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Continuous precipitation polymerization of vinylidene fluoride in supercritical carbon dioxide: A model for understanding the molecular-weight distribution

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) that is synthesized by precipitation polymerization in supercritical carbon dioxide ($scCO_2$) has a bimodal molecular weight distribution (MWD) and a very broad polydispersity index (PDI) under certain reaction conditions. Different models have been formulated to account for this behavior. This paper presents a homogenous model for a continuous stirred-tank reactor (CSTR) that includes the change of the termination reaction from kinetic control to diffusion control as the chain length of the polymeric radicals increases, and accounts for the change in the termination rate constant with macroradical chain length in the diffusion-controlled region. The model also includes the chain transfer to polymer reaction. Comparison of the model output with experimental data demonstrates that changes of the MWD, including the development of a bimodal distribution, with such reaction conditions as monomer concentration and average residence time are successfully predicted. In addition, the model can capture the occurrence of gelation, which appears to be responsible for a region of inoperability that was observed in the polymerization experiments. The success of this homogeneous model is consistent with recent research demonstrating that the CO_2-rich phase is the main locus of polymerization for the precipitation polymerization of vinylidene fluoride and vinylidene fluoride/hexafluoropropylene mixtures in $scCO_2$, at the conditions that have been studied to date.

1. Introduction

Poly(vinylidene fluoride) (PVDF) possesses unique properties such as excellent chemical, thermal and mechanical stability in addition to its pyroelectric and piezoelectric properties. Moreover, it has low surface energy, low water absorptivity, excellent weatherability and low flammability (Lovinger, 1982; Scheirs, 1997). Consequently, PVDF is used in applications requiring the highest purity, strength, and resistance to solvents, acids, bases, and heat, in addition to low smoke generation during a fire. Some typical applications for PVDF include coatings and films, cables, pipes, tubing in plastic heat exchangers, column packing, valves, and pumps. In addition, PVDF is an acceptable material for biological systems (Klinge et al., 2002).

The homopolymerization of vinylidene fluoride (VF2) in supercritical carbon dioxide ($scCO_2$) by both precipitation polymerization (Charpentier et al., 2000a, 1999; Galia et al., 2002; Liu et al., 2005; Mueller et al., 2005a; Saraf et al., 2002a, 2002b) and dispersion polymerization (Galia et al., 2006; Mueller et al., 2006; Tai et al., 2005a, 2005b, 2005c) has been reported in both continuous (Charpentier et al., 2000a, 1999; Saraf et al., 2002a, 2002b) and batch (Galia et al., 2002, 2006; Mueller et al., 2006; Tai et al., 2005a, 2005b, 2005c) reactors. The molecular weight distributions (MWDs) of the PVDF synthesized in $scCO_2$ exhibited bimodal distributions under certain reaction conditions, in both continuous (Saraf et al., 2002a, 2002b) and batch (Mueller et al., 2005a) operation. The main features associated with these bimodal MWDs (Saraf et al., 2002a) are: (1) the MWD changes from perfectly unimodal at low monomer concentrations to bimodal as the monomer concentration is increased at constant average residence time (τ), temperature and pressure; (2) the average residence time has no effect on the molecular weight and the MWD at low monomer concentration; (3) at high monomer concentrations, the polydispersity index (PDI) increases significantly with τ; and (4) the molecular weights, PDI, and the extent of bimodality decreases with increasing temperature.

High polydispersity indices and bimodality can contribute to better flow characteristics and processing behavior (Maccone et al., 2000; Tervoort et al., 2000). Therefore, the production of polymers with bimodal MWDs is potentially of commercial

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interest. Typically, broad and bimodal MWDs are obtained by polymer blending, which usually requires a multi-step process where low and high molecular weight fractions are synthesized independently and then mixed together. On the other hand, polymerization in $scCO_2$ is a single step process. However, in order to synthesize polymer with the desired properties, it is very important to understand the origin of the bimodal MWD and broad PDI, and to be able to control the relative amounts and molecular weights of the two fractions.

Four different hypotheses have been proposed to explain the MWD of PVDF synthesized in $scCO_2$. The first is imperfect mixing in the continuous stirred tank reactor (CSTR) that was used in some polymerizations (Saraf et al., 2002a). This hypothesis was influenced by the work of Zhang and Ray (1997) in which it was shown that broad MWDs with a shoulder can be generated by imperfect mixing. However, experiments by Saraf et al., showed that changing the agitation rate and/or agitator type during the continuous precipitation polymerization of PVDF did not affect the MWD significantly (Saraf et al., 2002a).

The second hypothesis is that long chain branching, a result of chain transfer to polymer, caused a second population of highly branched chains (Saraf et al., 2002a). In order to explore this possibility, Saraf et al. developed a homogeneous kinetic model that included a chain transfer to polymer (CTP) reaction. This model, which was based on the assumption that all the reactions took place in the continuous phase, i.e., in the supercritical fluid, was successful in predicting the PDI variation with inlet monomer concentration and residence time. In addition, the model predicted a region of inoperability for the CSTR, coincided with experimental results. However, bimodal MWDs could not be generated with the model (Saraf et al., 2002a).

