ABSTRACT

SARAF, Manish Kumar. Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide: Molecular Weight Distribution (Under the direction of Drs. George W. Roberts and Joseph M. DeSimone)

Conventional vinylidene fluoride polymerizations require the use of large amounts of water. Therefore, energy and cost-intensive drying and separation steps are required to isolate the polymer. Additionally, some conventional polymerizations use fluorosurfactants that belong to 3M’s ‘Scotchgard’ family of surfactants, which are being phased out due to environmental concerns. In this research, we investigate a "green" process for the continuous polymerization of vinylidene fluoride by free-radical precipitation polymerization in supercritical carbon dioxide (scCO₂). Significant technological and environmental improvements can be achieved by this technology, such as: 1) elimination of waste streams generated by conventional suspension, and emulsion processes; and 2) achievement of major energy savings, as the polymer is isolated in a dry form with no water or solvent to evaporate.

The experimental system used in this research consisted of a continuous stirred tank reactor (CSTR) for polymerization, and a polymer withdrawal system where polymer was collected, and continuously ejected to ambient conditions. The polymer was collected as a dry "free-flowing" powder, and was characterized by GPC (gel permeation chromatography), DSC (differential scanning calorimetry), and Fluorine-19 NMR (nuclear magnetic resonance spectroscopy). Experiments were carried out to study the effect of different parameters such as inlet monomer concentration ([M]₀ = 0.78 to 3.5 M), pressure (P=3050 to 4400 psig), temperature (T=65 to 85 °C), and average residence time (τ = 12 to 50 mins.), on the polymerization rate and the average molecular
weights. A homogeneous model based on classical free radical kinetics predicted the polymerization rate very well at the lower rates. However, this could not predict an inhibition in the rate that was observed at higher monomer concentrations.

A bimodal molecular weight distribution was obtained at inlet monomer concentrations greater than around 1.9 M. The second (high molecular weight) mode was more prominent at higher monomer concentrations, higher residence times, and lower temperatures. Two hypothesis, poor mixing and long chain branching, were investigated to explain these broad and bimodal molecular weight distributions (MWDs).

Agitation studies showed that poor mixing can account for the slower rate of polymerization at high monomer concentrations, but does not to bimodal MWDs. End group analysis using NMR showed that chain transfer occurs, probably to polymer. A homogeneous kinetic model was developed to investigate the effect of chain branching arising from chain transfer to polymer. This model showed that broad MWDs with large polydispersity indices (PDIs) are obtained at high monomer concentrations and at high residence times. These predictions matched very well with experimental data. However, the model predicted a unimodal MWD even at very high values of the rate constant for chain transfer to polymer.

Batch polymerization studies were carried out to develop alternate low temperature initiators, which could reduce operating and equipment costs and potentially produce high molecular weight polymer with reasonable yields. A fluorinated initiator obtained from hexafluoropropynl oxide dimer produced PVDF with very high molecular weights (~90 K) at reasonable yields.
POLYMERIZATION OF VINYLIDENE FLUORIDE
IN SUPERCritical CARBON DIOXIDE:
MOLECULAR WEIGHT DISTRIBUTION

By

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Manish Saraf was born on October 25th 1978 in Rajasthan, India. He moved with his family to Madras, India at the age of six. He completed his high school education from D.A.V. Senior Secondary School in 1995. After that, he attended the Indian Institute of Technology (IIT), Madras for his undergraduate studies. While at IIT, he worked with Dr. S.Pushpavanam on state and parameter estimation of a non-linear system using Kalman Filters. He obtained a Bachelor’s degree in Chemical Engineering at IIT in June 1999. In August 1999, he joined the graduate program in the Department of Chemical Engineering at North Carolina State University, Raleigh, NC, USA. During his graduate studies, he conducted research at the Kenan CO₂ Center and the NSF Science and Technology Center on Continuous Polymerizations in Supercritical Carbon Dioxide. He was jointly advised by Drs. George W. Roberts and Joseph M. DeSimone.
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CHAPTER 1     INTRODUCTION

Volatile organic compounds (VOCs) are widely used in the chemical industry for various processes. Many of these compounds are toxic and cause substantial harm to the environment. The polymer industry is a major user and emitter of VOCs into the atmosphere. As a result of the growing pressure from environmental groups and government regulations imposed on the use of these compounds (e.g., the Montreal Protocol in 1987 and the Clean Air Act Amendments in 1990), there has been considerable time and money spent on finding alternate solvents and processes that are environmentally benign. DeSimone and coworkers have shown that supercritical carbon dioxide (scCO$_2$) is a viable solvent for a number of polymerizations\textsuperscript{1-4}. In addition to being environmentally benign, carbon dioxide (CO$_2$) is cheap and easily available as it is the byproduct of many industrial processes such as ammonia, hydrogen, and ethanol synthesis. The most prominent advantages of using scCO$_2$ as a polymerization medium are: (1) no chain transfer to solvent, (2) high initiator efficiencies, (3) ability to control solvent quality and manipulate partition coefficient, (4) replacing toxic and environmentally aggressive solvents, (5) replacing water, thus eliminating the need for energy intensive drying steps required to produce a free flowing polymer powder and eliminating the need for waste water treatment.

There has been a considerable demand for poly(vinylidene fluoride) (PVDF) and its copolymers because of their excellent chemical, thermal and mechanical stability combined with their extraordinary piezoelectric and pyroelectric properties\textsuperscript{5}. Poly(vinylidene fluoride) is commercially produced by emulsion and suspension
polymerizations, both of which generate large quantities of waste water and require large quantities of energy to isolate the polymer as a free flowing powder. Moreover, the emulsion technique, and perhaps the suspension technique as well, involve the use of fluorosurfactants that belong to 3M’s ‘Scotchgard® family of surfactants. These surfactants contain perfluoro octanyl sulfonates (PFOs) that are non-biodegradable and with time could bioaccumulate in human fatty tissue. Perfluoro octanyl sulfonates have also been identified as persistent organic pollutants. This has prompted 3M to phase out the production of these surfactants. As a result, synthesis of PVDF in scCO$_2$ is even more important.

Kipp et.al.$^6$ have demonstrated the feasibility of synthesizing PVDF in scCO$_2$ using different types of initiators. This study is discussed in detail in §2.3. Charpentier et al.$^7$ have developed a continuous precipitation polymerization process in scCO$_2$ using diethylperoxydicarbonate(DEPDC). Most of these polymerizations were carried out at around 75 °C and 4000 psig. Such a continuous polymerization system could make commercial production of PVDF in scCO$_2$ feasible. However, it is very important to understand the kinetics and mechanism of polymerization in order to produce PVDF of desired properties such as molecular weights, microstructure etc. Additionally, there is an incentive to carry out these polymerizations at lower temperatures and pressures, in order to reduce capital and operating costs.

