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Cationic Dispersion Polymerizations in Liquid Carbon Dioxide

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ABSTRACT: The successful cationic dispersion polymerization of styrene in liquid carbon dioxide using amphiphilic block copolymers is reported. Vinyl ether block copolymers consisting of a CO_2-philic fluorinated segment and a poly(methyl vinyl ether) anchoring segment were employed to stabilize the growing polystyrene (PS) particles. The effect of stabilization in these polymerizations on molar mass, molar mass distribution, and polymer yield was studied as a function of temperature and surfactant composition. Scanning electron microscopy confirmed the formation of PS particles ranging in size from 300 nm to 1 μm in diameter.

Introduction

In contrast to the homogeneous polymerization of many fluorinated and silicone monomers in CO_2,[1] the polymerization of hydrocarbon monomers results in precipitation reactions that are often characterized by low yields,[2−7] broad molar mass distributions[2,6,8] and poorly controlled reactions.[2,9] In conventional solvent systems, these problems, associated with the low solubility of the growing polymer, can often be overcome by performing dispersion polymerizations. Dispersion polymerizations are characterized by the solubility of both the monomer and the initiator in the continuous phase and the insolubility of the resulting polymer in the continuous phase.[10,11] Because the polymer is stabilized as a colloid, higher yields and a higher degree of polymerization may be achieved compared to the analogous precipitation reaction in the absence of a stabilizer. Also, the polymer can be isolated as spherical particles (typically in the range of 0.1−10 μm in diameter), a form that facilitates processing and workup and is desirable in many applications.

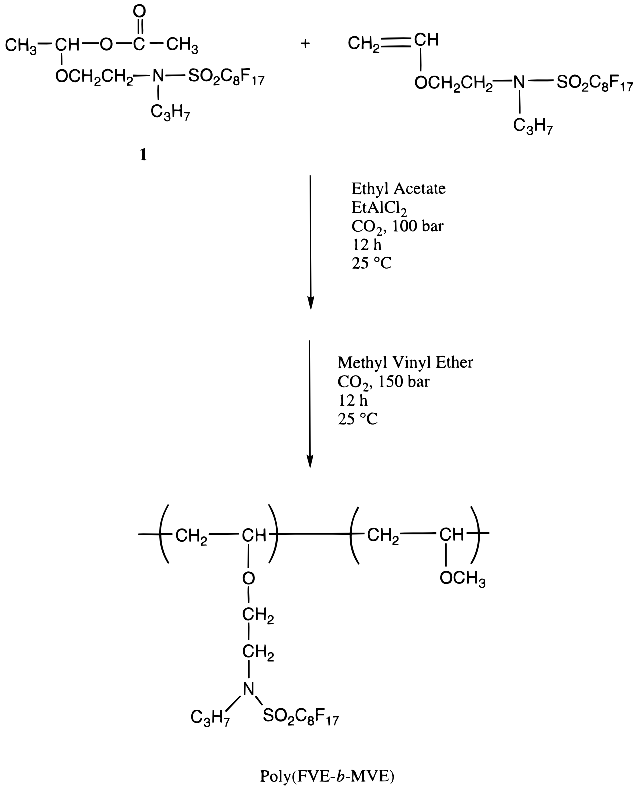
Free radical dispersion polymerizations have been performed by the use of steric stabilizers for a number of organic solvents[12−17] and carbon dioxide.[18−22] Anionic dispersion polymerizations of styrene in hexane have also been reported.[23] Both homopolymers and amphiphilic copolymers have been employed as stabilizers. However, reports indicate that block and graft copolymers are the best surfactants for the steric stabilization of polymer colloids in media of low polarity.[24]

Carbon dioxide exhibits many properties that make it an excellent choice as a reaction medium for cationic polymerizations such as a large diffusion coefficient, low viscosity, and low dielectric constant.[8] Further, it is nontoxic, inexpensive, nonflammable, abundant, easily recycled, and environmentally acceptable. As evidenced by these important features, CO_2 has been employed in numerous studies as a solvent for cationic polymerizations.[2−9,25,26] However, we are not aware of any report of cationic dispersion polymerizations in any solvent system, including CO_2. We report here the first cationic dispersion polymerization in CO_2, which allows for the production of oil-soluble polymers in high yields in the form of powders.

