Precipitation Polymerization of Acrylic Acid in Supercritical Carbon Dioxide

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ABSTRACT: We report the successful precipitation polymerization of acrylic acid in supercritical carbon dioxide at pressures ranging from 125 to 345 bar utilizing AIBN as a free radical initiator. Analyses by gel permeation chromatograpy (GPC) and scanning electron microscopy (SEM) indicate that for the pressure range studied there is no appreciable effect on product molecular weight, molecular weight distribution, or particle size or morphology. In addition, effective molecular weight control was demonstrated for precipitation polymerizations of acrylic acid in CO_2 through the use of ethyl mercaptan as a chain transfer agent.

Introduction

Increasing concern regarding the dissemination of chemical waste (both aqueous and organic) into our environment has prompted considerable interest in new technologies aimed at reducing current waste streams. Processes utilizing carbon dioxide in lieu of conventional solvents for chemical manufacturing and processing provide a viable route to achieving near-zero waste production for these important industries. The homogeneous (solution) polymerization[1,2] and telomerization[3] of several fluorinated monomers in supercritical carbon dioxide were recently reported by us. Utilizing supercritical carbon dioxide as a solvent alleviates the need for chlorofluorocarbons for the homogeneous synthesis of these fluorinated polymers and telomers in addition to providing other advantages, such as high mass transport rates, no Tromsdorff effects, and no chain transfer to solvent. Poly(1*H*,1*H*-perfluorooctyl acrylate) (3M) and poly(1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate) (Dupont) represent examples of a limited number of polymers which exhibit high enough solubility in CO_2 to allow the use of solution polymerization techniques (general classes of polymers which are highly soluble in CO_2 include amorphous fluoropolymers and silicones). Therefore, to extend the advantages of polymerization in supercritical CO_2 to other systems it is necessary to pursue heterogeneous polymerization processes. There are four basic heterogeneous polymerization processes: emulsion, suspension, dispersion, and precipitation. These processes can be distinguished by (i) the initial phase behavior of the polymerization mixture, (ii) the polymerization kinetics, and (iii) the mechanism of particle formation.[4] We recently reported the development of a dispersion polymerization process for methyl methacrylate in carbon dioxide.[5]

Poly(acrylic acid) is commonly prepared by aqueous solution polymerization, suspension polymerization, inverse emulsion polymerization in hydrocarbons, or precipitation polymerization in halohydrocarbons or aromatic hydrocarbons.[6] When solution, suspension, or emulsion processes are utilized to prepare cross-linked resins, it is necessary to utilize water-soluble cross-linking agents—many of which are sensitive to post-polymerization neutralization processes.[7] For emulsion and suspension processes there can often be problems with residual surfactants and stabilizers. In addition, there is usually additional expense associate with adding these materials (and removing them when necessary). For applications where clean, dry, poly(acrylic acid) or a poly(acrylic acid) derivative is desired (such as for use in superabsorbents), costly purification and drying processes are often necessary. Precipitation polymerization in organic media alleviates some of the cost associated with rigorous drying and allows the use of oil-soluble multifunctional comonomers, but there are obvious environmental concerns associated with the volatile organic compounds (VOCs) utilized for these processes. There are also health issues surrounding many of the conventional solvents, especially when products are for use in direct human contact, and for some solvent systems molecular weight can be limited by chain transfer to solvent.

Processes utilizing supercritical carbon dioxide as a dispersing medium for the manufacture of poly(acrylic acid) offer an attractive alternative to conventional methodologies in that reaction products are virtually free of organic and aqueous contamination. In addition, supercritical fluid extraction (SFE) processes[8] could be used *in situ* to remove small amounts of unreacted monomer and any surfactant or stabilizer added to aid in polymerization. This advantage would be especially beneficial for applications where such impurities would have deleterious consequences (cosmetics, toothpaste, etc.). Our previous work[1–3,5] and the work of others[9] have shown that CO_2 is an excellent medium in which to perform free radical reactions. There is virtually no chain transfer to CO_2, and mass transport rates for the solubilized monomer are significantly enhanced over those obtained in coventional solvents for the temperature and pressure ranges described here.[8] The polymerization of acrylic acid in the presence of CO_2 has been described previously in the patent literature, but these investigations were either focused on γ-ray-initiated processes or resulted in polymers that were not in a readily usable form[10] (hard chunks which resisted dissolution in water) and in other examples the products were intentionally cross-linked through the addition of difunctional comonomers; thus molecular weight characterization was not possible.[11,12]