The overall objective of this research work was to develop a better understanding of the synthesis of PVDF in scCO$_2$. Chapter II of this thesis presents a background on supercritical fluids (SFCs) and conventional and scCO$_2$ polymerizations with a focus on scCO$_2$ and PVDF. Chapter III presents an experimental study of the rate and molecular
weight distribution (MWD) of PVDF at different reaction conditions. Chapter IV presents a mathematical model to predict the rate of polymerization and MWD of the PVDF. In Chapter V, preliminary results using alternate, low-temperature initiator systems are presented.

The three main questions that this research work aims to answer are:

1) What are the effects of various parameters such as monomer (VF$_2$) concentration, reaction pressure, temperature and residence time on the rate of polymerization and the molecular weight distribution (MWD) of the PVDF synthesized in scCO$_2$?

2) Can we model the behavior seen in the experiments mentioned above?

3) Can we identify a low temperature initiator system that would allow operation at milder conditions and increase molecular weights, while maintaining reasonable yields?
Supercritical Fluids (SCFs) offer a great opportunity to discover and utilize new chemical phenomena that are not seen in conventional solvents. This is evident from the numerous research organizations that are investigating the applications of SCF solvents. Before going into details about the use of supercritical carbon dioxide (scCO$_2$) as a polymerization medium, it is important to review the properties of supercritical fluids to identify the features that make them attractive for a wide range of applications.

§ 2.1 Properties of Supercritical Fluids: Supercritical Carbon Dioxide.

Supercritical fluids are gases or liquids elevated above their critical temperature and pressure$^8$, $^9$. The shaded region in the P-T diagram of Figure 2.1 shows the supercritical region for a pure component. The supercritical state can be viewed as a distinct phase of matter with properties that often lie between those of liquids and gases. Consider two separate cases where the supercritical region is entered by isothermal compression of a gas (path 1 in Figure 2.1) or by isobaric heating of a liquid (path two in Figure 2.1). No distinct phase boundaries are crossed in either path. There are no first order transitions like those observed during phase changes (Solid-Liquid, Liquid-Gas, Gas-Solid). The fluid properties vary smoothly along paths 1 and 2, resulting in a SCF having properties between those of the gaseous and liquid states.
固体
液体
超临界流体

图2.1 P-T相图示意图纯成分。该区域P, T大于Pc(临界压力)和Tc(临界温度)分别代表超临界相。

此性质使得SCFs在许多应用中具有吸引力，因为可以利用在气态和液态中未发现的性质。例如，SCFs可以具有与气体相似的扩散性，这对反应动力学有重要影响，并且同时具有与液体相似的密度，使许多化合物能够溶化。

图2.2显示了CO2密度和电介质常数随压力的变化。通过改变压力和温度，可以改变密度并保持单一相系统。这种变化在靠近临界点时尤为重要，并可以用来调节SCF对特定溶质的溶解性。

这种SCFs的性质使得它们在许多应用中具有吸引力，因为可以利用在气态和液态中未发现的性质。例如，SCFs可以具有气体相似的扩散性，这对反应动力学有重要影响，并且同时具有液态相似的密度，使许多化合物能够溶化。此外，SCFs的性质可以通过简单地改变温度和压力来调节。

图2.2展示了二氧化碳的密度和电介质常数随压力的变化。通过改变压力和温度，可以改变密度并保持单一相系统。这种变化在靠近临界点时尤为重要，并可以用来调节SCF对特定溶质的溶解性。
Figure 2.2  Density (solid line) and dielectric constant (dotted line) of CO$_2$ as a function of pressure and temperature. Vertical line represents critical pressure (1030 psia). There is a sharp change in density and dielectric constant with pressure (while maintaining a single phase) near the critical point (31 °C and 1030 psia).\textsuperscript{11}

The variation of solvency of CO$_2$ with pressure is shown in Figure 2.3. In addition to the solvency, density and dielectric constant, other properties like the diffusivity, viscosity and thermal conductivity of SCF also can be tuned by changing the pressure and temperature.

Table 2.1 shows the critical point of a few common solvents. Supercritical carbon dioxide has a relatively accessible critical point: critical temperature of 31.1 °C and critical pressure of 1030 psia. This is easily obtainable and is reached in many industrial processes, making them ideal candidates for SCF adaptation.

The above factors put together have rendered scCO$_2$ a very attractive solvent for utilization in a number of applications such as extractions,\textsuperscript{13} homogeneous and heterogeneous free radical polymerizations,\textsuperscript{2, 14, 15} oil recovery,\textsuperscript{16} and fluoropolymer coatings\textsuperscript{17}. 
Figure 2.3  Variation of the Hildebrand solubility parameter of CO$_2$ with pressure. Below the critical temperature (e.g. at –31 °C), there is a step change in δ. However, above the critical temperature there is a continuous change in δ with pressure.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Critical Temperature ($^\circ$ C)</th>
<th>Critical Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>31.1</td>
<td>72.8</td>
</tr>
<tr>
<td>Water</td>
<td>374.2</td>
<td>217.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>318.6</td>
<td>40.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.5</td>
<td>111.3</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.3</td>
<td>48.2</td>
</tr>
<tr>
<td>Propane</td>
<td>96.7</td>
<td>41.9</td>
</tr>
</tbody>
</table>

Table 2.1  Critical conditions for various solvents.
§ 2.2 Polymerization Techniques

Polymerization processes are broadly divided into two groups known as step growth and chain growth polymerizations.\textsuperscript{18} In step growth polymerization, also known as condensation polymerization, polymer is formed by the condensation of two multifunctional molecules to produce one larger multifunctional molecule, with or without the elimination of a small molecule such as water. Chain growth polymerizations on the other hand involve a chain reaction in which the chain carrier can be an ion, a free radical, or a species that is covalently attached to a catalyst such as a transition metal.

Free radical polymerizations are further classified into homogeneous and heterogeneous polymerizations. In a homogeneous polymerization, all components – monomer, polymer, and initiator, form a single phase throughout the reaction. This category includes both bulk and solution (using a solvent) techniques. Bulk techniques do not require separation of the polymer from a solvent. However, bulk polymerization of vinyl monomers is very difficult, since the reactions are highly exothermic thus leading to problems associated with heat removal. Consequently, with the exception of poly(methyl methacrylate) and polystyrene, bulk polymerizations are seldom used commercially for the manufacture of vinyl polymers.\textsuperscript{18}

Heterogeneous polymerizations consist of at least two phases at some point during the reaction. They can be classified into four types: suspension, precipitation, dispersion and emulsion polymerizations, based on kinetics, initial state of the system and mechanism of particle formation.