The third hypothesis is also based on the assumption that all the reactions took place in the supercritical fluid phase; bimodality is attributed to the transition of the termination reaction from a kinetically controlled regime to a diffusion-controlled regime with increasing macroradical molecular weight (Ahmed et al., 2004). Accordingly, the rate constant for termination decreases with chain length in the diffusion-controlled regime, and the second mode of the MWD is a result of an increased population of high-molecular-weight macroradicals. In fact, the decrease in termination rate constant with radical chain length was previously reported to produce bimodal MWDs for the free-radical polymerization of methyl methacrylate in the presence of poly(methyl methacrylate) (Bogunjoko and Brooks, 1983).

In order to explore the third hypothesis, we previously proposed a homogeneous kinetic model for VF2 polymerization in a CSTR incorporating a termination rate constant that decreased with macroradical-chain-length for long chains (Ahmed et al., 2004). In this model, three termination reactions with different rate constants were used to approximate the actual termination scheme consisting of an infinite number of reactions and rate constants. The model captured the directional effect of the operating parameters, such as monomer feed concentration, residence time, and reaction temperature, on the MWD. However, the model seriously underestimated the PDIs that were observed in some experiments, and did not predict a region of inoperability. Presumably, these deficiencies resulted from ignoring the CTP reaction.

The fourth and final hypothesis is that bimodality results from simultaneous polymerization in both the supercritical fluid and the polymer phases (Mueller et al., 2005a; Saraf et al., 2002a, 2002b). Mueller et al. developed a mathematical model for the dispersion polymerization of poly(methyl methacrylate) in $scCO_2$ that accounted for simultaneous polymerization in both phases by taking into account the transport of polymeric radicals between the two phases (Mueller et al., 2004, 2005b). They then applied this model to the precipitation polymerization of PVDF in $scCO_2$ (Mueller et al., 2005a).

The "simultaneous polymerization" model included a large number of parameters. Mueller et al. made a considerable effort to estimate most of these parameters from independent sources. Nevertheless, three parameters had to be adjusted to model VF2 polymerization; two of these parameters had a very significant impact on the existence or the non-existence of a bimodal MWD (Mueller et al., 2005a). Mueller et al. compared the model predictions to batch polymerization data for PVDF and found reasonable agreement. That work establishes that the simultaneous polymerization in both the supercritical phase and the polymer particles can lead to bimodal molecular weight distributions. However, it does not establish that "simultaneous polymerization" is the cause of, or even a major contributor to, the bimodal MWDs that were observed for VF2 polymerization in $scCO_2$.

For precipitation/dispersion polymerization, two factors determine the importance of polymerization in the polymer phase relative to that in the fluid phase: (1) the time scale of the termination reaction compared to that of macroradical precipitation and/or transport between phases; and (2) the concentration of monomer dissolved in the polymer phase. Regarding the first factor, if the characteristic time for termination is much less than that for precipitation/transport, the polymer chains will terminate in the fluid phase before macroradicals transfer to the polymer phase and vice versa. Mueller et al. (2005a) introduced the Ω-parameter, i.e., the ratio of the characteristic time for interphase mass transport of radicals to that for termination, to quantify this relationship. They neglected the precipitation of macroradicals, which may be a more important means of radical transfer to the polymer phase, especially for long chain lengths. For precipitation polymerization of PVDF, the estimated values of Ω in the polymer phase were negligible, $\ll 1$, while the Ω parameter for the continuous phase was smaller than one, except for macroradicals with a very high degree of polymerization, where Ω values very close to one were obtained. These predictions suggest that both the polymer and fluid phases are possible loci of polymerization, at the conditions of the experiments. It is important to recognize that these values for the Ω-parameter depend on the specific interphase surface area of the polymer particles. This is one of the key adjustable parameters in the Mueller et al. (2005a) model, and has a significant impact on the model output. Small changes in the value of the total area of the particles are sufficient to completely change the MWD predicted by the model (Mueller et al., 2005a).

The second factor that has a significant impact on polymerization behavior is the solubility of VF2 in the polymer phase at reaction conditions. Recently, the simultaneous equilibrium sorption of CO_2 and VF2 into PVDF has been studied experimentally by Galia et al. (2008). They showed that the concentration of VF2 in the polymer particles is very low at the conditions used during the polymerization of VF2 in $scCO_2$. These results coincide with a similar study by our research group showing that the equilibrium partition coefficient of VF2 between PVDF and CO_2 is negligible at high pressures (Kennedy, 2003; Saraf et al., 2002b). The limited solubility of VF2 in PVDF in the presence of $scCO_2$ suggests that any radical initiated or captured in the polymer phase propagates under monomer-starved conditions that could compensate the autoacceleration effect arising from the impeded termination in the polymer phase (Galia et al., 2008), and lead to a very low rate of polymerization in the polymer phase.

Mueller et al. (2005a) used the Sanchez–Lacombe equation of state with the mixing rules proposed by McHugh and Krukonis (1994) to describe the partitioning of VF2 between the fluid and polymer phases. Experimental data (Kennedy, 2003) were used to