Continuous Precipitation Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide: Molecular Weight Distribution

*Manish K. Saraf, Louis M. Wojcinski II, Karen A. Kennedy, Sylvain Gerard, Paul A. Charpentier, Joseph M. DeSimone, and George W. Roberts**

North Carolina State University
Department of Chemical Engineering
Raleigh, NC 27695-7905, USA

Summary: The surfactant-free precipitation polymerization of vinylidene fluoride (VF2) in supercritical carbon dioxide was studied in a continuous stirred autoclave. The polymerization temperature ranged from 65 to 85 °C, the average residence time in the reactor varied from 10 to 50 min., and the pressure was between 210 and 305 bar. Diethyl peroxydicarbonate was used as the initiator. The fractional conversion of monomer varied from 7 to 26%, the number-average molecular weight of the polymer was between about 14,000 and 79,000, and the weight-average molecular weight was between about 21,000 and 700,000. In many cases, the polymer exhibited a bimodal molecular-weight distribution, especially at high monomer concentrations.

Introduction

Over the last several decades, considerable research has been devoted to finding environmentally benign solvents and processes for industrial use[1]. This effort has been driven by increasing regulation of emissions of volatile organic compounds (VOCs), and by the increasing cost of treating wastewater containing organic compounds. DeSimone and coworkers have shown that a variety of free-radical, cationic and step-growth polymerizations[2-5] can be carried out in supercritical carbon dioxide (scCO$_2$). Carbon dioxide is: 1) inert to highly electrophilic radicals, i.e., there is no chain transfer to solvent; 2) inexpensive (\$100-200/ton); 3) non-toxic and non-flammable, and; 4) environmentally benign. The use of carbon dioxide as a polymerization medium can lead to: a) a significant reduction in the energy required for polymer drying; b) elimination of organic solvents, and; c) a reduced requirement for wastewater treatment to remove monomers, surfactants, and emulsifiers[6]. Indeed, DuPont has announced its intention to manufacture Teflon™ commercially in CO$_2$ by 2006[7].

As industrial interest in using scCO$_2$ as a polymerization medium has grown, the need

CCC 1022-1360/00/\$ 17.50+.50/0

for continuous processes to harness the advantages of this medium is being recognized. A continuous system requires smaller, less expensive equipment for large volume polymers. Moreover, recycling of unreacted monomer and supercritical fluid is facilitated in a continuous system. We reported previously on a continuous process for the precipitation polymerization of various monomers, including acrylic acid, in $scCO_2$[8].

Poly(vinylidene fluoride) (PVDF) is a semicrystalline, thermoplastic polymer widely used for fabricating pipe, tubing in plastic heat exchangers, column packing, valves, and pumps[9]. This polymer is produced commercially in batch reactors by either emulsion or suspension techniques, at monomer pressures of between 10 and 200 bar and temperatures from 10 to 130 °C[10,11]. In the emulsion process, the latex is coagulated, thoroughly washed, and then spray-dried to form a free-flowing powder. The suspension technique requires separation of the polymer from the water phase, thorough washing, and then drying. In both processes, large quantities of wastewater are generated and large quantities of energy are required to dry the polymer. A continuous, environmentally-friendly process for PVDF manufacture would be attractive if it could eliminate the generation of waste streams, and minimize the need for polymer drying.

This paper describes an effort to understand the behavior of vinylidene fluoride (VF2) polymerization in $scCO_2$, initiated by the organic peroxide, diethyl peroxydicarbonate (DEPDC). Diethyl peroxydicarbonate was chosen because the starting materials for its synthesis are readily available and the synthesis itself is straightforward, as described below. Diisopropyl peroxydicarbonate (DIPPDC) is used in some suspension and emulsion processes, but the synthesis of this compound is more complex. The decomposition kinetics of DIPPDC and DEPDC are essentially the same[12].

A continuous stirred autoclave reactor was used. Experiments were carried out at monomer inlet concentrations ranging from 0.4 to 3.5 M, initiator inlet concentrations ranging from 8 to 50 x 10^{-4} M, temperatures from 65 to 85 °C, total pressures from 210 to 305 bar, and mean residence times from 10 to 50 minutes.