In suspension polymerizations, the initiator, monomer and the resulting polymer are insoluble in the polymerization medium, which forms the continuous phase.
Frequently, water is used as the polymerization medium. The initiator is usually dissolved in the monomer phase. The system is heterogeneous throughout the polymerization and the continuous phase acts as a dispersant and heat dissipation agent.

Precipitation polymerization refers to a process in which the initial ingredients – monomer, initiator are soluble in the continuous phase, resulting in a homogeneous solution. The polymer chains grow in length and start precipitating once they reach a critical molar mass, beyond which they are not soluble in the continuous phase, thus resulting in the formation of a polymer phase.

A dispersion polymerization is similar to a precipitation polymerization with respect to the solubility of the ingredients and the polymer. The difference is that surfactants are used to prevent coagulation or agglomeration of the polymer particles.

In emulsion polymerization, in contrast to dispersion polymerization the reaction mixture is initially heterogeneous. The initiator and the monomer are segregated with the initiator soluble in the continuous phase, which usually is water, and not in the monomer phase. Additionally, the polymer particles formed in emulsion techniques are typically around 10 times smaller than the smallest encountered in suspension polymerizations.

In heterogeneous polymerizations, both the monomer and the initiator may partition between the continuous phase and the polymer phase. Hence, polymerization may continue in both the phases as long as there is sufficient monomer and initiator present. Moreover, these techniques frequently involve water as the continuous phase. Consequently, they often require energy intensive drying steps to produce the final polymer.
§ 2.3 Poly(vinylidene fluoride)

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline, thermoplastic polymer produced by the free radical polymerization of 1,1-difluoroethylene (also known as Vinlylidene Fluoride – VF$_2$). There has been great interest in PVDF, especially since the 1980’s, because of its chemical inertness, extraordinary piezoelectric and pyroelectric properties, and lower cost compared to other fluoropolymers. Additionally, PVDF has excellent flame and smoke behavior in the event of fire, and has excellent mechanical and thermal properties that impart ease of moldability, processability and flexibility. These properties have resulted in PVDF being used in a wide variety of applications. These include many areas of chemical process industry such as tubing for heat exchangers, column packings, valves, pumps, etc; architectural coatings; plenum and nonplenum (insulation) wires and cables; and a variety of electrical and electronic devices. The global PVDF market in 1997 was estimated at 40 million pounds. Table 2.2 shows a breakdown of consumption and growth rate of PVDF by market segment in the U.S.19

There are some excellent review articles relating to synthesis and properties of PVDF. The first successful VF$_2$ polymerizations were performed in an aqueous medium using benzoyl peroxide (BPO) as the initiator. The polymerization was carried out at 89-91 °C and pressures of 860-955 atm. A subsequent patent in 1948 described VF$_2$ polymerizations using different types of initiators such as BPO, ammonium persulfate and sodium bisulfite with oxygen at pressures of around 300 atmospheres over a 20-250 °C range. The above-mentioned studies synthesized PVDF with a rather low molecular weight.
### U.S. Consumption of PVDF (millions of pounds)

<table>
<thead>
<tr>
<th>Year</th>
<th>Architectural Coatings</th>
<th>Plenum Cable</th>
<th>Other Wires and Cables</th>
<th>Chemical Processing and Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>10.3</td>
</tr>
<tr>
<td>1988</td>
<td>3.5</td>
<td>7.0</td>
<td>1.5</td>
<td>1.7</td>
<td>13.7</td>
</tr>
<tr>
<td>1991</td>
<td>4.4</td>
<td>6.7</td>
<td>1.5</td>
<td>2.5</td>
<td>15.1</td>
</tr>
<tr>
<td>1994</td>
<td>5.2</td>
<td>3.4</td>
<td>0.9</td>
<td>2.8</td>
<td>12.3</td>
</tr>
<tr>
<td>1997</td>
<td>8.5</td>
<td>3.3</td>
<td>0.8</td>
<td>4.5</td>
<td>17.1</td>
</tr>
<tr>
<td>2002*</td>
<td>11.4</td>
<td>3.6</td>
<td>0.9</td>
<td>5.7</td>
<td>21.6</td>
</tr>
</tbody>
</table>

### Average Annual Growth Rate (%)

| 1997-2002 | 6.0 | 2.0 | 2.0 | 5.0 | 4.8 |

Table 2.2 Consumption and growth rate of PVDF in the U.S. by market segment. *estimated

Commercially, PVDF is now produced in batch reactors by emulsion or suspension polymerizations. Emulsion polymerizations were first carried out at pressures of 25-60 atm and temperatures around 65 °C in the presence of water-soluble initiators, with or without an initiator dispersing agent. A chemically stable perfluorinated surfactant is usually added. Ammonium persulfate salts and organic peroxides have also been used widely as initiators. A number of patents with specific operating conditions of emulsion polymerizations are discussed in the review mentioned earlier. The product after an emulsion polymerization usually is a milky latex of suspended polymer particles.
of the order of 1 μm in diameter. The latex is coagulated, thoroughly washed and spray
dried to produce a free flowing powder.

Suspension polymerizations are usually carried out in an aqueous system using
peroxide based organic initiators that are soluble in the monomer phase. There are a
number of patents where suspension polymerizations of VF₂ using different initiator
systems have been reported. Suspension polymerization in a mixture of water, acetone
and methylcellulose, and dipropylperoxy dicarbonate as the initiator, at 90 °C and 40 atm.
has been reported in a Japanese patent.\textsuperscript{26} Subsequently, PVDF has been synthesized in
aqueous medium using an oil soluble initiator such as diisopropylperoxy dicarbonate at
60 °C.\textsuperscript{27} Suspension polymerizations in fluorocarbon media are also reported in
literature.\textsuperscript{20}

<table>
<thead>
<tr>
<th>PVDF Grade</th>
<th>Number Average Molecular Weight (M\textsubscript{n})</th>
<th>Weight Average Molecular Weight (M\textsubscript{w})</th>
<th>PDI \textsuperscript{*}</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kynar -710</td>
<td>7.52 x 10\textsuperscript{4}</td>
<td>1.93 x 10\textsuperscript{5}</td>
<td>2.6</td>
<td>Unimodal</td>
</tr>
<tr>
<td>Kynar -740</td>
<td>1.0 x 10\textsuperscript{5}</td>
<td>3.03 x 10\textsuperscript{5}</td>
<td>3.0</td>
<td>Unimodal</td>
</tr>
<tr>
<td>Kynar -741</td>
<td>9.8 x 10\textsuperscript{4}</td>
<td>2.69 x 10\textsuperscript{5}</td>
<td>2.7</td>
<td>--</td>
</tr>
<tr>
<td>Kynar -761</td>
<td>9.99 x 10\textsuperscript{4}</td>
<td>4.05 x 10\textsuperscript{5}</td>
<td>4.1</td>
<td>Unimodal</td>
</tr>
</tbody>
</table>

