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Dispersion Polymerizations in Carbon Dioxide Using Siloxane-Based Stabilizers

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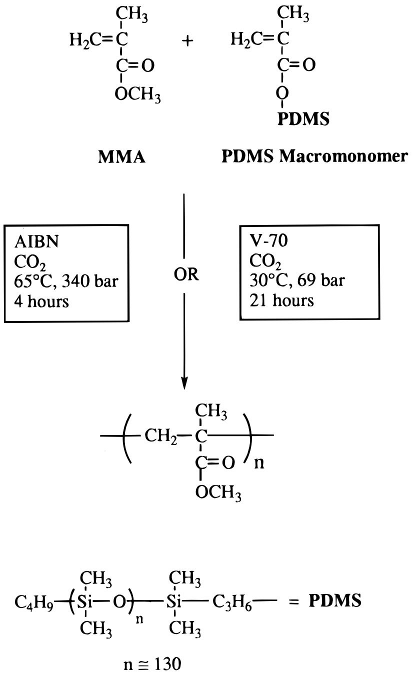
In the past three years, the number of polymerization reactions that have been conducted in CO_2 has increased considerably.[1] Herein we report the dispersion polymerization of olefinic monomers in carbon dioxide using a polymerizable, CO_2-soluble poly(dimethylsiloxane) (PDMS) macromonomer as the stabilizer. This study builds upon the dispersion polymerization of methyl methacrylate (MMA) in CO_2 reported by DeSimone *et al.* which utilized poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)] homopolymer as the steric stabilizer.[2,3]

Although many fluoropolymers and silicone polymers have been identified as being soluble in CO_2[4−8] or "CO_2-philic",[9] a silicone-based material has not previously been used to stabilize a heterogeneous polymerization in CO_2. The advantages of using silicone-based materials as stabilizers are 2-fold. First, silicone-polymers are much less expensive than their fluorinated counterparts (ca. \$0.80−\$1.30/lb), and second, the solubility of silicone polymers in both CO_2 and conventional organic solvents makes for facile characterization of the products obtained using commonly available solvents.

Macromonomers[10−12] are polymers with terminal functional groups that can further polymerize and are most commonly used in the preparation of well-defined graft copolymers.[13−15] A relatively new use for macromonomers is in the stabilization of emulsion and dispersion polymerizations.[16−19] These reactions are sterically stabilized by graft copolymers that form *in situ* during the polymerization. A recent article by Kawaguchi *et al.* discusses the mechanism of dispersion copolymerizations in detail.[16] Herein, we describe the dispersion polymerizations of MMA and styrene in CO_2, stabilized by the addition of a commercially available PDMS macromonomer. The colloidal particles which are produced using this methodology may find use in applications such as printing inks, paints, toner, adhesives, chromatographic column packing, and drug delivery systems to name a few. Preliminary results show that the dispersion polymerization of MMA can be conducted in both supercritical and liquid CO_2. The relatively low pressure utilized in the latter, coupled with the environmental and toxicity advantages afforded by CO_2 and the commercial availability of the stabilizer, makes this heterogeneous polymerization process much more attractive.

Our synthetic procedure is shown in Scheme 1. The specific methacryloxy functional PDMS macromonomer utilized had a $\langle M_n \rangle$ of 1.13×10^4 and a molecular weight distribution (MWD) of 1.1.[20] Using ^{29}Si NMR, the macromonomer was also shown to be 100% functionalized.[21] Polymerizations were conducted in a 10-mL high-pressure view cell[22] using analytical or SFC/SFE grade CO_2[23] and either 2,2′-azobis(isobutyronitrile) (AIBN; Eastman Kodak) or 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako) as the initiator. When AIBN was used as the initiator, reactions were necessarily conducted at high pressures (340 bar) in order to solubilize the PDMS macromonomer at the desired reaction temperature of 65 °C. In contrast, relatively low pressures were necessary to solubilize the PDMS macromonomer in liquid CO_2. Unreacted PDMS macromonomer was removed from the polymers by either washing with hexanes[24] or extraction with liquid CO_2 (345 bar, 23 °C).[25] The washings were concentrated *in vacuo* and shown by ^{1}H NMR to contain unreacted PDMS macromonomer, not PMMA-*g*-PDMS or PDMS macromonomer that had reacted. The products were characterized before and after purification using GPC (in THF versus polystyrene standards), ^{1}H NMR spectroscopy (Bruker, 200 MHz), and scanning electron microscopy (SEM).

