

CONTINUOUS POLYMERIZATION IN SUPERCRITICAL CARBON DIOXIDE

Roberts, G. W.^{1,*}, Liu, T.^{1,3}, Ahmed, T. S.¹, and DeSimone, J. M.^{1,2}

¹North Carolina State University, Department of Chemical and Biomolecular Engineering, Box 7905, Raleigh, NC 27695-7905

²University of North Carolina at Chapel Hill, Department of Chemistry, CB #3290, Chapel Hill, NC 27599-3290

³Current Address: Bayer Technology and Engineering Company (Shanghai) Co., LTD., Block F3, Mu Hua Road, Shanghai Chemical Industry Park, Shanghai, 201507, P. R. China

* To whom correspondence should be addressed: groberts@eos.ncsu.edu, Fax: 919-515-3465

ABSTRACT

Poly(vinylidene fluoride), poly(acrylic acid), and various compositions of poly(vinylidene fluoride-co-hexafluoropropylene) have been synthesized in scCO₂ using a continuous stirred-tank reactor. The first two polymers are formed via precipitation polymerization. The copolymer can be formed by either precipitation or solution polymerization, depending on the CO₂ pressure, the molecular weight, and the hexafluoropropylene content. Cross-linked poly(acrylic acid) also was synthesized by adding a multi-functional monomer to the feed to the reactor.

These studies covered a range of pressures from 20 to 40 MPa, temperatures from 40 to 90 °C, average residence times from 10 to 48 minutes, and total monomer concentrations from 0.3 to 6.5 moles/L. The effects of reaction conditions on the rates of polymerization and the molecular weights are discussed. The behavior of the rate of polymerization and the polymer molecular weight was distinctly different for poly(acrylic acid) than it was for the fluoropolymers.

INTRODUCTION

Supercritical carbon dioxide (scCO₂) is a low-cost, environmentally-benign medium for carrying out polymerization reactions. The beneficial features of scCO₂ include: elimination of pollution associated with the use of water and organic solvents, and reduction of the energy required for polymer drying. The possibility of improved material properties has also been suggested, but this dimension has not been fully explored.

A large number of chain-growth and step-growth polymers have been synthesized in scCO₂, primarily by either precipitation or dispersion polymerization in small batch reactors (view cells) [1]. The mode of polymerization in scCO₂ is usually different than the commercial mode of the polymerization, in part because of the limited solubility of most polymers in scCO₂.

Only a few polymerizations have been carried out *continuously* in scCO₂, despite the potential practical and scientific advantages of continuous operation. Continuous polymerization is an economic requirement for many high-volume polymers. Relative to batch polymerization, continuous processing requires smaller equipment per unit of throughput, and therefore is less capital intensive. This is a particular advantage for processes involving scCO₂ because relatively high pressures are intrinsic. Continuous polymerization also leads to a more uniform product, to easier recycle of unreacted monomer

and CO₂, and to the potential to couple polymerization with continuous downstream processing.

This paper demonstrates the feasibility of producing several different polymers by polymerization in scCO₂ using a continuous stirred-tank reactor (CSTR). These polymers are: 1) poly(vinylidene fluoride) (PVDF); 2) poly(acrylic acid) (PAA), uncrosslinked and cross-linked to varying degrees, and; 3) poly(vinylidene fluoride-co-hexafluoropropylene) (poly(VF2-co-HFP)). The first two polymers are formed via precipitation polymerization. The copolymer can be formed by either precipitation or solution polymerization, depending on the CO₂ pressure, the molecular weight, and the hexafluoropropylene (HFP) content. These three systems were chosen for study in part because of their ability to illuminate the scientific fundamentals of polymerization in scCO₂, and in part because they may be potential candidates for commercial manufacture in scCO₂. Poly(acrylic acid) is currently manufactured primarily by continuous solution polymerization in water, which leads to a high energy requirement. The fluoropolymers are produced commercially by either emulsion or suspension polymerization in water [2]. Both processes require high pressures and may involve perfluorooctanoic acid surfactants, which are being phased out for environmental reasons [3].

In addition to providing a basic demonstration of feasibility, the present studies show that polymers produced in scCO₂ can have distinct physical and structural differences relative to similar polymers produced by conventional methods.