\textbf{Table 2.3}  Molecular weight data for commercial PVDF samples.\textsuperscript{28, 29}

\textsuperscript{*}Polydispersity index (= M\textsubscript{w}/M\textsubscript{n})

Table 2.3 shows the average molecular weights and the molecular weight
distributions for four different commercially available grades of PVDF. Kynar-740 data
was obtained from Dinoia et al.\textsuperscript{28} and the rest were obtained from Atofina. All molecular weights given in Table 2.3 are relative to poly(methyl methacrylate) (PMMA) standards.

Most of the literature on VF\textsubscript{2} polymerization is in the form of patents. There is very little reported work on the kinetics of VF\textsubscript{2} polymerization. Russo et al.\textsuperscript{30} have investigated the kinetic features of VF\textsubscript{2} radical polymerization in three different solvents – acetone, ethyl acetate and methyl acetate. They reported a deviation in the order of the polymerization rate, with respect to the monomer and initiator concentrations, from the classical values of 1 and 0.5. This was accounted for by the presence of reactions interfering with the normal process of bimolecular termination, such as degradative chain transfer,\textsuperscript{31} (primarily to solvent), primary radical termination,\textsuperscript{32} or degradative addition.\textsuperscript{33} Values of chain transfer constants to solvent for all three cases were also reported.

Microstructure analysis of PVDF has been the focus of a number of publications\textsuperscript{34-39}. Most of this work has been focused on estimating the amount of reverse defects using NMR. Figure 2.4 depicts the normal and defect additions of VF\textsubscript{2} units. Each reverse addition is typically followed by another head-head addition, which corrects the defect. Estimation of percentage reverse defects using NMR is discussed in a later section. It has been shown that reverse defects are unavoidable during conventional polymerization of vinyl monomers. Such defects occur to a significant extent in PVDF and affect the crystallization and properties of the polymer.\textsuperscript{40} The number of reverse defects in PVDF has been found to be dependent on the temperature of polymerization\textsuperscript{41}: it increases from around 3.5 \% at 20 °C to about 6\% at 140 °C.
Normal addition of monomer

\[
\left( \text{CH}_2 - \text{CF}_2 \right)_n
\]

Normal (Head-Tail) and defect addition of Vinylidene Fluoride

\[\text{CH}_2 - \text{CF}_2 - \text{CH}_2 - \text{CF}_2 - \text{CF}_2 - \text{CH}_2 - \text{CH}_2 - \text{CF}_2 - \text{CH}_2 - \text{CF}_2\]

a : Reverse (Tail-Tail) monomer addition
b : Defect correction (Head-Head addition)

In addition to homopolymers of VF2, a number of its copolymers are of commercial interest because of their improved thermal, chemical and mechanical properties. The primary co-monomers are hexafluoropropylene (HFP) and tetrafluoroethylene (TFE).

§ 2.4 Supercritical CO2 Polymerizations

Carbon dioxide was shown to be a viable medium for free radical precipitation polymerizations as early as 1968. However, in the 1990s there was an explosion of research in this area. DeSimone and coworkers have shown that a variety of heterogeneous and homogeneous polymerizations can be carried out in scCO2.[1-4,43]

In Chapter 1, the need to use environmentally benign systems for the polymerization of PVDF was discussed. Supercritical carbon dioxide is the ideal choice as a new reaction medium for PVDF polymerizations, for a number of reasons. They are:

1. Carbon dioxide is inert and there is no chain transfer to solvent (CO2) in the case of
free radical polymerizations. This is a special problem with VF₂ polymerizations because
the growing VF₂ end (~VF₂⁺) easily abstracts a proton from many organic compounds.

(2) The critical temperature and pressure of CO₂, T_c = 31.1 °C and P_c = 72.8 atm, are
similar and in some cases much lower than the conditions for many of the VF₂
polymerization techniques discussed in §2.3. Hence, it is easier to adapt VF₂
polymerizations to scCO₂ than for many other monomers.

(3) Carbon dioxide is a gas at ambient pressures, hence the polymer can be isolated as a
dry free flowing powder by simple depressurization. Moreover, only a small fraction of
the CO₂ needs to be depressurized while the rest can be recycled in the compressed state.
Thus, energy and cost intensive polymer drying and solvent removal steps can be
eliminated.

(4) Supercritical CO₂ also can plasticize polymers, i.e., lower the polymer glass transition
temperature, T_g.8,44-46 This plasticization can facilitate removal of residual monomers,
incorporation of additives, and formation of foams.

(5) Supercritical CO₂ has gas like properties such as low viscosities, (μ = 0.06 centipoises
at 75 °C and 4000 psig) resulting in high mixing rates, while maintaining liquid like
densities (ρ = 0.74 g/ml at 75 °C and 4000 psig) which enhances its ability to dissolve
organic compounds.10

Although CO₂ is a good solvent for molecules of low molar mass, and for highly
fluorinated polymers, most high molecular weight polymers are insoluble in scCO₂. The
pressures and temperatures required to dissolve most polymers in CO₂ are so high that
they are not practical for large-scale manufacturing. Consequently, most polymers are
synthesized in scCO₂ by heterogeneous polymerization techniques. Amorphous
fluoropolymers and silicone polymers, however, are soluble in scCO$_2$ and can be synthesized by homogeneous polymerization techniques.

§ 2.4.1 Polymerization of VF$_2$ in scCO$_2$

Poly(vinylidene fluoride) with higher molar mass is not soluble in scCO$_2$ and its monomer, VF$_2$, even at very high temperatures and pressures. In contrast, VF$_2$ is soluble in CO$_2$. Therefore, polymerizations of VF$_2$ in CO$_2$ are either precipitation or dispersion polymerizations, depending on whether stabilizers are used. Precipitation polymerizations have an added advantage because no additives are used, potentially resulting in a purer product.

Polymerization of VF$_2$ in scCO$_2$ was first reported by Combes et al.$^{48}$ Telomers of VF$_2$, with degrees of polymerization ranging from 1 to 9, were synthesized using perfluorbutyliodide (PCR) as the telogen and azobis(isobutryonitrile) (AIBN) as the initiator. The reactions were carried out in a stainless steel view cell for 24 hours, at a temperature of 60 °C, and pressure ranging from 280 to 340 bars. These telomers were soluble in scCO$_2$, resulting in a homogeneous system.