Scheme 1. Dispersion Polymerization of MMA in CO_2



For polymerizations conducted in supercritical CO_2, the effect of PDMS macromonomer concentration on the resulting poly(methyl methacrylate) (PMMA) product was investigated. The results of this study are summarized in Table 1. The SEMs used to determine the particle sizes and size distributions reported in Table 1 are shown in Figure 1. When no PDMS macromonomer was added to the polymerization, only a low conversion, precipitation polymerization resulted. Although adding a relatively small amount of PDMS macromonomer to the reaction increased both the yield and molecular weight of the polymer obtained considerably, larger amounts of PDMS macromonomer were necessary to adequately stabilize the dispersion polymerization of MMA in supercritical CO_2. As shown in Table 1, powdery products comprised of relatively monodisperse polymer particles were obtained when at least 3.5 wt % PDMS macromonomer was added to the polymerization. In addition, bimodal particle size distributions were evident when less than 3.5 wt % PDMS macromonomer was used. This indicates that an ag-

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Table 1. Dispersion Polymerization of MMA in Supercritical CO_2[a]

entry	stabilizer	% PDMS feed[b]	% PDMS incorporated[c]	yield, %	$\langle M_n \rangle$,[d] kg/mol	MWD[d]	product	particle size,[e] μm
1	none	0	na[f]	24	65	3.7	tacky solid	
2	PDMS	6.8	0.38, 0.72	51	210	2.5	hard solid	
3	PDMS macromonomer	0.05	0.00, na	56	271	2.4	hard solid	
4	"	0.26	0.25, 0.00	67	280	2.1	hard solid	2.8 (1.52)
5	"	1.7	0.11, 0.08	70	200	2.6	mixed	2.8 (1.12)
6	"	3.5	0.01, na	80	383	2.1	powder	2.8 (1.03)
7	"	5.2	0.14, na	89	378	2.1	powder	2.2 (1.02)
8	"	6.7	0.24, 0.26	87	386	2.1	powder	2.0 (1.01)
9	"	16	0.41, 0.68	88	363	2.3	powder	1.1 (1.05)

[a] Reactions were conducted at 65 °C and 340 bar for 4 h with 2.1 g of MMA and 0.0070 g of AIBN. [b] wt % PDMS based on monomer plus PDMS or PDMS macromonomer added to the reaction. [c] wt % PDMS remaining in the product after washing with hexanes (first value) or extraction with liquid CO_2 (second value), as determined by ^{1}H NMR spectroscopy. [d] Values obtained for samples after washing with hexanes to remove PDMS or unreacted PDMS macromonomer. [e] D_n, number average diameter. The value in parentheses is the PSD (particle size distribution) $= D_w/D_n$.[35] Particle size reported only when well-defined particles were obtained. [f] na = not applicable; no CO_2 washing experiments conducted for this sample.

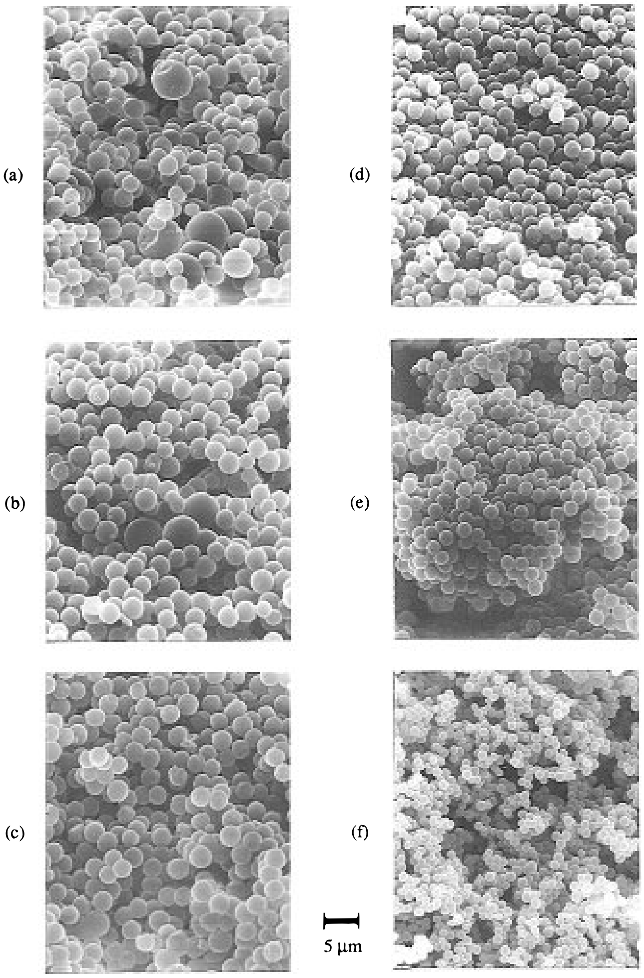

Figure 1. SEMs of PMMA particles synthesized in supercritical CO_2 with (a) 0.26 wt % PDMS macromonomer, (b) 1.7 wt % PDMS macromonomer, (c) 3.5 wt % PDMS macromonomer after washing with hexanes, (d) 5.2 wt % PDMS macromonomer after washing with hexanes, (e) 6.7 wt % PDMS macromonomer after extraction with liquid CO_2, and (f) 16 wt % PDMS macromonomer after extraction with liquid CO_2.

glomeration mechanism may be operating in the absence of sufficient stabilizer to protect the total particle surface.[26]

Table 2. Dispersion Polymerization of MMA in Liquid CO_2 Stabilized with PDMS Macromonomer[a]

entry	% PDMS feed[b]	% PDMS incorporated[c]	yield, %	$\langle M_n \rangle$[d] kg/mol	MWD[d]	product	particle size[e] μm
10	0		46	14	5.3	tacky solid/ powder	
11	2.5	0.05	94	123	2.3	hard solid/ powder	5.8 (1.17)
12	4.3	0.18	88	141	2.5	powder	2.9 (1.52)
13	6.2	0.41	89	151	2.3	powder	2.9 (1.22)