Experimental Section

Reagents and Solvents. Unless otherwise indicated, all solvents and reagents were purchased from Aldrich, were of reagent grade, and were used without further purification. SFC grade carbon dioxide was supplied by Air Products. Ethyl acetate and styrene were distilled twice under argon from calcium hydride prior to use. 2-(*N*-Propylperfluorooctanesulfonamido)ethyl vinyl ether (FVE) (Dainippon Ink Company) was recrystallized three times from ethanol and dried under vacuum. The initiator **1** (Scheme 1) was synthesized by treating FVE with acetic acid at 60 °C for 24 h and distilling under vacuum.

Scheme 1. Synthesis of FVE-*b*-MVE Copolymers in CO_2



Physical Methods. A Waters 150-CV gel permeation chromatograph (GPC) with Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosities in THF was used with PS standards to determine the molar mass and the molar mass distribution of the PS samples. M_n and M_w were estimated for the block copolymers using a Waters 610 GPC with 10^3 and 10^4 Å columns in a mixed solvent of 75%:25% trifluorotoluene toluene (v/v) vs PS standards. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-400 NMR spectrometer using $CDCl_3$ as the solvent. Scanning electron microscopy (SEM) was performed on a JEOL 6400 FE scanning electron microscope.

Stabilizer Syntheses. The 25 mL high-pressure Hastelloy reaction vessel has been described previously.[8] The block

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Scheme 2. Cationic Dispersion Polymerization of Styrene in Carbon Dixoide

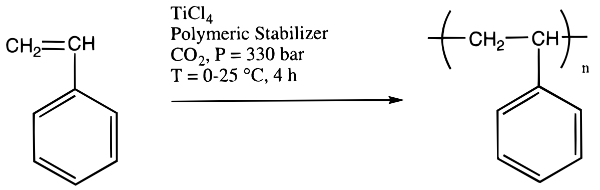

Table 1. Vinyl Ether Block Copolymers

sample	M_n total[a]	M_n fluorinated block[b]	PDI[c]	T_g (°C)
1	20K	18K	1.09	−59, −25.4
2	17K	16K	1.10	−55, −1.7
3	18K	17K	1.10	−45, −1.5

[a] Number average molecular weight determined by GPC against PS standards. [b] Calculated from composition determined by ^{1}H NMR. [c] Polydispersity index determined by GPC.

copolymers were synthesized by living cationic methods using sequential monomer addition.[8,27] First, the fluorinated alkyl sulfonamide vinyl ether monomer, ethyl acetate, and **1** were added to the body of the cell, and ethyl aluminum dichloride (1 M solution in hexane) was added to a Hastelloy dish located within the body of the cell. The reagents were mixed as the cell was pressurized to 100 bar with CO_2. The reaction temperature was maintained at 25 °C, and the reaction was allowed to proceed for 12 h. Methyl vinyl ether (MVE) was then added to the cell using a high-pressure syringe pump (High Pressure Equipment), and a sufficient amount of CO_2 was added to give a final pressure of 150 bar. The reaction was allowed to proceed for another 12 h, then the CO_2 was vented through a pressure relief valve, and the reaction was terminated by the addition of deoxygenated methanol (Scheme 1). The polymers were dissolved in THF, filtered to remove fluorinated homopolymer and washed with water to remove poly(methyl vinyl ether) homopolymer. The synthesis of the other stabilizer investigated, poly(styrene-*b*-dimethylsiloxane), has been previously described.[28] The homopolymer poly(FVE) used for surfactant comparison studies was synthesized according to literature procedures.[8]

Dispersion Polymerizations. Styrene monomer and the polymeric stabilizer were added to the body of the cell, and titanium tetrachloride was added to the Hastelloy dish. Carbon dioxide was then added to a pressure of 330 bar, and the reaction was stirred for 4 h. The reaction mixture was initially homogeneous, but minutes after the polymerization was initiated the solutions became cloudy and opaque with the appearance characteristic of a latex. Latex stability depended upon the particular surfactant used in each reaction. At the end of the reaction, the CO_2 was removed by venting into methanol, and additional methanol was added to the cell to quench the remaining mixture (Scheme 2). The polystyrene products were dried overnight under vacuum, and yields were determined gravimetrically. For comparison, control reactions were also conducted in the absence of stabilizer.