Precipitation polymerization of VF$_2$, using scCO$_2$ as the reaction medium in a batch mode, using a variety of initiators has been reported.$^6$ The initiators studied were lauroyl peroxide (LP), isobutyryl peroxide (IBP), bis(perfluor-2-propoxypropionyl) peroxide (HFPO- hexafluoropropylene- oxide dimer acyl peroxide), 2,2,-azobis(2,4-dimethyl—methoxypentanitrile) (V-70 Wako) and AIBN. Azo based initiators, AIBN and V-70 Wako, proved inefficient; very little PVDF was obtained. A series of experiments were carried out at different monomer and initiator concentrations, using
LP, IBP, or HFPO dimer at 65, 35, or 25 °C, respectively. HFPO dimer was the most efficient, with conversions as high as 85% for a reaction time of around 15 hours at 25 °C. Although these reactions were not optimized, the molecular weights of the PVDF synthesized (\(\bar{M}_n\) ranged from 11 to 24 kg/mole) were lower than commercially useful.

Charpentier et al. have developed a continuous polymerization system for scCO\(_2\) polymerizations.\(^{49}\) Continuous polymerizations in scCO\(_2\) have a number of added benefits beyond the advantages of CO\(_2\) that have been discussed previously. They are (1) A continuous system is essential for large volume, commodity polymers. Moreover, a continuous system requires a smaller and hence cheaper reactor as compared to a batch system. (2) A continuous system can facilitate continuous removal of polymer as a dry powder. (3) There is a potential of coupling the polymer removal system with downstream processing. (4) Monomer recycle can be facilitated, thus enabling operation at lower conversions, indirectly leading to higher rates of polymerization. (5) A continuous system in scCO\(_2\) can be exploited to incorporate in-situ steps to purify the resultant polymer by supercritical fluid extraction. (6) There is a potential to produce uniform product because the conditions in the reactor are constant once steady state is reached.

Initial continuous polymerization experiments using AIBN and DEPDC as the polymerization initiators showed that DEPDC was more effective. Consequently, further work was focused on DEPDC.\(^7\) Charpentier et al. studied the decomposition kinetics of DEPDC in scCO\(_2\)\(^{50}\) so that VF\(_2\) polymerization could be understood. These studies showed that the decomposition is first order. The activation energy, the pre-exponential factor and the initiator efficiency were similar to those reported in conventional organic
solvents. Additionally, pressure did not have any significant effect on the decomposition rate constant. These results are presented in Table 2.4.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Initiator Efficiency(f)</th>
<th>Initiator Decomposition Constant (K_d x 10^-4)s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.61</td>
<td>2.4</td>
</tr>
<tr>
<td>70</td>
<td>0.69</td>
<td>4.3</td>
</tr>
<tr>
<td>75</td>
<td>0.59</td>
<td>10.3</td>
</tr>
<tr>
<td>85</td>
<td>0.63</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Table 2.4  Kinetic parameters for decomposition of DEPDC in scCO_2^7

Kinetic studies on the rate of polymerization of VF_2 in scCO_2^7 showed that the order of the reaction was approximately 1.0 with respect to monomer and approximately 0.5 with respect to initiator. Experimental data suggested the presence of an inhibitor. A kinetic model that assumed that the inhibitor was present in the monomer or that the monomer itself was the inhibitor, predicted the measured polymerization rates reasonably well. This model was based on the kinetic scheme shown in Figure 2.5. The parameters α and β, and the respective activation energies, E_a^α and E_a^β, were calculated from the experimental data using a non-linear regression. The ratio $K_p/K_d^{0.5}$ was calculated from α and $fK_d$. These results are summarized in Table 2.6.
\[ I \xrightarrow{K_d} 2fR^* \]  
(Decomposition)

\[ R^* + M \xrightarrow{K_a} P_1^* \]  
(Initiation)

\[ P_n^* + M \xrightarrow{K_p} P_{n+1}^* \]  
(Propagation)

\[ P_n^* + P_m^* \xrightarrow{K_i} P_{n+m} / P_n / P_m \]  
(Termination by combination and/or disproportionation)

\[ P_n^* + Q \xrightarrow{K_Q} Pn \]  
(Inhibition)

**Figure 2.5**   Kinetic scheme to model rate of polymerization.\(^7\)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Kp/Kt(^{0.5}) L/mol(^{0.5}).s</th>
<th>(\alpha) x10(^{-3}) (L(^{0.5})/mol(^{0.5}).s)</th>
<th>(\delta) x10(^{-4}) (L/mol(^{0.5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.10</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>70</td>
<td>0.15</td>
<td>2.4</td>
<td>3.4</td>
</tr>
<tr>
<td>75</td>
<td>0.20</td>
<td>5.0</td>
<td>7.1</td>
</tr>
<tr>
<td>80</td>
<td>0.32</td>
<td>10.1</td>
<td>14.2</td>
</tr>
<tr>
<td>85</td>
<td>0.43</td>
<td>20.1</td>
<td>28.1</td>
</tr>
</tbody>
</table>

**Table 2.5**   Kinetic parameters for polymerization of VF\(_2\) in scCO\(_2\). \(^7\)

\[ \alpha = K_p(fK_d/K_t)^{0.5}\text{ and } \delta = (K_Q/4K_d)/(fK_d/K_t)^{0.5}. \]

In this research, the above work has been extended to focus on the average molecular weights, the molecular weight distribution and the effect of reaction conditions on these. The kinetic model has been extended to predict the molecular weights obtained from the experimental study. These studies are discussed in detail in Chapters 3 and 4.
A number of experiments have been conducted to study the effect of different reaction parameters, i.e., monomer (VF$_2$) concentration, pressure, temperature and residence time, on the molecular weight distribution (MWD) and the rate of polymerization ($R_p$). The initiator chosen for these studies was diethylperoxy dicarbonate (DEPDC). Previous work has demonstrated the feasibility of using this initiator for VF$_2$ polymerizations in scCO$_2$. Previous studies predominantly were carried out at temperatures around 75 °C, pressures around 4000 psig, monomer (VF$_2$) inlet concentrations between 0.8 and 2.8 M, and residence times between 10-50 minutes.

§ 3.1 Experimental

§ 3.1.1 Materials.

