading to discrete spherical particles with diameters in the range expected from dispersion polymerization. Unusual morphologies are observed at high initiator concentration and at lower stabilizer concentration. Surprisingly, high yields of polymer are still formed even at very low concentrations of stabilizer (e.g., 10^{-4} wt % with respect to monomer).

Introduction

The desire to replace conventional hydrocarbon and halocarbon solvents with more environmentally benign systems has led to increased interest in the use of supercritical fluids as reaction media.[1] Supercritical carbon dioxide ($scCO_2$) has been investigated extensively, as it is a relatively cheap, nonflammable, environmentally acceptable solvent.[2] One area of interest has been the free radical polymerization of acrylates and in particular methyl methacrylate.[1] The product, poly(methyl methacrylate) [PMMA], is insoluble in $scCO_2$, and hence a stabilizer must be added. This leads to a dispersion polymerization and a significant improvement in the yield, molecular weight, and morphology of the resultant material.

DeSimone et al. have demonstrated that methyl methacrylate (MMA) undergoes a dispersion polymerization in supercritical carbon dioxide utilizing homopolymeric stabilizers, e.g., poly(1,1-dihydroperfluorooctyl acrylate) [PFOA], or block copolymer stabilizers where the soluble section is either poly(dimethylsiloxane) [PDMS] or [PFOA].[3,4] Others have developed similar materials.[1,5] By contrast, Beckman et al. have synthesized a series of graft copolymers, poly(methyl methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropyl oxide), which are also effective stabilizers for the dispersion polymerization of MMA in $scCO_2$.[6]

An alternative approach is the use of siloxane-based macromonomers (PDMS macromonomers) for the dispersion polymerization of methyl methacrylate in $scCO_2$.[4,7−10] Macromonomers are oligomers or polymers with a polymerizable terminal functional group, which are commonly used for the formation of graft copolymers. The drawback to the use of such materials is that they are necessarily incorporated into the PMMA product.

We recently reported the use of a different system, a carboxylic acid-terminated perfluoropolyether [Krytox 157FSL] as stabilizer for the free radical polymerization of methyl methacrylate.[11] The anchoring of this stabilizer to the growing polymer particles is proposed to be through a hydrogen bond between the terminal acid functionality of the stabilizer and the ester grouping of MMA leading to a pseudo-graft copolymer. We have also shown that the same principle can be extended to carboxylic acid functionalized graft copolymers.[12] It should be emphasized that at the end of the polymerization process there are no detectable residues of the perfluoropolyether material in the product PMMA. This paper details our investigations into the effect of varying the reactant concentrations (monomer, stabilizer, and initiator) on the molecular weight, yield, and morphology of the PMMA product.

Experimental Section

The initiator 2,2′-azobis(isobutyronitrile) [AIBN] [BDH Ltd.], Krytox 157FSL [Dupont], and methyl methacrylate [Ineos, inhibited with 2 ppm of Topanol (a mixture of hindered amines)] were used as received unless otherwise stated. Polymerizations were performed in a 60 mL stainless steel autoclave (NWA GmbH) equipped with magnetic stirrer. High-purity carbon dioxide (BOC Gases, SFC grade) was passed initially through a drying column. In a typical polymerization, the autoclave was loaded with reactants and sealed. The cell was then pressurized up to 3000 psi with high grade N_2, to leak test the equipment and to degas the reactants. The cell was vented before being filled with CO_2, stirred, and heated to the reaction temperature using a preheated block. The correct pressure was obtained by adding additional CO_2.

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

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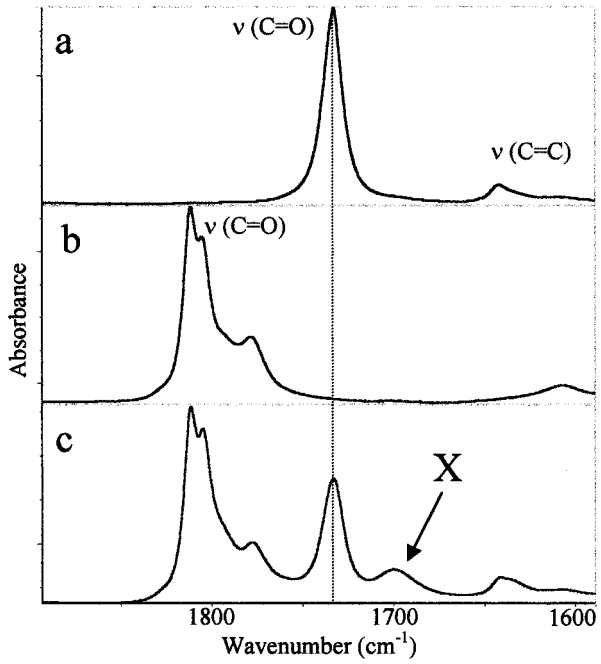