Herein we describe the successful precipitation polymerization of acrylic acid in supercritical carbon dioxide utilizing 2,2′-azobis(isobutyronitrile) (AIBN) as

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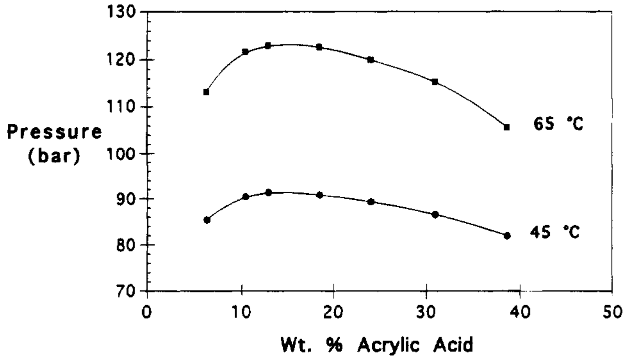

Figure 1. Partial two-component phase diagram for acrylic acid and carbon dioxide at 45 and 65 °C.

a free radical initiator to form high molecular weight linear polymer. Two independent studies are presented: a survey conducted to determine the effect of pressure on product molecular weight, molecular weight distribution, and particle size and morphology, and a series of reactions carried out to demonstrate the effectiveness of a common chain transfer agent, ethyl mercaptan, in precipitation polymerizations of acrylic acid in supercritical CO_2.

Experimental Section

Acrylic acid (99%, inhibited with 200 ppm hydroquinone monomethyl ether) and ethyl mercaptan (97%) were obtained from Aldrich and used as received. 2,2′-Azobis(isobutyronitrile), obtained from Eastman, was recrystallized twice from methanol before use. Carbon dioxide (instrument grade, 99.9%), obtained from Sunox, was purified by passing through columns of molecular sieves, activated BASF catalyst, and phosphorus pentoxide prior to use.

In a typical reaction, 2.5 mL of deoxygenated acrylic acid was charged to a 25-mL, stainless steel high-pressure view cell containing a magnetic stir bar. The cell was then sealed and enough liquid CO_2 was added to form a homogeneous solution occupying approximately half the cell volume. The temperature was then gradually increased to the desired reaction temperature of 62 °C. Carbon dioxide was then added to achieve the desired reaction pressure through a small tube containing a preweighed amount of AIBN.[13] For the experiments involving chain transfer agent, ethyl mercaptan was added with the acrylic acid. The only deviation from this protocol was for two of the reactions in the pressure series—in those cases monomer was added to the cell first and the cell was brought to temperature. Once at the desired temperature, all of the CO_2 was added through the tube containing initiator.[14] All reactions were allowed to proceed for 4 h at which time the cell was cooled and vented slowly. The product was collected as a fluffy, white, free-flowing powder. All reactions were run at 10 wt/vol % solids with 1.0 wt/vol % initiator (based on monomer). Reactions conducted in the presence of chain transfer agent were performed at 345 bar. In all instances, >90% conversion was achieved (based on ^1H NMR).

Scanning electron micrographs were taken by Dr. Dale Bachelor at North Carolina State University, and aqueous GPC analyses were conducted by researchers at Rohm and Haas Co.

Results and Discussion

The two-component phase diagram for acrylic acid and CO_2 mixtures has been previously determined and is partially reconstructed in Figure 1 for 45 and 65 °C.[11] This diagram shows that acrylic acid is highly soluble in carbon dioxide even at moderate pressures. Poly(acrylic acid) is essentially insoluble even at very low molecular weight. Based on these observations and commonly accepted solubility criteria for different heterogeneous polymerization processes,[4] precipitation and dispersion methodologies are most appropriate for the heterogeneous polymerization of acrylic acid in carbon dioxide continuous phases. This is highlighted by our recent success in the dispersion polymerization of methyl methacrylate.[5] Suspension and emulsion polymerization processes require that the monomer exhibit low solubility in the continuous phase. At densities where acrylic acid exhibits low solubility in CO_2, potential surfactants or stabilizers for these processes may also exhibit low solubility in the gaslike CO_2 phase, perhaps limiting the viability of emulsion and suspension processes for acrylic acid polymerization in CO_2. Based on this analysis we have pursued the precipitation polymerization of acrylic acid in CO_2.