Results and Discussion

The fluorinated block copolymers were synthesized (Scheme 1) using FVE and MVE. The reaction mixtures remained homogeneous throughout the course of the polymerization of the fluorinated monomer but became slightly cloudy as the methyl vinyl ether was consumed. (For simplicity, the surfactants will be noted by listing the M_n of the CO_2-soluble fluorinated or siloxane block followed by the M_n of the anchoring block.) Table 2 lists the results of the cationic dispersion polymerization of styrene in CO_2 at three temperatures using the 17K/1K surfactant. The results are compared with reactions performed under identical conditions without surfactant.

Table 2. Cationic Dispersion Polymerizations of Styrene Using 17K/1K Surfactant

sample	% surfactant[a]	temp (°C)	molar mass[b]	PDI[b]	% yield
1	4	0	5.0×10^3	2.6	6
2	4	0	2.4×10^3	5.4	24
3	0	15	6.3×10^3	6.2	42
5	1	15	1.5×10^4	4.2	95
4	4	15	1.8×10^4	4.0	97
6	0	25	3.9×10^3	3.1	57
7	0	25	4.0×10^3	3.1	60
8	4	25	4.9×10^3	2.6	82
9	4	25	4.2×10^3	1.9	79

[a] Weight percent compared to monomer. [b] Determined by GPC against PS standards.

Polymerizations conducted at 0 °C with added stabilizer resulted in low yields and no apparent stabilization by the surfactant. The polymer precipitated from the reaction medium without evidence of a stable polymer colloid and the SEM's of the product showed no particle formation. The absence of stabilization by the surfactants is attributed to their low solubility in CO_2 at 0 °C, rendering them ineffective as stabilizers and resulting in low yields and broad PDI's.

Reactions performed at 15 °C with the 17K/1K surfactant (either 1 or 4 wt %) resulted in polymerizations which had a uniform milky white appearance characteristic of a stabilized polymer colloid. The molar masses of the stabilized polystyrene samples were nearly an order of magnitude higher than those synthesized at 0 °C, and essentially quantitative yields of polystyrene were obtained. In contrast, polymerizations performed without surfactant at 15 °C resulted in a lower yield and a lower M_n. For the stabilized reactions, polystyrene products could be isolated from the reactor as free-flowing powders, while those polymerized in the absence of stabilizer were isolated as fused masses. The stabilized polystyrene products redispersed when placed in Freon-113. SEM analysis of the polymer synthesized at 15 °C with 1% stabilizer indicated the formation of spherical particles with diameters of approximately 1 μm and a broad particle size distribution. Increasing the surfactant concentration to 4% resulted in an increase in the surface area that could be covered by the surfactant and smaller particles with a more uniform particle size distribution. Figure 1 shows the scanning electron micrographs of the polystyrene samples synthesized at 15 °C in the presence of 1% and 4% surfactant.

Overall, molar masses obtained at 25 °C are lower than those for reactions conducted at 15 °C. This effect is attributed to a higher rate of chain transfer to monomer at the higher temperature. However, the yield is higher and the polydispersity index is smaller when the 17K/1K surfactant is added to the polymerization mixture. As with the polymerizations conducted at 15 °C, the reaction mixtures had the milky appearance characteristic of a latex in the presence of surfactant. The molar masses of the polymers synthesized at 25 °C were independent of the surfactant concentration. The scanning electron micrographs of a stabilized polystyrene sample and an unstabilized sample synthesized at 25 °C are shown in Figure 2. Although particle formation is evident from the micrograph in 2(b), significant particle coagulation is observed, possibly due to the lower yield and lower molecular weight of the polystyrene.