Figure 1. FTIR spectra of the carbonyl region of (a) methyl methacrylate, (b) Krytox, and (c) a dilute solution of methyl methacrylate/Krytox in supercritical carbon dioxide (65 °C, 2500 psi). X indicates a new carbonyl peak arising from the hydrogen-bonding interaction between methyl methacrylate and Krytox.

and were gold coated. ^{1}H NMR data were collected using a Bruker 300 MHz spectrometer.

Results and Discussion

There is an extensive literature detailing the effects of reactant concentrations and reaction conditions on dispersion polymerization processes.[13] In particular, the concentrations of monomer, stabilizer, and initiator are well-known to have dramatic effects upon the yield, molecular weight, and particle size of the product polymers. Several studies in $scCO_2$ have compared and contrasted these effects for a range of different steric stabilizer and macromonomer systems.[4,6−8] In this paper, we report on experiments that were carried out to investigate the effects of varying independently the concentration of monomer, initiator, and Krytox 157FSL stabilizer. The changes in yield, molecular weight, and morphology of the product PMMA are compared to those observed with other stabilizer systems in $scCO_2$.

The anchoring mechanism for the carboxylic acid-terminated perfluoropolyether to PMMA is proposed to occur through a hydrogen bond between the carboxylic acid group and the carbonyl functionality in methyl methacrylate. We previously reported thin-film FTIR studies that demonstrated such an interaction for liquid mixtures of the stabilizer and MMA at room temperature.[11] Clearly, it is important to know that the same interaction still occurs in $scCO_2$ at the higher temperatures encountered in free radical polymerization. FTIR measurements have been performed in a high-pressure FTIR cell[14−16] and clearly demonstrate shifts in the carbonyl region of the FTIR spectrum (Figure 1) for an $scCO_2$ solution containing the stabilizer and MMA. The spectral changes observed are consistent with those observed for the thin-film experiments[11] and with other studies in supercritical fluids,[17] confirming that hydrogen bonding does indeed occur in $scCO_2$.

Effect of Monomer Concentration on Polymerization. The monomer concentration of methyl methacrylate was varied between 4.2% and 25 wt % with respect to CO_2 (2.5 g to 15 g in a 60 mL autoclave) in order to investigate the effect upon the PMMA produced. The experiments were conducted at 70 °C and 170 atm (2500 psi) using AIBN as the initiator (1 wt % with respect to monomer), and reactions were allowed to proceed for 4 h. Under these conditions, the starting solution is known to exist as one phase.[18] The results are summarized in Table 1.

In all of these experiments, PMMA is produced in high yield, and the yield changes very little with monomer concentration. The yields at lower monomer concentration are likely to be slightly lower because the smaller scale of experiment tends to exaggerate the effects of loss of the PMMA product (entries 1−3) from the autoclave. The molecular weights and molecular weight distributions also remain essentially constant and are close to those values that would be expected in the absence of chain transfer agent. Increasing the monomer concentration is known to have a substantial effect on the solvency of the medium and to affect the morphology of the product. It is well-known that, as more monomer is added to the reaction, the solvency of the medium increases for both the product polymer and the stabilizer. This in turns allows larger particles to be formed.[13,19]

At the lowest monomer level (2.5 g; Table 1, entry 1) only aggregated particles of PMMA are produced, and it is difficult to estimate their diameter (~2 μm). On increasing the reaction scale from 2.5 g through to 15 g, the particles become more discrete and clearly increase in size. These data indicate that at the low monomer concentration the stabilizer dissolves preferentially in the $scCO_2$ and does not appear to partition as effectively between the growing polymer and the reaction medium as in the cases where the monomer conditions are higher. Thus, affecting the quality of the dispersion formed. At the higher concentrations there is now sufficient monomer in the reaction medium to form a stable dispersion observed in view cell experiments. The SEM images of the PMMA product demonstrate formation of discrete particles (Figure 2) and increase in diameter from ca. 2 to 3.6 μm. The PMMA