Vinylidene fluoride monomer was generously donated by Solvay Research, Belgium and used without further purification. Carbon dioxide (SFE/SFC grade-99.999% pure) was generously donated by Air Products & Chemicals, Inc. and further purified by passage through columns containing 5 Å molecular sieves (Aldrich) and copper oxide (Aldrich) to remove excess water and oxygen, respectively. The initiator, DEPDC was synthesized as described below and all other chemicals were obtained from Aldrich.
§ 3.1.2 Initiator Synthesis.

Diethylperoxy dicarbonate was synthesized as described in literature\textsuperscript{51, 52}, using water as the reaction medium and extracting the initiator into Freon\textsuperscript{®} 113 (HPLC Grade). All manipulations of the initiator were performed in an ice bath and the final product was stored in a freezer at \(-20^\circ\text{C}\). The iodine titration technique, ASTM Method E 298-91, was utilized to determine the concentration of active peroxide in the solution. The concentration of the initiator solution synthesized was typically around 0.4 M in active peroxides and was checked periodically.

§ 3.1.3 Polymerization Apparatus

Figure 3.1 shows a schematic of the continuous polymerization system. The polymerization system is similar to that described elsewhere,\textsuperscript{7, 49} the only change being a more efficient polymer withdrawal system. The main component of the system is a continuously-stirred, thermostated, 800 mL stainless steel autoclave. A magnetically coupled dispersimax impeller is used to provide mixing of the ingredients in the CSTR. Isco syringe pumps are used to feed the reactants continuously. A chiller/heater unit and a heated control valve, which functions as a back pressure regulator (BPR), are used to control the temperature and pressure respectively.

A countercurrent heat exchanger is used to cool the effluent stream from the reactor to ambient temperatures. This stream is then directed by a 4-way ball valve into one of three filter housings containing 1\(\mu\)m filters where the solid polymer is collected. The exit stream after filtration, containing the unreacted VF\(_2\), CO\(_2\) and initiator, flows through a heated control valve (BPR) after being sampled through a gas chromatograph.
Polymer withdrawal system: The main approach taken was to isolate the polymer removal system from the reactor and simultaneously use a CO$_2$ flow in the reverse direction through the high-pressure filters, to dislodge the polymer cake formed around the filter element. An Isco syringe pump is used to provide a CO$_2$ flow in the reverse direction through two of the three filters. These two high-pressure filter housings are connected to a bag filter, which is at ambient pressures, through two on-off valves in
series. The polymer collected in these high-pressure filter housings is moved continuously into the bag filter by using the reverse CO$_2$ flow and simultaneously actuating the on-off valves one after the other.

§ 3.1.4 Experimental procedure

The polymerization procedure has been described in detail elsewhere.$^{49}$ The reactor was first heated to the desired temperature and the agitation speed was set to 1800 rpm. The type and speed of agitation were changed for a few experiments to study the effect of mixing. These changes are described in a later section. The reactor was then purged using a nitrogen (N$_2$) flow. Next, the system was pressurized with CO$_2$ to the desired pressure. Once the reactor reached the set pressure, a small CO$_2$ flow rate, typically around 5ml/min, was set and the system allowed to stabilize to the desired temperature and pressure.

When the system had stabilized, the inlet VF$_2$, CO$_2$ and initiator flow rates were set to operate at the desired concentrations and residence times. The initiator was fed as ca. 0.4 M solution in Freon113. Densities of VF$_2$ and CO$_2$ in the cooled syringe pumps and the heated reactor required to determine the feed flow rates were obtained from data provided by Solvay (VF$_2$) and by NIST$^{53}$ (CO$_2$).

The three feed streams VF$_2$, CO$_2$, and DEPDC, were fed continuously using the ISCO syringe pumps operated in a constant flow mode. Polymerization took place continuously in the highly agitated, heated 800 mL CSTR. The reactor volume was reduced to 500 mL using an insert in a few experiments carried out at very low residence
times. The temperature (T) and pressure (P) control of the reactor during the polymerization was typically ±1 °C, and ±1 bar respectively.

Polymer was initially collected in non-SS filter F2 until it was completely filled with polymer. Valves V1 and V2 were then switched to filter F3 thus isolating the filter F2 from the rest of the reactor system while the polymer was being collected in F3. Filter F2 was cleaned using a CO₂ flow in the reverse direction. A syringe pump maintained at a pressure slightly greater than the pressure in the CSTR provided the reverse CO₂ flow. Valves V5 and V6 were then actuated sequentially, with V5 being closed before V6 was opened, thus allowing the polymer to flow from the high-pressure filter housing to the bag filter, which is at ambient pressure. This process was repeated a few times before the system was switched back to filter, F2. Filter F3 was then cleaned using the same procedure. This was repeated until the reactor had been operating at the desired conditions for 5 residence times. At that point, the stream leaving the reactor was switched to the steady state filter F1 and steady state polymer was collected until filter, F1 was completely filled with polymer. The system was then switched back to its original state, vented, and the polymer in F1 was collected and weighed.

§ 3.2 Analytical Techniques
§ 3.2.1 Gas Chromatograph (GC).

The rate of polymerization, \( R_p \) was calculated from the weight of steady state polymer collected per unit time. The steady state monomer concentration, \( [M]_{\text{out}} \) in the reactor and monomer conversion, \( X \) were calculated from \( R_p \) by a mass balance on VF₂.\(^7\) A SRI 8610C GC was also used in select cases to calculate the conversion. The GC
contained a 3 ft × 1/8 in. packed silica gel column, while the oven temperature was isothermal at 55 °C. The GC sampled the exit stream directly (after filtration) through a high performance liquid chromatograph (HPLC) valve.

The concentration of VF₂ in the exit stream from the filters does not always represent the concentration in the reactor outlet stream because of the back-flush with CO₂. Therefore, the GC was used only when SS polymer was collected for a sufficiently long time, around 5 filter housing residence times, without any intermittent back-flushing with CO₂. The conversion calculated from the GC agreed reasonably well with that determined from the measured rate of polymerization. Appendix A presents the calibration curve of the GC and the calculations in detail.

§ 3.2.2 Gel Permeation Chromatography (GPC).

All GPC measurements on the polymer samples were performed by Solvay Research (Belgium) at 40 °C on a Waters-Alliance HPLC system with 2 × HR5E and 1 × HR2E columns, using N,N-dimethylformamide (DMF) modified with 0.1 M lithium bromide (LiBr). 100 µL of a 1 g/L sample was used for the analysis. The GPC was calibrated at 40 °C using narrow molecular weight standards of poly(methyl methacrylate) (PMMA) purchased from Polymer Laboratories Ltd. The Mark-Houwink constants $K$ and $a$ used to calculate absolute average molecular weights are: PMMA $K=1.89 \times 10^{-4}$ and $a = 0.63$ ; PVDF $K=3.3 \times 10^{-4}$ and $a = 0.63$.