Table 1. Summary of Molecular Weight and Molecular Weight Distribution Data for Acrylic Acid Precipitation Polymerizations in Supercritical Carbon Dioxide and Controls Conducted in Conventional Dispersing Media

pressure (bar)	mol fract AA/CO_2	M_n	MWD
125	0.118	149K	3.9
205	0.083	144K	3.8
275	0.075	146K	3.9
345	0.071	146K	3.8
controls			
benzene	N/A	134K	2.8
toluene	N/A	46K	2.1
methylene chloride	N/A	121K	2.6

For all of the precipitation polymerizations described here the reaction began as a homogeneous solution of carbon dioxide, monomer, initiator, and chain transfer agent in some cases. The onset of polymerization could be observed shortly after initiator was added as the reaction turned yellow, then orange (the growing first particles were just large enough to scatter visible light), and then white and cloudy. Within minutes white particles of solid precipitate could be observed settling to the cell bottom, and well before the allotted reaction time had elapsed the cell was filled with precipitated polymer. Upon venting the carbon dioxide, the products of all reactions were isolated as dry, free-flowing powders which readily dissolved in water. Analyses of products from reactions carried out at four different CO_2 pressures from 125 to 345 bar (Table 1) indicate that there was no discernible pressure effect on product molecular weight, molecular weight distribution, or particle size or morphology within this pressure range. Product molecular weights for these reactions are all just below 150 kg/mol with molecular weight distributions of 3.8–3.9. Electron micrographs of the products prepared at 125 and 345 bar are shown in Figure 2 (top and bottom, respectively). The micrographs show large aggregates of primary particles <100 nm in size and are representative of each of the reactions in this series.

Also shown in Table 1 are data for controls carried out in coventional solvents. Note that the relatively low monomer concentration and high initiator concentration used for all of the reactions represented in this study probably set limits for the obtained molecular weight. Therefore, expected deviations in molecular weight due to chain transfer to solvent were not obvious except in the case of toluene. Figure 3 shows a lower magnification comparison of reaction products obtained from dense CO_2 (345 bar) and from benzene (top and bottom, respectively). The micrographs are quite similar and show that poly(acrylic acid) prepared via precipitation polymerization in supercritical carbon dioxide compares favorably to that prepared in dispersing media commonly use by industrial manufacturers.

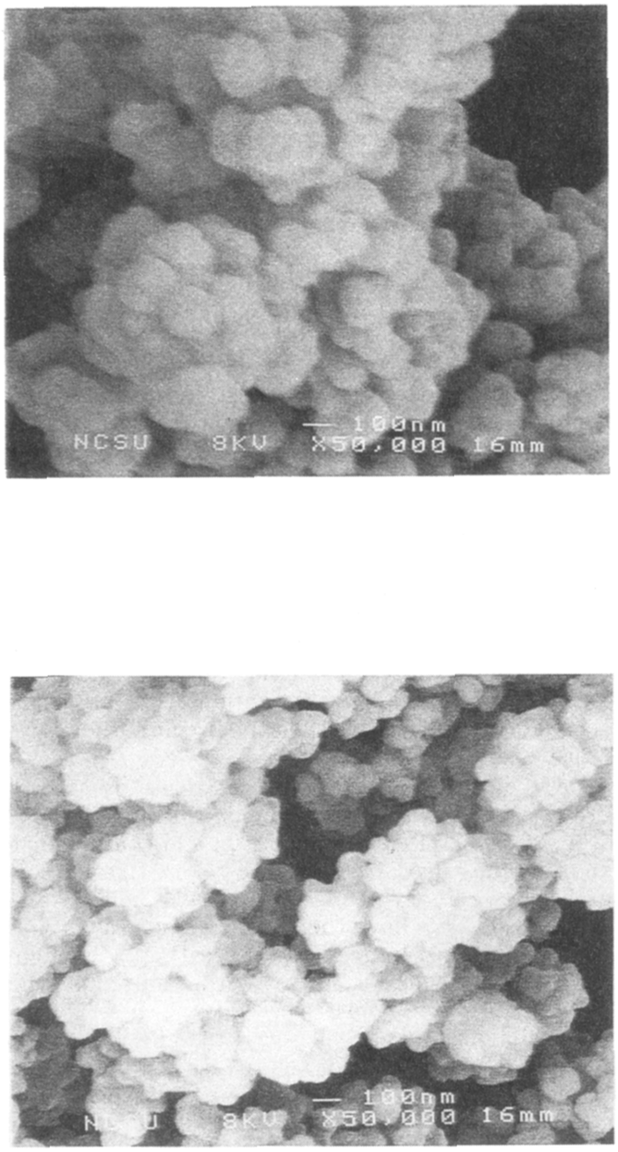

Figure 2. Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization in supercritical carbon dioxide at different pressures: (A, top) 125 bar; (B, bottom) 345 bar.