[a] Reactions were conducted at 30 °C and 69 bar for 21 h with 2.1–2.3 g of MMA and 0.0260 g of V-70. No attempt was made to optimize the reaction time. [b] wt % PDMS based on monomer plus PDMS macromonomer added to the reaction. [c] wt % PDMS remaining in the product after washing with hexanes, as determined by ^{1}H NMR spectroscopy. [d] Values obtained for samples after washing with hexanes to remove unreacted PDMS macromonomer. [e] D_n, number average diameter. The value in parentheses is the PSD (particle size distribution) $= D_w/D_n$.[35]

PDMS homopolymer (lacking the reactive MMA terminus) was not very effective in stabilizing the dispersion polymerization of MMA in supercritical CO_2. As shown in Table 1, the results obtained for a control reaction conducted with 6.8% PDMS homopolymer ($\langle M_n \rangle = 1.33 \times 10^4$ and MWD $= 1.1$[27]) were similar to those obtained for the reaction conducted with 0.05 wt % PDMS macromonomer. These results are consistent with those obtained by Pelton *et al.* for the AIBN-initiated dispersion polymerization of MMA conducted in heptane in the presence of either of two different PDMS homopolymers ($\langle M_n \rangle$ ca. 1.39×10^5 and 3.08×10^5).[28] Pelton *et al.* attributed their results to the stability of PDMS to hydrogen abstraction by AIBN and by growing PMMA chains,[28] which prevented the *in situ* formation of PDMS-*g*-PMMA and subsequent stabilization of the polymerization.

Results for dispersion polymerization of MMA conducted in liquid CO_2 are summarized in Table 2. Comparison of polymerizations conducted with and without added PDMS macromonomer shows that the addition of PDMS macromonomer was necessary to obtain high yields of high molecular weight polymers. For reactions conducted with added PDMS macromonomer, the yields and molecular weights of the polymers obtained did not change significantly as the concentration of the PDMS macromonomer was varied. In contrast to the reactions conducted in supercritical CO_2 over a similar macromonomer concentration range, the particles obtained from the polymerizations conducted in liquid CO_2 were much larger and had much larger particle size distributions.[30]

The GPC analysis of the PMMA prepared in CO_2 with added PDMS macromonomer showed a low molecular weight shoulder at ca. 1.4 x 10^4 prior to washing and extraction, which corresponded to unreacted PDMS macromonomer. As shown in Tables 1 and 2, analysis of ^{1}H NMR spectra of the products obtained before and after washing and/or extraction showed that only a fraction of the PDMS macromonomer added to the polymerizations was incorporated into the PMMA obtained. Comparison of entries 5−8 in Table 1 with entries 11−13 in Table 2 shows that slightly more PDMS was incorporated into the polymers prepared in liquid CO_2 than in supercritical CO_2. It should be noted that when MMA and PDMS macromonomer are copolymerized in toluene, a good solvent for both MMA monomer and the PDMS macromonomer, the amount of PDMS incorporated into the polymer obtained is relatively close to the amount added to the reaction.[31] The results obtained in the present study are consistent with the low macromonomer reactivities observed for copolymerizations conducted in a selective solvent for the macromonomer.[32]

To show the versatility of PDMS macromonomer as a stabilizer for dispersion polymerizations conducted in CO_2, the dispersion polymerization of styrene (2.0 g) was conducted in CO_2 at 340 bar and 65 °C for 24 h. Using 0.040 g of AIBN and 2.5 wt % PDMS macromonomer, a powdery product was obtained in 71% yield with a $\langle M_n \rangle$ of 1.8×10^4 and a MWD of 3.1. In contrast, when stabilizer was not added to the reaction, polystyrene with a $\langle M_n \rangle$ of 4.3×10^3 and a MWD of 3.2 was obtained in 30% yield. These results are comparable to those obtained for the dispersion polymerization of styrene in supercritical CO_2 stabilized by polystyrene-*b*-poly(FOA).[33] However, as expected,[34] the polymer particles obtained from the reaction conducted with macromonomer were much larger than those obtained from a reaction conducted with a comparable amount of block copolymer. It should be noted that both reactions conducted in CO_2 yielded polystyrene particles with broad size distributions.

In conclusion, a commercially available PDMS macromonomer has been used to stabilize the dispersion polymerization of MMA in liquid and supercritical CO_2 and of styrene in supercritical CO_2. Purification of the PMMA obtained showed that only a fraction of the macromonomer added to the polymerization actually copolymerized. We are currently investigating the role that unreacted PDMS macromonomer plays in stabilizing these dispersion polymerizations and are extending the use of PDMS-based macromonomers to the stabilization of the other heterogeneous polymerizations in CO_2.

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Supporting Information Available: Experimental details of the polymerizations in supercritical and liquid CO_2 (2 pages). Ordering information is given on any current masthead page.

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