MATERIALS AND METHODS

The experimental system and the materials that were used in this research have been described in detail in a number of publications [4-8]. Briefly, scCO₂, the monomer(s), and the initiator solution were fed via syringe pumps into a stirred autoclave that behaved as an ideal CSTR [9]. The reaction, either a precipitation polymerization or a solution polymerization, took place in the autoclave. The exit stream from the autoclave was cooled to quench the reaction. In some cases, it also was necessary to add an inhibitor solution to ensure that polymerization did not take place downstream of the reactor [6]. For most precipitation polymerizations, the polymer particles were collected in parallel filters that operated near reactor pressure. For solution polymerizations, and for the precipitation polymerizations of amorphous fluoropolymers, the polymer was collected by adding a cosolvent continuously at high pressure, passing the fluid through a control valve to atmospheric pressure, collecting the solution and evaporating the CO₂ and the cosolvent. In addition, during copolymerizations where a polymer containing more than about 20 mol% HFP was produced, the condition of the stream leaving the reactor was visually observed via a sight glass in the exit line from the reactor [7].

The rate of polymerization (R_p) was determined gravimetrically, by weighing the polymer collected over a known period of time after the reactor had reached steady state. Gel permeation chromatography was used to determine the molecular-weight distribution (MWD) of the fluoropolymers. The viscosity-average molecular weight of PAA was determined from the measured intrinsic viscosity. The HFP content of poly(VF2-co-HFP) was obtained by elemental F analysis and by ¹⁹F NMR.

RESULTS

a. Rate of polymerization

When polymer precipitates during the polymerization, the various polymerization reactions can take place either in the supercritical fluid phase, in the precipitated polymer

particles, or simultaneously in both phases. Mueller et al. [10] have developed mathematical models of the polymerization process, and have provided a methodology for understanding and predicting the relative contributions of the two different loci. However, a large number of parameters must be known *a priori* in order to use these models in a predictive mode.

In a CSTR, the question of polymerization locus can be studied by means of a simple set of experiments where the amount of polymer in the reactor is varied at constant temperature and reaction pressure. This can be accomplished by changing the inlet monomer concentration, and/or the inlet initiator concentration, and/or the space time (average residence time). The results of such a study with PAA are shown in Figure 1 [11]. In these experiments, 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65B) was used as the free-radical initiator. The theory behind this plot is developed elsewhere [11]. The figure shows that the rate of polymerization depends on the square root of the volume fraction of polymer in the reactor ($v_p^{0.5}$). This dependency results from assuming that the polymerization takes place uniformly throughout the polymer particle, with no polymerization occurring in the supercritical fluid phase. The experimental data at both temperatures are very consistent with this model.

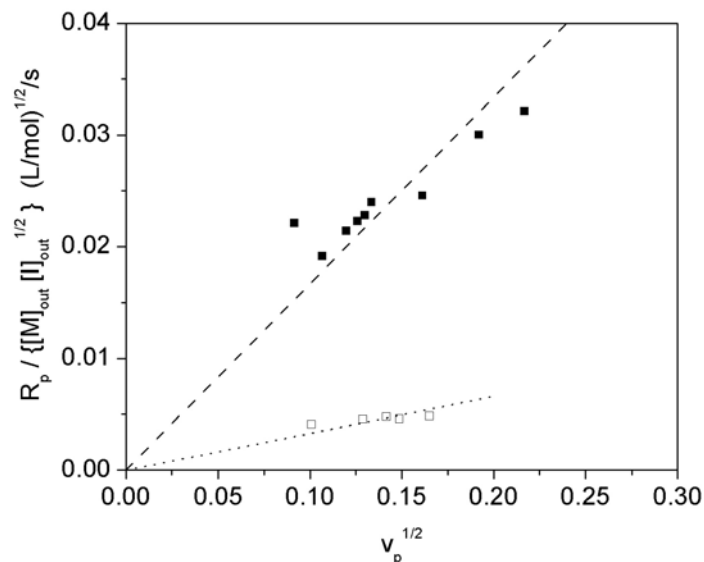


Figure 1: Test of Polymerization Rate Data Against Model based on Polymerization Throughout the Polymer Particles - Acrylic Acid Polymerization (207 bar; 50 °C (unfilled squares), 90 °C (filled squares)) [11]

The question of where polymerization takes place is of both theoretical interest and practical importance. For example, if acrylic acid (AA) polymerizes only inside the polymer particles, it should be possible to produce a cross-linked polymer simply by adding a multifunctional monomer (cross-linker) to the acrylic acid that is fed to the reactor. Figure 2 shows the results of several experiments in which different concentrations of the tetrafunctional monomer tetraallylpenterithritol (APE4) were added to the feed in the polymerization of AA [12]. By varying the APE4 concentration, the product could be made soluble, partially soluble, or insoluble in water.