Table 1. Polymerization Conditions for Varying the Concentrations of Monomer[a]

entry	monomer mass (g)	monomer w/v % in CO_2[b]	yield (%)	M_n[c] (Da)	M_w[c] (Da)	PDI[c]	morphology	particle diameter (μm)[d]
1	2.5	4.2	86	102 700	218 900	2.1	aggregated	n/a
2	5	8.3	91	128 800	306 300	2.4	aggregated particles	2.1
3	7.5	12.5	84	105 600	249 900	2.4	aggregated particles	2.2
4	10	16.7	99	99 200	249 800	2.5	particles	2.7
5	12.5	20.8	98	95 000	241 400	2.5	particles	2.7
6	15	25.0	97	77 000	206 100	2.6	particles	3.6

[a] Reactions carried out at 2500 psi at 70 °C for 4 h using 1% AIBN and 1 wt % Krytox with respect to monomer. [b] Calculated for 60 mL volume. [c] As determined by GPC analysis. [d] Particle diameter as determined by SEM.

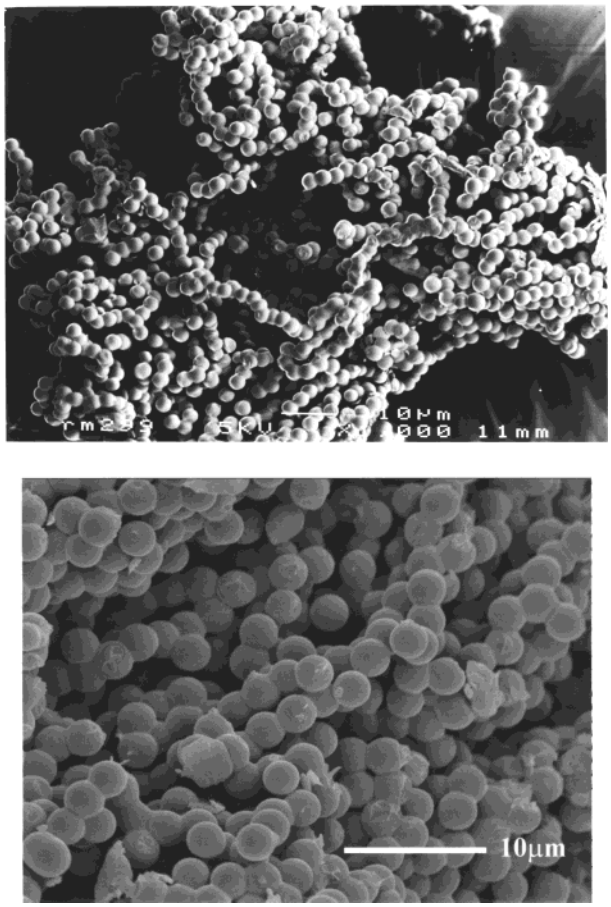

Figure 2. SEM showing particles formed using 1% AIBN, 1% Krytox: (a, top) 2.5 g of methyl methacrylate; (b, bottom) 15 g of methyl methacrylate. The SEMs show that aggregation occurs with a low monomer concentration, but discrete particles are formed at higher concentrations.

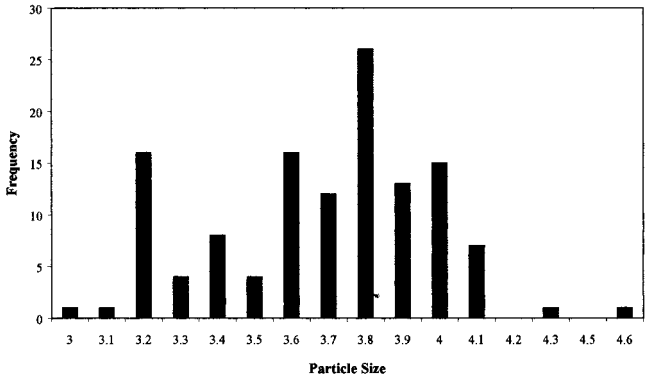

Figure 3. Graph showing the particle size distribution (1.08) for PMMA obtained from SEM images (for Table 1, entry 6; 125 particles were measured).