Experimental

Materials. Vinylidene fluoride monomer was generously donated by Solvay Research, Belgium and used without further purification. Carbon dioxide (SFE/SFC grade) was generously donated by Air Products & Chemicals, Inc. and further purified by passage through columns containing 5A molecular sieves (Aldrich) and copper oxide (Aldrich) to remove excess water and oxygen, respectively. All other chemicals were obtained from the Aldrich Chemical Company.

Initiator Synthesis. The DEPDC initiator was synthesized as previously reported, using water as the reaction medium and extracting the initiator into Freon® 113 (HPLC Grade)[13,14]. All manipulations of the initiator were performed in an ice bath and the final product was stored in a cold chest at -20 °C. The iodine titration technique, ASTM Method E 298-91, was utilized to determine the concentration of active peroxide in the solution. The decomposition of DEPDC in $scCO_2$ obeyed a first-order rate law[12]. No significant solvent or pressure dependence was observed. The measured initiator efficiency, $f \cong 0.6$, is typical for an organic peroxide[15].

Polymerization Apparatus. Figure 1 is a schematic diagram of the experimental apparatus. The equipment and the procedure has been described in detail elsewhere[8,16]. Polymerization took place continuously in an agitated, 800 mL autoclave. Three streams, CO_2, VF2, and DEPDC in Freon® 113, were fed continuously to the reactor with individual syringe pumps. The produced polymer, CO_2, and unreacted VF2 and DEPDC, left the reactor continuously. Control of the reactor temperature (T) and pressure (P) was excellent during a polymerization ($T = \pm 0.3$ °C and $P = \pm 1$ bar). Feed rates of initiator and monomer from the syringe pumps were ± 0.1%.

The residence time distribution (RTD) of the experimental reactor, and the decomposition kinetics of DEPDC, were determined in independent experiments, as reported elsewhere[14]. For all conditions studied, the RTD of the reactor agreed closely with that of an ideal, continuous stirred tank reactor (CSTR).

The mean residence time of the reactor, τ, is defined as the reactor volume, V, divided by the volumetric flowrate, v. Collection of "steady-state" polymer normally was started after the reactor had been operating for five mean residence times by switching from one of the parallel filters, shown in Figure 1, to the other. As reported previously[8], essentially all of the formed polymer was collected on 1 μm filters.

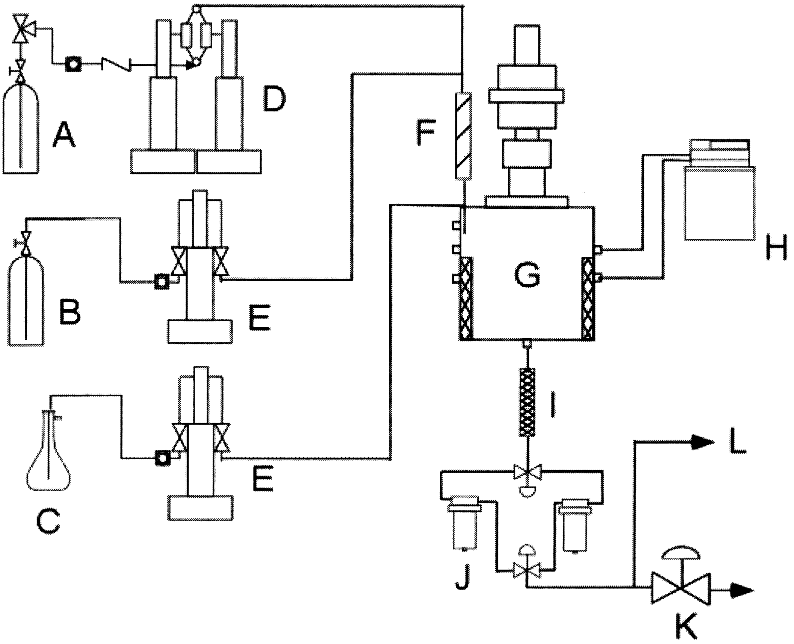

Figure 1. Continuous Polymerization Apparatus: A-CO_2 Cylinder; B-Monomer; C-Initiator Solution; D-Continuous CO_2 Pump; E-Syringe Pumps; F-Static Mixer; G-Thermostated Autoclave; H-Chiller/Heater Unit; I-Effluent Cooler; J-Filters; K-Heated Control Valve; L-Gas Chromatograph.