Table 2. Summaryof Molecular Weight and Molecular Weight Distribution Data for Precipitation Polymerizations of Acrylic Acid in Supercritical Carbon Dioxide with Ethyl Mercaptan Chain Transfer Agent Present

[EtSH]	[AA]	M_n	MWD
0.0012	1.34	153K	2.88
0.0060	1.34	68.1K	2.23
0.063	1.34	6.5K	1.71
0.169	1.34	2.9K	1.26

A series of reactions performed in the presence of varying amounts of ethyl mercaptan as a chain transfer agent demonstrate the achievement of effective molecular weight control. The molecular weight data and corresponding reagent concentrations for these reactions are given in Table 2. A plot of $1/X_n$ (X_n = number-average degree of polymerization) vs [ethyl mercaptan]/[acrylic acid] is linear with a correlation coefficient of 0.99 (Figure 4). The slope of this plot yields a chain transfer constant of 0.20. A value of 1.6 from solution telomerization studies was reported by other researchers.[15]

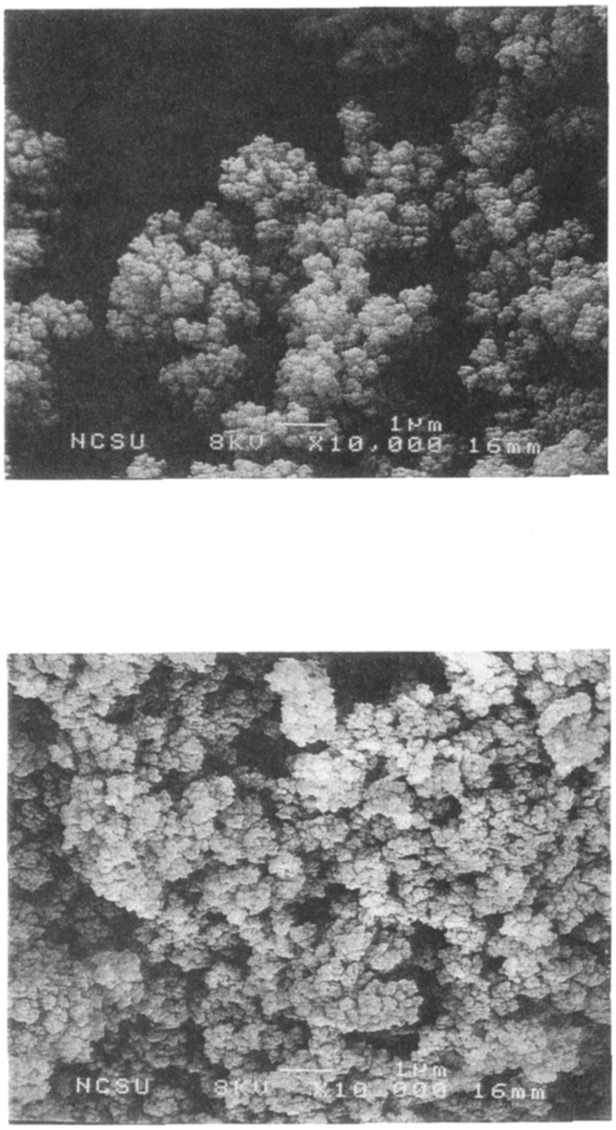

Figure 3. Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization: (A, top) in supercritical carbon dioxide at 345 bar; (B, bottom) in benzene.

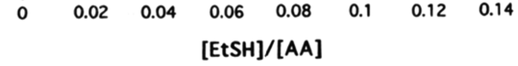

Figure 4. Plot of $1/X_n$ (X_n = number-average degree of polymerization) vs [ethyl mercaptan]/[acrylic acid] for acylic acid polymerizations in supercritical carbon dioxide with ethyl mercaptan added as a chain transfer agent; slope = 0.20, R = 0.99.

Conclusions

Acrylic acid has been polymerized in supercritical carbon dioxide utilizing AIBN as a free radical initiator at pressures ranging from 125 to 345 bar with no appreciable effect of pressure on product molecular weight, molecular weight distribution, or particle size or morphology. Effective molecular weight control was achieved for precipitation polymerizations of acrylic acid in CO_2 through the addition of ethyl mercaptan as a chain transfer agent. Molecular weight data and electron micrographs for poly(acrylic acid) prepared in carbon dioxide and for poly(acrylic acid) prepared in conventional solvents show that CO_2 compares favorably with conventional solvents as a dispersing media for the preparation of poly(acrylic acid).

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