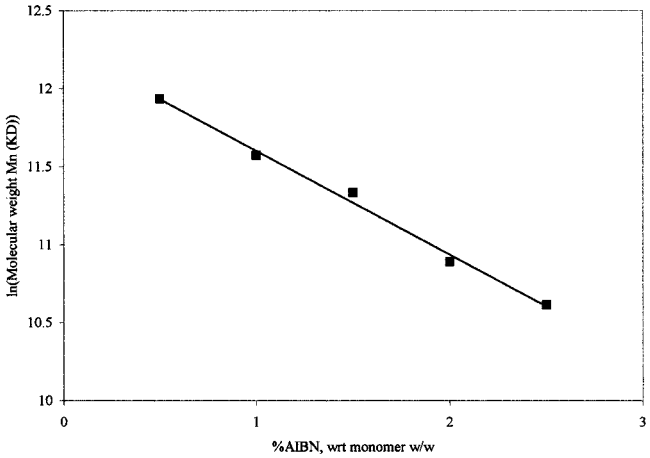

Figure 4. Mayo Walling plot of ln(molecular weight (M_n)) against initiator concentration (Table 2).

produced at 15 g scale also has a narrow particle size distribution (1.08) as illustrated in Figure 3. Interestingly, no "second crop" of smaller particles is observed in these experiments as was noted elsewhere.[22] The observed trend in particle size with monomer concentration using the Krytox stabilizer does indeed follow that observed for polymerizations in conventional solvents and can be related to the solvency of the reaction medium. These results also match closely those observed by others in $scCO_2$ for fluorinated stabilizers.[20] However, the change in particle size was much less marked for siloxane-based block copolymer systems.[21]

Effect of Initiator Concentration. Increasing the initiator concentration leads to a decrease in molecular weight because of increased number of radicals in the medium.[13] Moreover, a decrease in particle size is generally observed because of the formation of more nucleation sites. We have investigated the concentration of initiator over the range 0.5−2.5 wt % with respect to monomer at constant monomer and stabilizer concentration, and the results obtained are summarized in Table 2.

Table 2 shows that as the initiator concentration is increased, there is a controlled decrease in molecular weight, the M_n falling from 152 000 to 40 700 when the initiator concentration changed from 0.5% (Table 2, entry 1) to 2.5% w/w (Table 2, entry 5). A similar trend has also been seen using other systems in $scCO_2$.[22] Both the molecular weight distribution and yield of the polymerization are largely unaffected by the initiator concentration.

The effect of initiator concentration on molecular weight for a dispersion polymerization in conventional solvents can be described by the Mayo−Walling equation, where the molecular weight is proportional to the inverse of initiator concentration.[13] A log plot of molecular weight against initiator should therefore give a straight line and is shown for the Krytox system in Figure 4.

Table 2. Polymerization Conditions for Varying the Initiator Concentration [AIBN]

entry	%AIBN in the reaction	yield (%)	M_n[b] (Da)	M_w[b] (Da)	PDI[b]	morphology	particle size[c] (μm)
1	0.5	98	152 300	316 300	2.1	discrete particles	2.5
2	1	99	106 000	280 400	2.6	discrete particles	2.8
3	1.5	97	83 500	214 400	2.6	strings and particles	3.0
4	2	98	53 600	141 800	2.6	strings and particles	n/a
5	2.5	97	40 700	118 500	2.6	strings	n/a

[a] Reactions performed at 2500 psi and 70 °C with a reaction time of 4 h using 1 wt % Krytox with respect to monomer (10 g). [b] As determined by GPC analysis. [c] Particle diameter as determined by SEM.