Gel Permeation Chromatography (GPC). Gel permeation chromatography measurements on the polymer samples were performed by Solvay Research, Belgium at 40 °C on a Waters-Alliance HPLC system with 2x HR5E and 1x HR2E columns, using N,N-Dimethylformamide (DMF) modified with 0.1M LiBr. The GPC was calibrated at 40 °C using narrow molecular weight distribution standards of poly(methyl methacrylate) (PMMA) purchased from Polymer Laboratories Ltd.

Results

Experimental Phase Behavior. Under the experimental conditions studied, VF2 and DEPDC were completely miscible with CO_2, while the formed polymer powder, PVDF, was imiscible in CO_2. These studies were performed in a variable-volume view cell, similar in design to that reported elsewhere[1]. Our observations on the solubility of PVDF in CO_2 agree with recently reported data on PVDF/CO_2 and PVDF/CH_2F_2[17]. This phase behavior indicates a precipitation polymerization[15].

Figure 2 shows the molecular weight distribution (MWD) as a function of the concentration of VF2 in the feed to the reactor, at otherwise constant conditions. At low monomer concentrations, the MWD is unimodal and the polydispersity index ($PDI = \overline{M}_w / \overline{M}_n$) is close to 1.5. This suggests that termination is primarily by combination at these conditions. At higher monomer concentrations, the MWD broadens and begins to exhibit a second mode. The second mode becomes increasingly prominent as the monomer concentration is increased. The *PDI* increases from approximately 1.5 at the lowest monomer concentration to 5.6 at the highest. The broad *PDI* and bimodality can contribute to improved flow characteristics and processing behaviour[18].

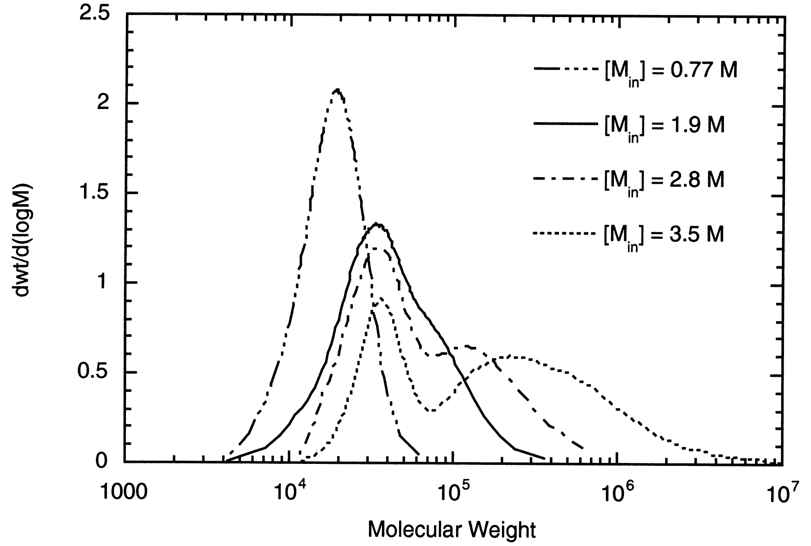

Figure 2. Effect of Inlet Monomer Concentration on Molecular Weight Distribution.

Temperature = 75 °C; Pressure = 277 bar; Mean Residence Time = 21 min; DEPDC Inlet Concentration = 2.85 mM.

The average molecular weights of the polymers shown in Figure 2 span a range that is typical of the commercial grades of PVDF. However, it is believed that the bimodal MWD is unique to the present process.

Figure 3 shows the MWD as a function of total pressure, at otherwise constant conditions. There are subtle shifts in the MWD with pressure. The most prominent feature is the high-molecular-weight tail at the highest pressure. In fact, the measured *PDI* at 304 bar (4400 psig) was about 10.