Table 3 compares the results of the 18K/2K, 16K/1K, and 17K/1K FVE-*b*-MVE block copolymer surfactants

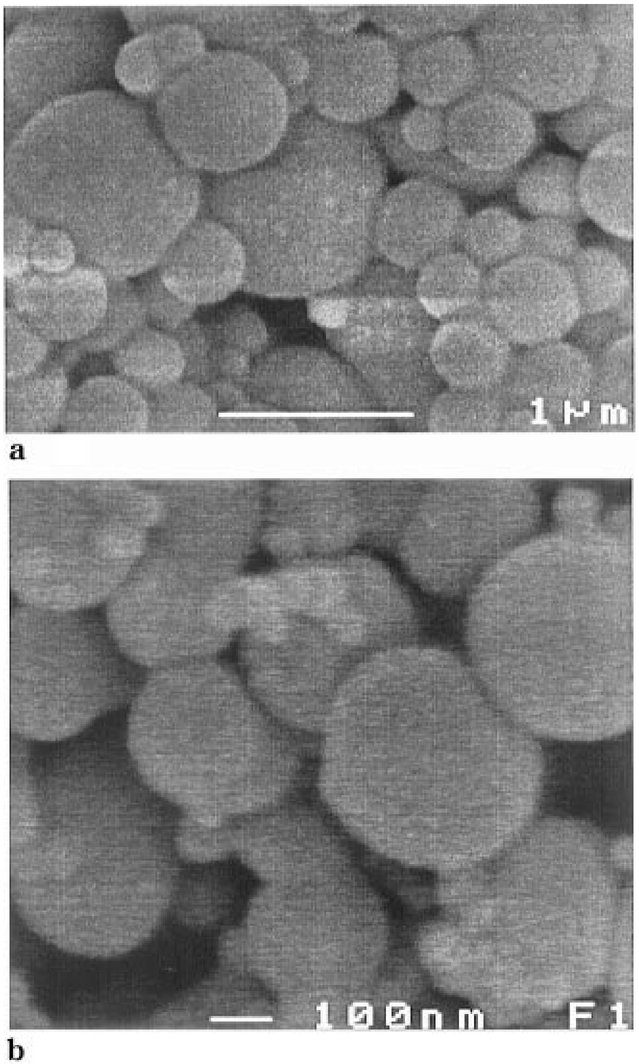

Figure 1. (a) SEM of PS made with 1% (17K/1K) p(FVE-*b*-MVE) surfactant at 15 °C. (b) SEM of PS made with 4% (17K/1K) p(FVE-*b*-MVE) surfactant at 15 °C.