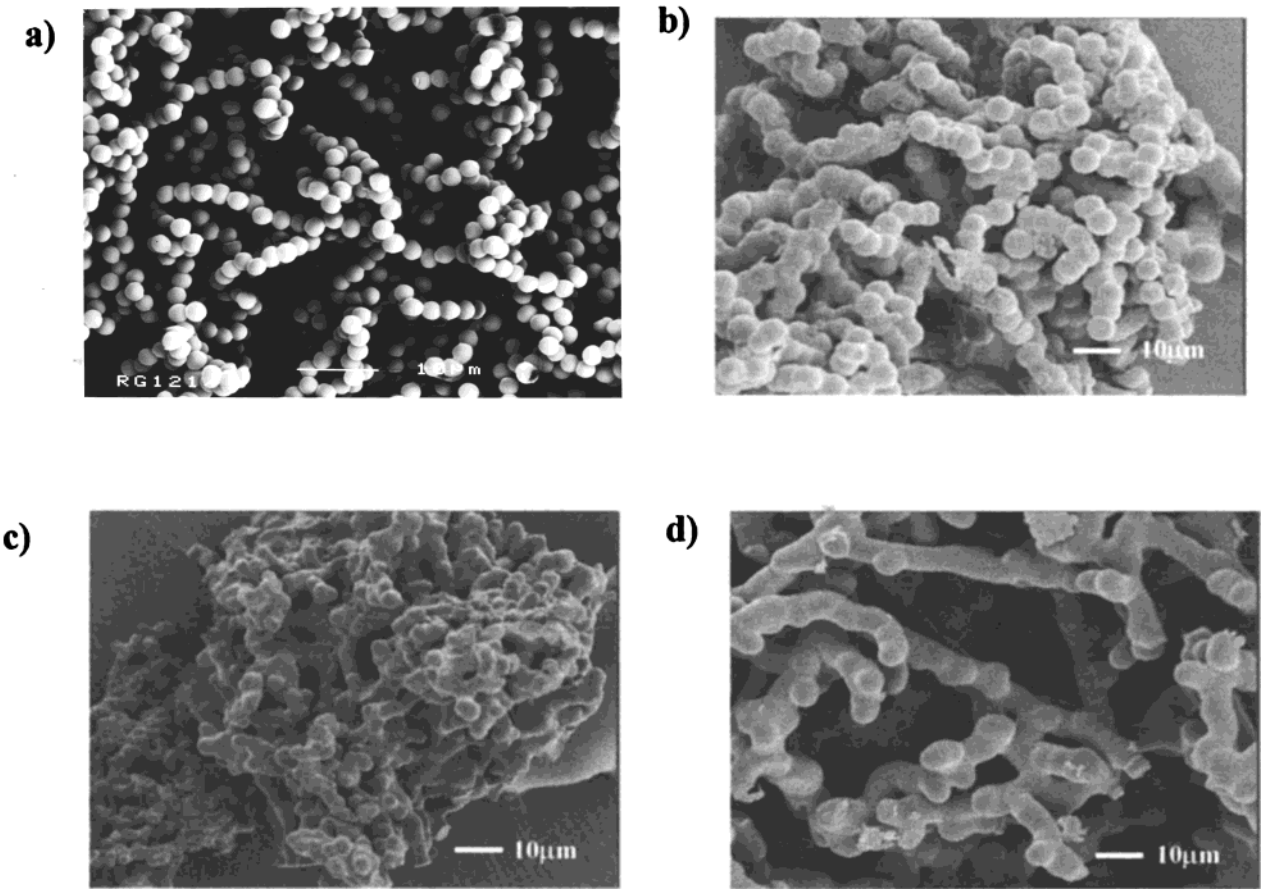

Figure 5. SEM images showing (a) discrete particles formed using 1% Krytox, 0.5% AIBN, (b) 1.5% AIBN, (c) 2% AIBN, and (d) "string"-like structure formed using 2.5% AIBN.

Table 3. Polymerization Conditions for Different Stabilizer Concentrations[a]

entry	% Krytox w/w[a]	yield (%)	M_n[b] (Da)	M_w[b] (Da)	PDI[b]	morphology	particle diameter[c] (μm)
1	0	29	10 900	69 900	3.6	foamed	n/a
2	0.0001	89	32 300	129 300	4.0	foamed	n/a
3	0.01	88	31 700	206 400	6.0	aggregated particles	6.0
4	0.1	90	94 400	218 800	2.3	strings and particles	4.6
5	1.0	87	125 100	279 800	2.2	particles and some strings	3.5
6	10.0	95	115 600	254 200	2.2	particles	1.8
7	32.0	96	116 300	269 800	2.3	particles	1.7

[a] Reactions carried out at 2500 psi at 70 °C using 1% AIBN with respect to monomer. [b] As determined by GPC analysis. [c] Particle diameter as determined by SEM.