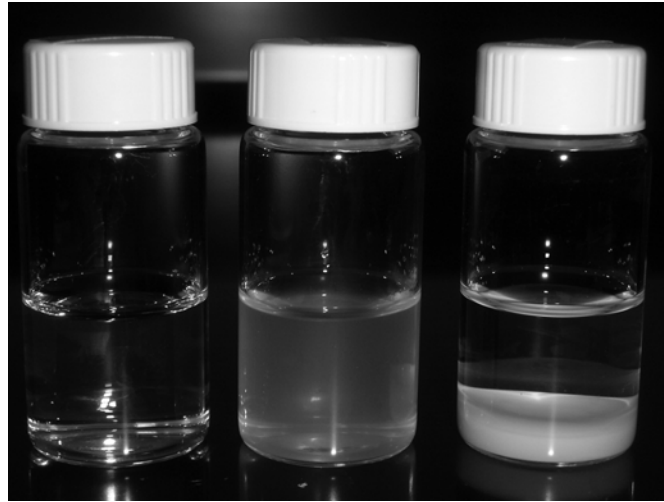


Figure 2. Solubility behavior of cross-linked PAAs in Deionized Water (left – [APE4] = 0.1 wt%; middle – [APE4] = 0.4 wt%; right – [APE4] = 5 wt%) [12].

Figure 3 shows the same plot as in Figure 1, this time for the precipitation polymerization of vinylidene fluoride (VF2) in $scCO_2$. The initiator used for these experiments was diethyl peroxydicarbonate (DEPDC). Clearly, the behavior of the polymerizations of AA and VF2 is quite different. There is little or no dependence of the rate of VF2 polymerization on the volume fraction of polymer in the reactor.

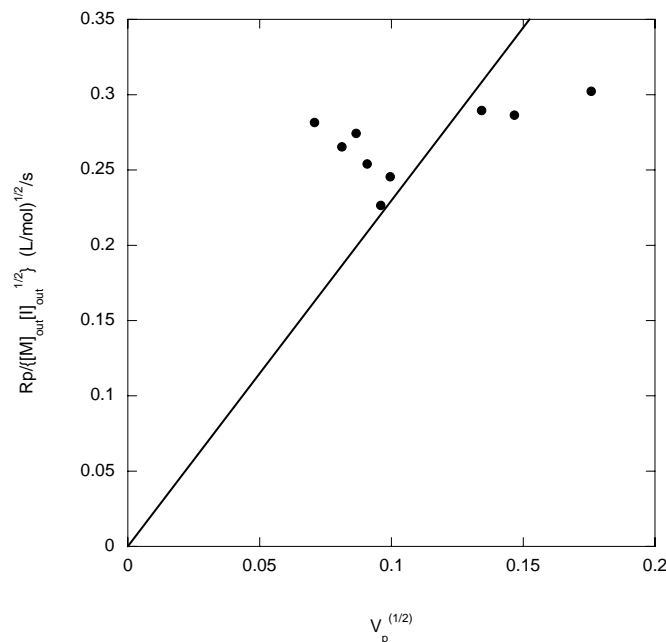


Figure 3: Test of Polymerization Rate Data Against Model based on Polymerization Throughout the Polymer Particles – Homopolymerization of VF2 (277 bar; 75 °C)

The poor fit of the experimental data to the model based on polymerization throughout the polymer particle suggests that VF2 polymerization does not take place inside the polymer particles. In fact, further study has shown that polymerization occurs primarily in the supercritical fluid when fluoromonomers such as VF2 and HFP are polymerized [13]. When

the reaction occurs predominantly in the fluid phase, and if there is a mechanism for cross-linking, such as chain transfer to polymer plus termination by combination, it is possible to form a tough, essentially insoluble polymer that fills the whole reactor. In fact, such a situation occurred in the laboratory during experiments on the homopolymerization of VF2 monomer [5].