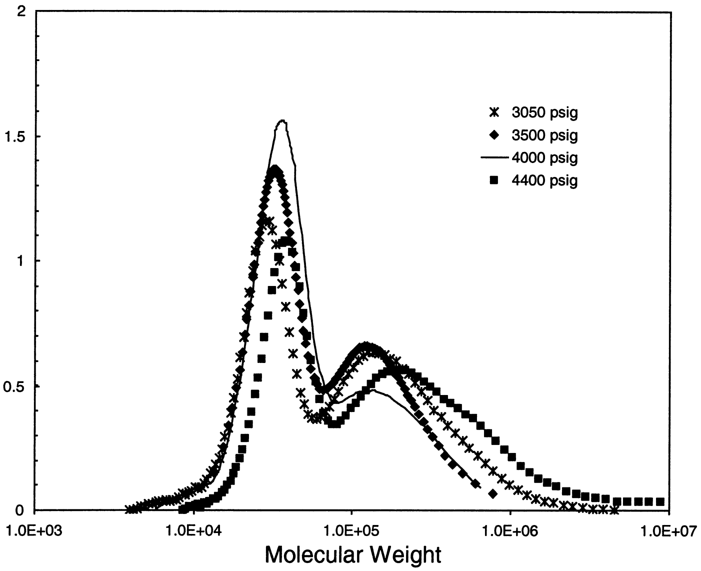

Figure 3. Effect of Total Pressure on Molecular Weight Distribution. Temperature = 75 °C; Mean Residence Time = 21 min; DEPDC Inlet Concentration = 2.85 mM; Inlet Monomer Concentration = 2.83 M.

Figure 4 shows the effect of reaction temperature on the molecular weight distribution. The higher-molecular-weight peak appears to diminish as temperature increases.

Two possible explanations for the bimodal MWD's and high PDI's are being investigated:

1. Polymerization occurs in two different phases, the supercritical fluid and the CO_2-swollen polymer particles. The higher-molecular-weight mode presumably results from polymerization in the particles.

2. Long-chain branching occurs at the conditions of the experiments.

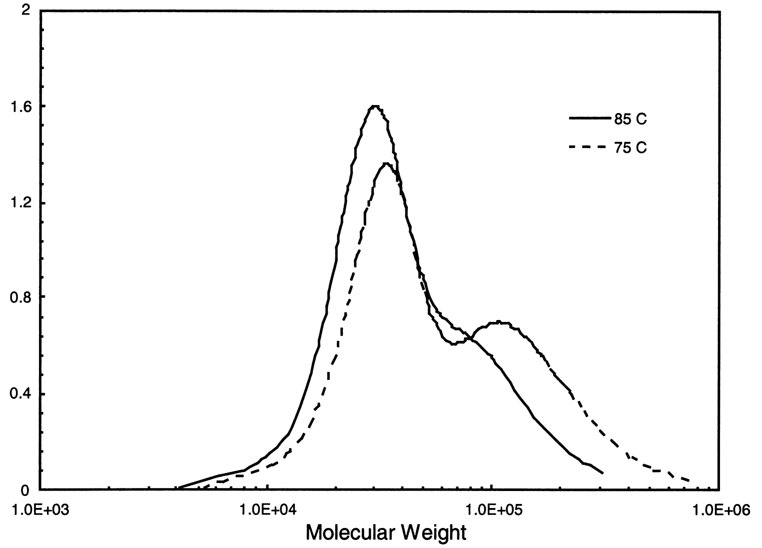

Figure 4. Effect of Temperature on Molecular Weight Distribution. Pressure = 277 bar; Mean Residence Time = 21 min; DEPDC Inlet Concentration = 2.85 mM; Inlet Monomer Concentration = 2.83 M.