The polymer morphology is also found to be very dependent upon initiator concentration. Figure 5a shows discrete particles with a diameter of 2.8 μm, formed at 0.5% AIBN. On increasing the initiator to 2.5%, the same particles are still formed but have very clearly aggregated in a rather unusual fashion to form "string"-like structures as shown in Figure 5d. We have already reported similar such morphologies with an alternative, but related, stabilizer system.[12] At all initiator concentrations, the molecular weight of the PMMA is above 40-mer, and at these relatively high molecular weights, there is known to be no substantial change in glass transition temperature (T_g).[23] The T_g of the PMMA is lowered considerably by $scCO_2$ plasticization[24] and could perhaps account for the observed morphologies. However, one would expect that the T_g of all materials at all the molecular weights observed would be depressed uniformly, indicating that perhaps this is not a viable explanation. At higher initiator concentrations, we also detected no substantial increase in internal autoclave temperature.

Such unusual morphologies have been observed with only one other stabilizer system[12] and may be a consequence of the unique mode of action of the hydrogen bonding type stabilizer. Work is currently underway to investigate the exact mechanism for the formation of these structures.

Effect of Stabilizer Concentration. The concentration of stabilizer controls the morphology of the material produced, with higher concentrations generally leading to smaller particles. To investigate this, a number of polymerizations were performed over a wide range of Krytox concentrations (0.0001−32%).

In the absence of stabilizer, PMMA was produced in low yield (29%) and with a low molecular weight (Table 3, entry 1). However, addition of only a very small amount of the Krytox stabilizer (0.0001%) increases the yield to nearly 90% with a corresponding increase in molecular weight (Table 3, entry 2). Clearly the amount added is insufficient to stabilize a dispersion, and SEM of the polymer produced shows the expected aggregated and foamed material (SEM not shown). However, the