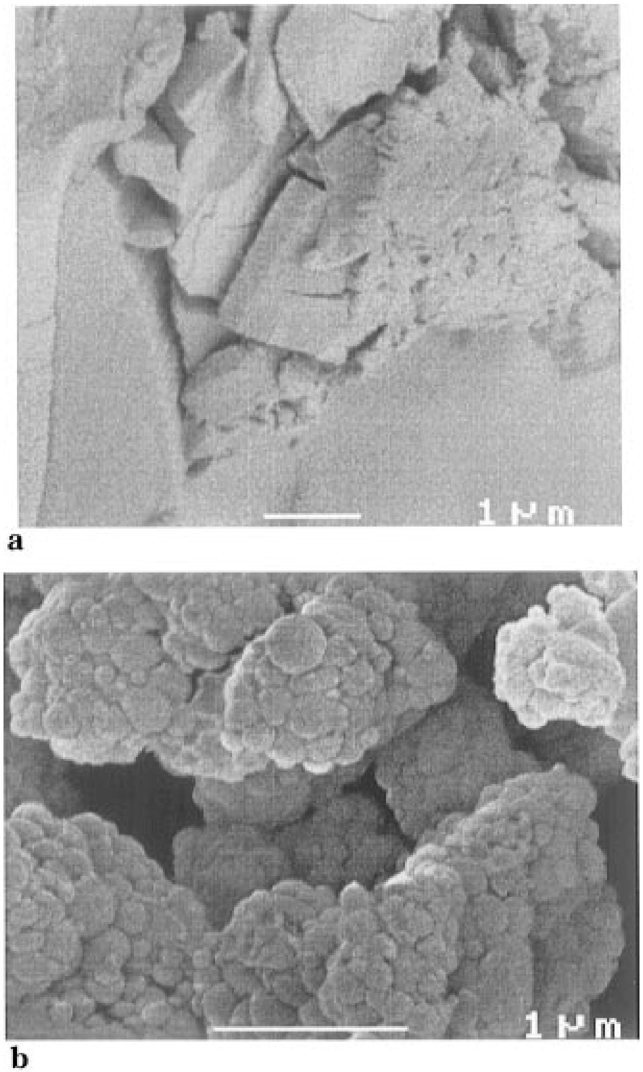

Figure 2. (a) SEM of PS made with no surfactant at 25 °C. (b) SEM of PS made with 4% (17K/1K) p(FVE-*b*-MVE) surfactant at 25 °C.

Table 3. Styrene Dispersion Polymerizations with Different Vinyl Ether Stabilizers

sample	surfactant[a]	temp (°C)	molar mass[b]	PDI[c]	yield
1	18K/2K[d]	15	3.8×10^3	4.2	25
2	16K/1K[d]	15	3.1×10^4	4.0	94
3	17K/1K[d]	15	1.5×10^4	4.2	95

[a] 4% surfactant relative to monomer. [b] Determined by GPC against PS standards. [c] Polydispersity index (M_w/M_n). [d] Number average molar mass (M_n) of first block (FVE)/M_n of second block (MVE).

to stabilize polystyrene polymerizations at 15 °C in carbon dioxide. The surfactant with the higher MVE content (18K/2K) did not sufficiently stabilize the growing polystyrene particles, as indicated by the low yield and molar mass and the lack of latex formation during the polymerization. The longer MVE chain may reduce the solubility of the block copolymer in CO_2, thus inhibiting the stabilization of the growing polymers. In contrast, as the MVE content was decreased, successful stabilization of the polymerization was achieved which resulted in higher product molar mass and yield.

The cationic dispersion polymerization in CO_2 was also attempted at 15 °C using the homopolymer poly(FVE) as a stabilizer. Although the reaction appeared milky white, even when stirring was stopped, polymer precipitation was observed on the windows of the cell and the resulting polymer product was in the form of chunks and a fused mass. The milky white appearance was probably due to only a slight stabilization by the homopolymer, with the majority of the product being formed as a precipitate. SEM confirmed the absence of particle formation. The yields were much lower than those of the 17K/1K surfactant, but were higher than the reaction performed without surfactant. The yields ranged from about 45 to 65% and were not reproducible, as opposed to those reactions employing effective stabilizers. These results indicate that the homopolymer is not a suitable stabilizer for the dispersion polymerization of styrene in CO_2. This result is not surprising since the homopolymer lacks a suitable anchoring group to the polystyrene particle, rendering insufficient stabilization.

Poly(dimethylsiloxane-*b*-styrene) (PDMS-*b*-PS) copolymers have been shown to be suitable surfactants for free radical dispersion polymerizations of polystyrene in CO_2.[28] In order to compare the efficiency of the vinyl ether surfactants to previously studied surfactants, cationic polymerizations of styrene were carried out using the PDMS-*b*-PS stabilizers. This surfactant was not suitable for the stabilization of polystyrene by cationic dispersion polymerization. The products were obtained in low yields (<40%) and had low molecular weights (M_n < 4000). Further, the results were highly irreproducible. GPC analysis of the surfactant before and after treatment with titanium tetrachloride in CO_2 indicated that the PDMS chain was decomposed by $TiCl_4$, making it an undesirable stabilizer for the reaction conditions studied here.

Conclusion

We have successfully conducted cationic dispersion polymerizations in CO_2. This constitutes a rare example of a cationic dispersion polymerization in any solvent and the first example in CO_2. A reaction temperature near 15 °C appears to work best for suppression of chain transfer to monomer while maintaining solubility and surface activity of the stabilizer. The vinyl ether stabilizers synthesized here show higher chemical stability under cationic conditions and greater versatility than other PDMS-based surfactants. The use of amphiphilic polymeric stabilizers for cationic dispersions in CO_2 allows for the utilization of carbon dioxide's unique solvent properties while bypassing the problems inherent to polymer precipitation.

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