Monomer Partitioning. In order to test the first hypothesis, the equilibrium partition coefficient of VF2 between the polymer and the supercritical fluid was measured. For present purposes, the partition coefficient is defined as the monomer concentration in the polymer divided by the monomer concentration in the fluid:

$$K_c = [VF2]_{polymer}/[VF2]_{fluid}$$

Figure 5 shows the measured partition coefficient for VF2 as a function of the total pressure at two different temperatures. A commercial grade of PVDF, Solef 1010, was used for these measurements. At 75 °C, the temperature of the experiments in Figures 2 and 3, the partition coefficient is immeasurably small at the pressures of Figure 2. If the rate of polymerization within the polymer particles is significant compared to the rate in the fluid phase, the monomer concentration in the polymer should be comparable to that in the fluid. Clearly, this is not the case at the pressures of most of the polymerization experiments.

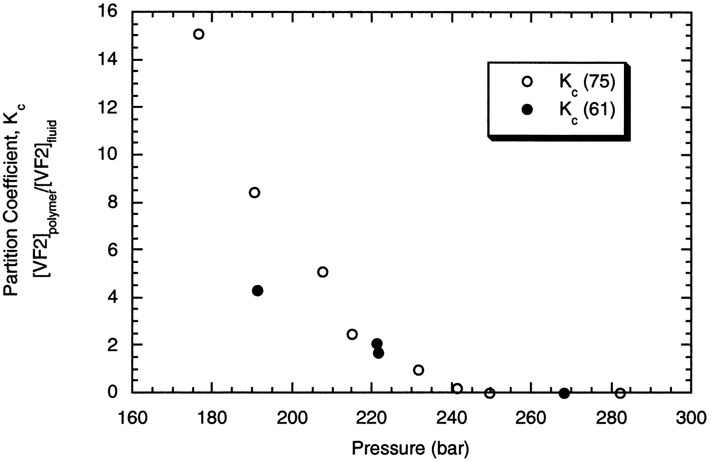

Figure 5. Partition Coefficient for Vinylidene Fluoride between Poly(Vinylidene Fluoride) and Supercritical Carbon Dioxide.

The behavior of the partition coefficient is inconsistent with the measured MWDs in two other respects. First, Figure 3 shows that a high-molecular-weight tail develops at the highest pressures. In addition, the *PDI* increases from about 4 at the lowest pressure to about 10 at the highest. However, Figure 5 shows that K_c decreases with pressure, indicating that the equilibrium monomer concentration inside the polymer particles goes down as pressure is increased. Second, Figure 4 shows that the MWD becomes more unimodal as the reactor temperature is increased, i.e., the higher-molecular-weight peak becomes less prominent at the higher temperature. However, Figure 5 shows that the partition coefficient increases with temperature.

Long-Chain Branching. It has been established that branching can occur via chain-transfer to polymer in polymers containing VF2 monomer[18]. The effect of long-chain branching on the molecular-weight distribution first was examined almost 50 years ago[19]. Various studies have shown that chain transfer to polymer coupled with termination by disproportionation does not lead to a bimodal MWD[19-22]. There does not appear to be any published research that defines whether chain transfer to polymer coupled with termination by combination can give rise to a bimodal MWD. The discrepancies between the behavior of the MWD and the behavior of the phase equilibrium for VF2, as noted above, have caused us to re-examine the question of whether branching can lead to a bimodal MWD.

A mathematical model of VF2 polymerization has been developed, assuming a homogeneous reaction and an ideal CSTR operating at steady-state. A preliminary version of the model was presented previously[16]. That publication focused exclusively on the rate of polymerization. The model has now been extended to include chain transfer to polymer, and to include computation of the number- and weight-average molecular weights and the average number of branches per molecule.

The model that was used in this research is based on four reactions: initiator decomposition with a rate constant k_D and an initiator efficiency f; propagation with a rate constant k_p; termination by combination with a rate constant k_c; and; chain transfer to polymer with a rate constant k_{tp}. Values of k_d and f for DEPDC in $scCO_2$ were determined in previous research[12]. The value of $k_p/(k_c)^{0.5}$ also was determined previously[16] by fitting data for the rate of polymerization. The value of k_{tp}/k_p was determined from the present *PDI* data, as described below.