b. Molecular Weight

One of the striking features of the polymer that is produced by homopolymerization of VF2 is the sensitivity of the MWD to changes in the feed monomer concentration and to the average residence time in the reactor. The MWDs for a set of experiments at constant temperature and residence time, but with varying feed monomer concentration, are shown in Figure 4 [4]. These experiments were carried out using DEPDC as the free-radical initiator.

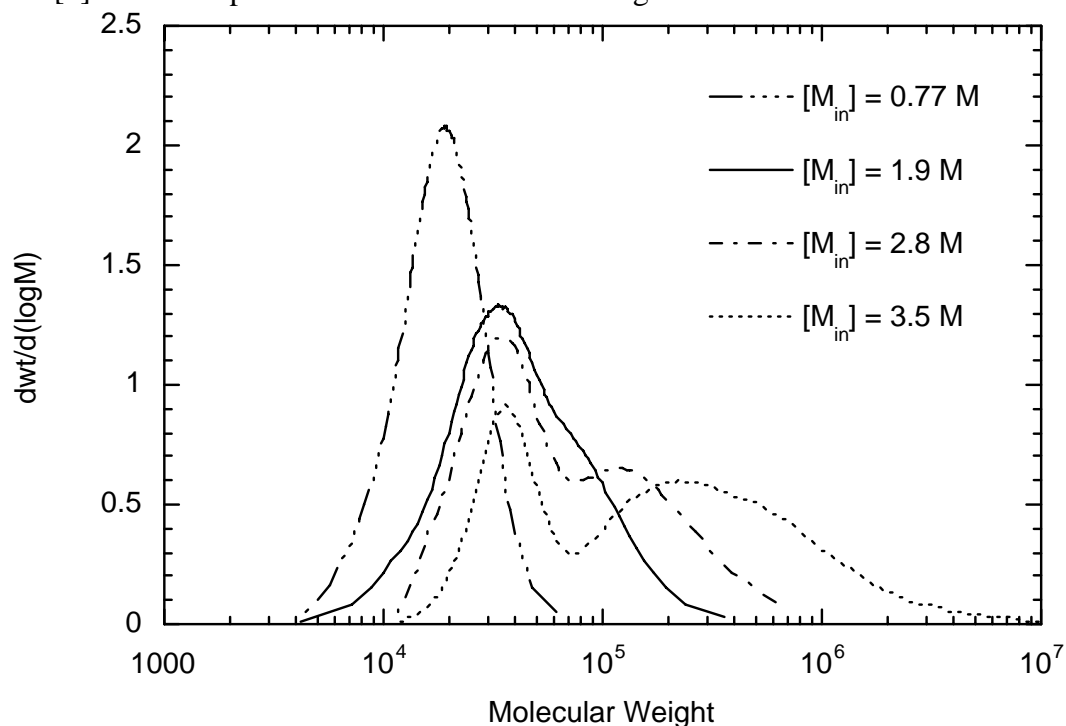


Figure 4: Effect of Monomer Concentration in Feed to Reactor on Molecular Weight Distribution. Temperature = 75 °C; Pressure = 277 bar; Mean Residence Time = 21 min; Inlet [DEPDC] = 2.85 mM.

Clearly, the feed monomer concentration had a pronounced effect on the MWD. As monomer concentration was increased, the average molecular weight increased, the MWD became bimodal, and the breadth of the MWD increased. The bimodal MWD may result in improved rheological properties of the polymer. This molecular-weight behavior may arise from the transition of the termination reaction from a kinetically-controlled regime to a diffusion-controlled regime with increasing macroradical molecular weight, coupled with a chain-transfer-to-polymer reaction [15]. This same hypothesis can account for the effects of temperature and pressure on the MWD of PVDF [14,15], and for the MWD's of VF2/HFP copolymers relative to PVDF homopolymer [7,8].