GPC measurements were also carried out by Atofina to confirm the results obtained from Solvay. The conditions for the GPC analysis and the results are presented in Appendix B.
§ 3.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy.

All NMR spectra were obtained on a Bruker 400 MHz (\textsuperscript{1}H) NMR spectrometer using XWIN-NMR software. The polymer was dissolved in DMF, and the spectra were obtained using a 2.5 µs pulse with a 5 s delay.

§ 3.2.4 Differential Scanning Calorimetry (DSC)

All DSC analysis were performed by Atofina (Philadelphia). All the melting temperatures reported were second heats, where the polymer sample was ramped through the following cycle: 25-190°C (10°C/min), 5 min hold, 190-25°C (also 10°C/min), 5 min hold, 25-190°C (10°C/min).

§ 3.3 Results and Discussion

§ 3.3.1 Polymerization Mechanism.

The presumed polymerization mechanism, experimental phase behavior and other aspects such as mixing and attainment of steady state have been discussed in detail elsewhere\textsuperscript{7, 50}. The experimental phase behavior suggests a heterogeneous precipitation polymerization. It has been shown that the reactor behaved as an ideal CSTR, and the concentrations and rates reached a steady state value after operation for around 5 residence times\textsuperscript{7, 50}. Additionally, it has been shown that the speed and type of agitation did not have any significant effect on the conversion and molecular weights. These mixing studies were performed at low inlet monomer concentrations (0.78 M). Mixing studies carried out at higher inlet monomer concentrations are discussed in a later section.
§ 3.3.2 Molecular Weight Distribution (MWD) and Rate Studies.

Effect of Monomer Concentration.

A few runs were carried out with inlet monomer concentrations varying from 0.78 M to 3.5 M, at otherwise constant conditions. The reaction conditions, polymerization rates, and average molecular weights for these runs are given in Table 3.1. The initiator concentration \([I]_{\text{out}}\), was calculated using \([I]_{\text{out}} = \frac{[I]_{\text{in}}}{1 + K_d \tau}\). The decomposition rate constant, \(K_d\) was obtained from Table 2.4. The conversion was calculated from the measured \(R_p\) as described earlier. The rate of polymerization and conversion for run 5 could not be obtained because of operator error in recording the time for which steady state polymer was collected.

\[
\begin{array}{cccccccccc}
\text{Run #} & [I]_{\text{in}} & [I]_{\text{out}} & [M]_{\text{in}} & \tau & R_p & X & M_n & M_w & \text{PDI} \\
\text{mmol/L} & \text{mmol/L} & \text{mol/L} & \text{mins} & \text{g/min.L} & & \% & & & \\
1 & 2.94 & 1.28 & 0.78 & 21.5 & 0.42 & 18.0 & 1.43 \times 10^4 & 2.11 \times 10^4 & 1.5 \\
2 & 2.79 & 1.26 & 1.46 & 20.3 & 0.73 & 15.5 & 2.88 \times 10^4 & 5.95 \times 10^4 & 2.1 \\
3 & 2.95 & 1.27 & 1.68 & 22.0 & 0.81 & 16.1 & 2.96 \times 10^4 & 5.55 \times 10^4 & 1.9 \\
4 & 2.84 & 1.24 & 2.79 & 20.5 & 1.58 & 17.4 & 5.65 \times 10^4 & 1.45 \times 10^5 & 2.6 \\
5 & 3.32 & 1.47 & 3.53 & 21.1 & & & 7.85 \times 10^4 & 4.43 \times 10^5 & 5.6 \\
\end{array}
\]

Table 3.1 Effect of inlet VF₂ Concentration on rate of polymerization and average molecular weights; Temperature, T=75 °C, Pressure P=4000 psig
The rate of polymerization $R_p$, increases almost linearly with increasing VF$_2$ concentrations, which is typical of homogeneous free radical kinetics. Additionally, the monomer conversion does not change much as the initiator concentration is essentially a constant. In fact, Charpentier et.al.\textsuperscript{7} showed that a plot of $R_p$ vs. $[M]_{out}$ at a constant $[I]_{out}$ is linear for low to medium (~ 0 to 2 M) values of monomer concentration.

The number average molecular weight, $\bar{M}_n$, increases from 14000 at 0.78 M to 78000 at 3.5 M. This last $\bar{M}_n$ is comparable to the commercial $\bar{M}_n$'s shown in Table 2.3. In classical free radical polymerizations, the average chain length is given by the ratio of THE rate of polymerization, $R_p$ to the rate at which polymer chains are formed. The rate at which chains are formed depends on the type of termination. It varies from $R_i$, when termination is purely by disproportionation to $R_i/2$, when termination is purely by combination. Hence, $\bar{M}_n$ is bounded by

$$\bar{M}_n = \frac{R_p}{2R_i} \cdot m \quad \text{and} \quad \bar{M}_n = \frac{R_p}{R_i} \cdot m \quad \text{(3.1)}$$

where m is the molar mass of the monomer unit, $R_i$ is the rate of initiation given by

$$R_i = 2fK_d[I]_{out} \quad \text{(3.2)}$$

Since $[I]_{out}$, f, $K_d$ are the same for the first four runs shown in Table 3.1, $\bar{M}_n$ should be proportional to $R_p$. Figure 3.2 shows a plot of $\bar{M}_n$ vs. $R_p$ for the data shown in Table 3.1. A straight line through the origin fits the data reasonable well. This indicates that the homogeneous kinetics described by Equations 3.1 and 3.2, predict the trend in the rate and number average molecular weight reasonably well.
Figure 3.2  Plot of $M_n$ vs. $R_p$ at constant initiator concentration. Data obtained from Table 3.1

The weight average molecular weight, $M_w$, increases more sharply with increasing inlet monomer concentration than $M_n$. This increase is reflected in the very high polydispersity indices (PDIs) at the higher monomer concentrations. Figure 3.3 shows the MWD as a function of monomer concentration in the feed to the reactor. At the lowest inlet monomer concentration, a unimodal MWD with a PDI ($M_w/M_n$) of around 1.5 is observed. This suggests that the termination is primarily by combination. At higher VF$_2$ concentrations, the MWD broadens and begins to exhibit a second mode. In fact, at a VF$_2$ concentration of 3.5 M, the PDI is 5.6 and a bimodal MWD with a distinct high molecular weight mode is observed. Such behavior is not commonly seen in homogeneous free radical polymerizations as the PDI typically varies from 1.5 (termination by combination only) to 2 (termination by disproportionation only).
Figure 3.3 Effect of inlet monomer concentration on molecular weight distribution. Temperature = 75 °C; Pressure = 4000 psig;

Effect of Pressure.