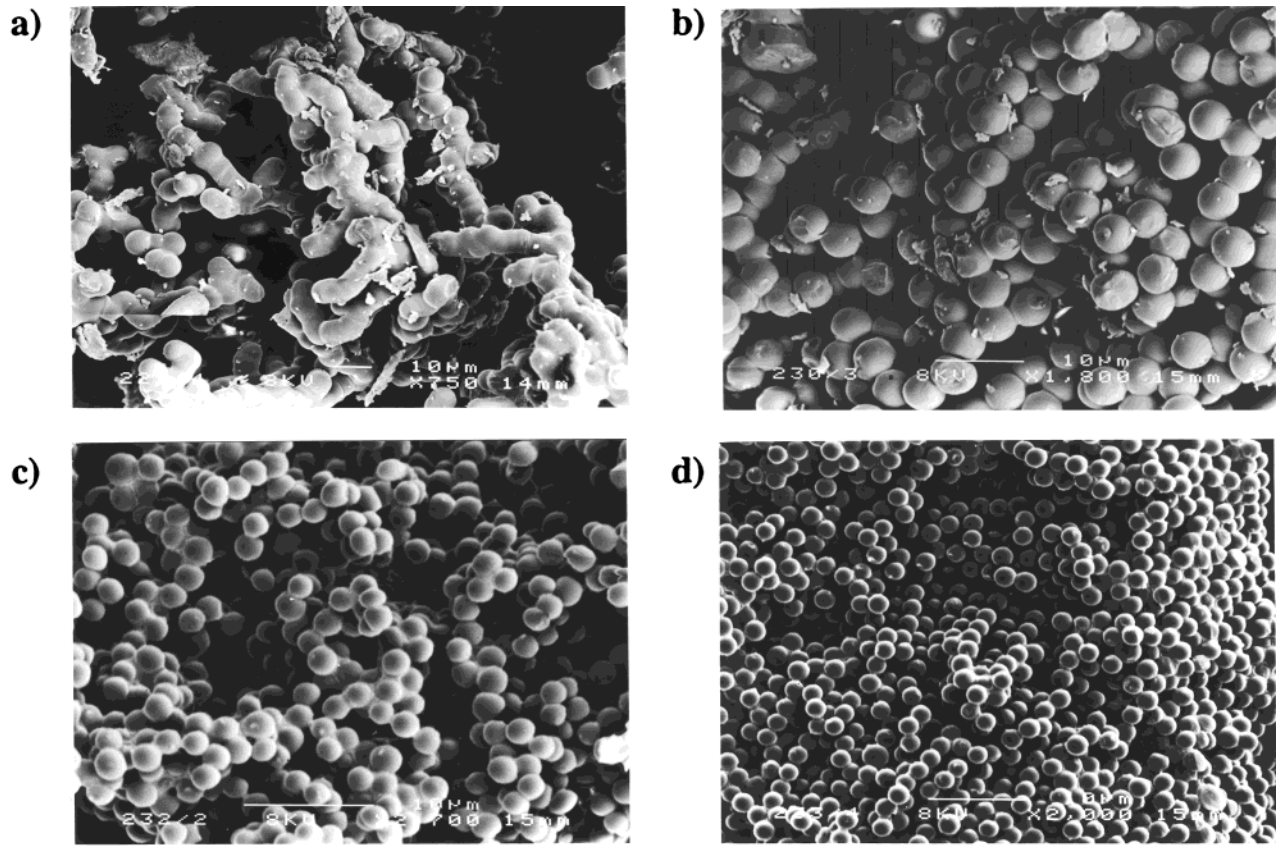

Figure 6. SEM images showing the materials formed using 1% AIBN and (a) 0.01% Krytox, (b) 0.1% Krytox, (c) 10% Krytox, and (d) 32% Krytox. Scale bar in each case represents 10 μm.

increase in yield clearly indicates an interaction that is promoting polymerization. Exhaustive repetition of these experiments and careful cleaning of the autoclave vessel between successive experiments demonstrate that the stabilizer can be completely removed and that the yield and molecular weight do indeed return to the lower values (Table 3, entry 1) in the absence of Krytox.

On increasing the stabilizer concentration to 0.1% (Table 3, entry 4), there is further increase in molecular weight and yield, and the SEM micrographs reveal a trend from foamed morphology through to a mixture of discrete particles and "strings". Careful inspection of Figure 6a,b shows the presence of stringlike morphologies that are reminiscent of those obtained at higher AIBN concentrations. At higher stabilizer concentrations (1−32 wt %) discrete particles are produced (Figure 6c,d). These very high stabilizer concentrations demonstrate that particle size may be controlled, and a decrease in diameter is observed. This is in agreement with the results observed for dispersion polymerizations in conventional solvents[13,19] and for the other stabilizer systems in supercritical carbon dioxide.[3,4] However, even at the very highest stabilizer concentrations, no residues of perfluoropolyether stabilizer can be detected in the product PMMA following $scCO_2$ extraction (in-line extraction vessel; 300 atm, 50 °C for 3 h) by ^{19}F NMR.[11] It should be pointed out that the Krytox stabilizer is certainly soluble in the NMR solvent $CDCl_3$ and hence should produce a characteristic NMR signal if present These results contrast with those obtained by others[1,3] where significant residues of stabilizer, which cannot be extracted, are detected in the product polymer. The molecular weight of the Krytox is below the entanglement density of PMMA, thus aiding removal from the product polymer. Moreover, the complete absence of C−H bonds or copolymerizable end groups in the structure of the stabilizer ensures that there is no grafting or incorporation by hydrogen abstraction, leading to covalent bonding to PMMA.

Conclusions

Krytox 157FSL is an effective stabilizer for the polymerization of methyl methacrylate in supercritical carbon dioxide. The morphology and molecular weight of the materials produced depend greatly on the concentration of reactants employed, with new "pearl necklace" stringlike structures being observed. Such structures may well have very high surface areas and could show utility as support materials. The stabilizer interacts through a hydrogen bond with the carbonyl group of methacrylate monomer. In addition, Krytox gives remarkably high yields of polymer at stabilizer concentrations, which are substantially lower than those previously reported and, even at very high stabilizer concentration, there are no detectable residues of perfluoropolyether in the PMMA product. These factors, along with the relatively low cost and ready availability of the stabilizer, indicate potential as a commercially viable stabilizer for polymer synthesis in $scCO_2$.

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