Increasing the pressure of the polymerization caused the average molecular weight to shift to higher values, and caused a broadening of the molecular-weight distribution. Thus, the polymer properties can also be “tuned” by adjusting the reaction pressure.

CONCLUSIONS

The use of scCO₂ as a polymerization medium offers important options for “tuning” the properties of the polymers produced, and, in some cases, creating microstructures that are not found in polymers of the same composition produced by “conventional” methods. Thus, the MWD of certain fluoropolymers can be controlled by adjusting the polymer feed concentration and/or the reaction pressure.

It is important to understand the mechanism of the polymerization reaction in scCO₂, and especially to identify the locus of polymerization. This understanding can be used to exploit some of the unique features of scCO₂ as a polymerization medium, and to design continuous processes that produce products with unique properties.

ACKNOWLEDGEMENTS

This research was supported by the STC Program of the National Science Foundation under Agreement No. CHE-9876674, and by Solvay Advanced Polymers, Inc.

REFERENCES:

- [1] Shaffer, K. A., DeSimone, J. M., Trends Polym. Sci., Vol. 3, **1995**, p.146; Canelas, D. A., DeSimone, J. M., Adv. Polym. Sci., Vol. 133, **1997**, p.103; Kennedy, K. A., Roberts, G. W., DeSimone, J. M., Adv. Polym. Sci., Vol. 175, **2005**, p.329.
- [2] Drobny, J.G., Technology of Fluoropolymers, **2001**, CRC Press, Boca Raton, FL, USA
- [3] Preliminary Risk Assessment: Perfluorooctanoic Acid (PFOA) and Fluorinated Telomers: U. S. Environmental Protection Agency: April, **2003**; 2010/15 PFOA Stewardship Program: U. S. Environmental Protection Agency: January, **2006**.
- [4] Saraf, M. K., Wojcinski, L. M. II, Kennedy, K. A., Gerard, S., Charpentier, P. A., DeSimone, J. M., Roberts, G. W., “Continuous Precipitation Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide: Molecular Weight Distribution”, pp. 119-129 in Macromolecular Symposia 182, “Free-Radical Polymerization: Kinetics and Mechanism”, Buback, M. and German, A. L. (eds), **2002**, Wiley-VCH, Weinheim, Germany.
- [5] Saraf, M. K., Gerard, S., Wojcinski, L. M. II, Charpentier, P. A., DeSimone, J. M., Roberts, G. W., Macromolecules, Vol. 35, **2002**, p.7976.
- [6] Liu, T., DeSimone, J. M., Roberts, G. W., J. Poly. Sci. Part A: Poly. Chem., Vol. 43, **2005**, p.2546.
- [7] Ahmed, T. S., DeSimone, J. M., Roberts, G. W., Macromolecules, Vol. 41, **2008**, p.3086.
- [8] Ahmed, T. S., DeSimone, J. M., Roberts, G. W., Macromolecules, Vol. 40, **2007**, p.9322.
- [9] Charpentier, P. A., DeSimone, J. M., Roberts, G. W., Chem. Engng. Sci., Vol. 55, **2000**, p.5341.
- [10] Mueller, P. A., Storti, G., Morbidelli. M., Chem. Engng. Sci., Vol. 60, **2005**, p.377; Mueller, P. A., Storti, G., Morbidelli. M., Chem. Engng. Sci. Vol. 60, **2005**, p.1911; Mueller, P. A., Storti, G., Morbidelli. M., Macromolecules, Vol. 38., **2005**, p.7150.
- [11] Liu, T., DeSimone, J. M., Roberts, G. W., Chem. Engng. Sci., Vol. 61, **2006**, p.3129.
- [12] Liu, T., DeSimone, J. M., Roberts, G. W., Polymer, Vol. 47, 2006, p.4276.
- [13] Ahmed, T. S., DeSimone, J. M., Roberts, G. W., Macromolecules, Vol. 42, **2009**, p.148.
- [14] Ahmed, T. S., DeSimone, J. M., Roberts, G. W., Chem. Engng. Sci., Vol. 59, **2004**, p.5139.
- [15] Ahmed, T. S.; DeSimone, J. M.; Roberts, G. W., “Continuous Precipitation Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide: A Model for Understanding the Molecular-Weight Distribution”, submitted to Chem. Engng. Sci., **2009**.