Figure 6 shows the predicted and measured *PDIs* for the experiments in Figure 2.

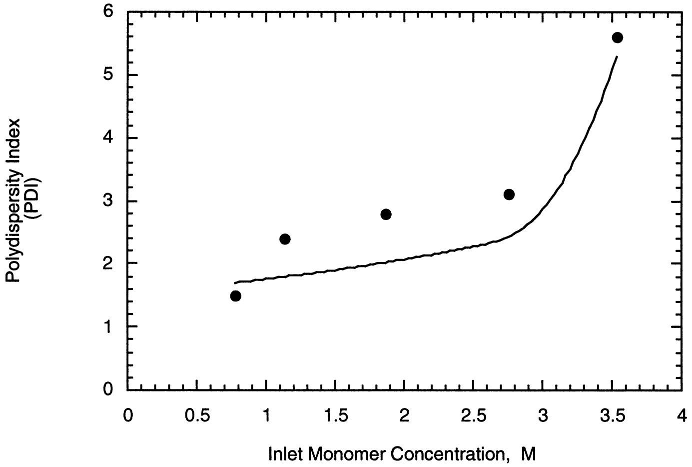

Figure 6. Polydispersity Index as a Function of Inlet Monomer Concentration. Experimental Conditions as Given in Figure 2. Solid line – Model; Points – Experimental Data. Parameters for Model: $k_D = 0.00103\ s^{-1}$; $f = 0.60$; $(k_p/k_c^{0.5}) = 0.141$ L/mol,s$^{0.5}$; $(k_{tp}/k_p) = 0.002373$.

In order to apply the model, a value of k_{tp}/k_p was calculated from the data point at the highest inlet monomer concentration; the same value was used at the lower concentrations. Both the model results and the experimental data show that the *PDI* increases with inlet monomer concentration, at otherwise constant conditions. There is reasonable agreement between the data and the model. One of the interesting features of both the model predictions and the experimental data is the abrupt increase in the *PDI* at an inlet monomer concentration of about 3 M.

The model also permits the extent of branching to be predicted. The average number of branches per molecule of PVDF increases from about 0.1 at the lowest monomer concentration in Figure 6 to about 0.4 at the highest. These predictions compare reasonably well with measurements on a VF2/hexafluoropropylene/tetrafluoroethylene (72/18/10) polymer synthesized at a similar temperature[18]. This comparison is relevant because this terpolymer is composed primarily of VF2, and because branching on hexafluoropropylene and tetrafluoroethylene units is unlikely since there are no H atoms on either molecule.

Nuclear magnetic resonance (^{19}F NMR) studies were carried out on some of the polymers produced in this research, in an attempt to detect branching. However, at the extents of branching mentioned above, the branch points are very difficult to detect and impossible to quantify by conventional ^{19}F NMR.

Conclusions

The polymerization of vinylidene fluoride in supercritical carbon dioxide was studied in a continuous stirred autoclave at about 75 °C using diethyl peroxydicarbonate as the initiator. Polymer with a bimodal molecular weight distribution was produced at many of the operating conditions investigated. As the monomer concentration was increased, the polydispersity of the polymer increased, and the high-molecular-weight mode of the distribution became more prominent.

The cause of the bimodal MWD is not clear at this time. The measured equilibrium concentration of vinylidene fluoride in the polymer is low at the conditions of the polymerization experiments. Moreover, the partitioning of vinylidene fluoride between the polymer and supercritical phase does not follow the same trends with temperature and pressure as the MWD.

A model of the polymerization that includes chain transfer to polymer predicts the increase in polydispersity that was observed as the monomer concentration was increased. However, it is not clear whether long-chain branching can be the source of the bimodal molecular-weight distribution.

Acknowledgements

This work was supported in part by Solvay Advanced Polymers, Inc. through the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing, and in part by the STC Program of the National Science Foundation under Agreement No. CHE-9876674. We thank Solvay Research, Belgium for performing GPC analyses of the PVDF samples. We extend special thanks to Dr. Roland Martin of Solvay Research, Belgium for many helpful suggestions and insightful criticisms.

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