A few experiments were carried out at pressures varying from 3050 – 4400 psig at otherwise similar conditions in order to study the effect of pressure on the MWD. Table 3.2 presents the reaction conditions and the average molecular weights for these polymerization runs.
The rate of polymerization, $R_p$, does not vary significantly with pressure. For homogeneous free radical kinetics, $R_p$ is given by

$$R_p = K_{app} \cdot [M]_{out} \cdot [I]_{out}^{1/2} \quad (3.3)$$

where $K_{app}$ is the apparent rate constant for the rate of polymerization. From Table 3.2, $[M]_{in}$ and the conversion are almost the same for the different runs. Therefore, $[M]_{out}$ can be assumed constant for all the runs. Additionally, $[I]_{out}$ is also a constant. Therefore, from Equation 3.3, the only parameter that can change the $R_p$ for the different runs in Table 3.2 is $K_{app}$.

From transition state theory the effect of pressure on a rate constant is given by

$$K_p = K_0 \exp\left(-\frac{\Delta V^*}{RT}(P-P_0)\right) \quad (3.4)$$

where, $K_0$ is the rate constant at some reference pressure, $P_0$; and $\Delta V^*$ is the activation volume. The above equation is valid under the assumption that $\Delta V^*$ and the dielectric constant (see Fig 1.2) are essentially constant in the pressure range under consideration.
Though there is no literature data on the activation volume for the apparent rate constant for $R_p$ in the case of $\text{VF}_2$ polymerizations, it lies between $-5$ to $-30$ cm$^3$/mole for most polymerizations.\textsuperscript{54} The ratio of rate constants at 75$°$C and two different pressures \textit{viz.} 4400 and 3050 psig ($K_{3050}/K_{4400}$) calculated assuming a value of $\Delta V^*$ of $-20$ cm$^3$/mole, equals 1.052. This suggests an increase of only about 5% in the rate constant. Therefore, the $R_p$ does not vary significantly with pressure within the pressure range studied herein.

The number average molecular weight $\overline{M}_n$, is expected to show a similar behavior as $R_p$. However, in contrast to $R_p$, $\overline{M}_n$ shows a significant increase when the pressure increases from 4000 to 4400 psig. From equations 3.1-3.3, it can be seen that at a constant $K_{app}$, $[M]_{out}$ and $[I]_{out}$, $\overline{M}_n$ depends only on $f$ and $K_d$. It has been shown that the rate constant for initiator decomposition does not change with pressure.\textsuperscript{50} Guan et.al.\textsuperscript{55} have shown that $f$ for the decomposition of AIBN in scCO$_2$ does not change with pressure. However, the effect of pressure on $f$ for DEPDC decomposition is not known. A sharp decrease in $f$ with pressure between 4000 and 4400 psig could be a possible cause for the increase in $\overline{M}_n$.

From Table 3.2, the weight average molecular weight, $\overline{M_w}$ and the PDI increase abruptly, leading to a very broad MWD with a PDI of around 10, when the pressure is increased from 4000 to 4400 psig. Figure 3.4 shows the effect of pressure on the MWD. All the MWDs are bimodal and no consistent trend with increasing pressure is seen. The MWD at 4400 psig shows a long tail leading to very high values of the PDI and weight average molecular weight. The cause for this tail at a pressure of 4400 psig is not clear.
Effect of Temperature.

A couple of experiments were carried out at 75 and 85 °C to study the effect of temperature. The corresponding results and reaction conditions are presented in Table 3.3 and Figure 3.3.

The rate of polymerization at 85 °C is greater than that at 75 °C, in spite of a lower initiator concentration ([I]_{out}). This is attributed to the higher value of the polymerization rate constants at the higher temperature (85 °C). Both the average molecular weights decrease with increasing temperature. The effect of temperature on the rate and molecular weights is discussed in detail, using a classical free radical polymerization model, in chapter 5. The PDI and extent of bimodality decrease with increasing temperature.

Figure 3.4 Effect of Pressure on Molecular Weight Distribution; T = 75 °C, \( \tau \sim 15 \) mins., \([M]_n \sim 2.8\) M, \([I]_{out} \sim 1.4\) M
<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>[I]_n (mmol/L)</th>
<th>[I]_out (mmol/L)</th>
<th>[M]_n (mol/L)</th>
<th>( \tau ) (mins)</th>
<th>( X )</th>
<th>( Mn ) (g/min. L)</th>
<th>( Mw ) (mmol/L)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>85</td>
<td>2.56</td>
<td>0.82</td>
<td>2.62</td>
<td>10.8</td>
<td>2.00</td>
<td>12.5</td>
<td>3.22 \times 10^4</td>
<td>5.75 \times 10^4</td>
</tr>
<tr>
<td>11</td>
<td>75</td>
<td>2.67</td>
<td>1.59</td>
<td>2.75</td>
<td>11.2</td>
<td>1.48</td>
<td>9.3</td>
<td>4.26 \times 10^4</td>
<td>1.03 \times 10^5</td>
</tr>
</tbody>
</table>

**Table 3.3**  Effect of temperature on rate of polymerization and average molecular weights; \( P = 4000 \) psig

**Figure 3.5**  Effect of temperature on the MWD; Pressure = 4000 psig
**Effect of Residence Time:**

Two sets of experiments were carried out to study the effect of average residence time (\(\tau\)). The experimental conditions and results are presented in Table 3.4. One set of experiments was at a low \(\text{VF}_2\) inlet concentration (0.78 M) and the other at a high \(\text{VF}_2\) concentration (~2.8 M).

<table>
<thead>
<tr>
<th>Run #</th>
<th>([I]_{in})</th>
<th>([I]_{out})</th>
<th>([M]_{in})</th>
<th>([M]_{out})</th>
<th>(\tau)</th>
<th>(X)</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mmol/L</td>
<td>mmol/L</td>
<td>mol/L</td>
<td>mol/L</td>
<td>mins</td>
<td>g/min.L</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>12</td>
<td>2.89</td>
<td>1.83</td>
<td>0.78</td>
<td>0.70</td>
<td>9.6</td>
<td>0.58</td>
<td>11.0</td>
<td>1.47 x 10^4</td>
<td>2.04 x 10^4</td>
</tr>
<tr>
<td>1</td>
<td>2.94</td>
<td>1.28</td>
<td>0.78</td>
<td>0.65</td>
<td>21.5</td>
<td>0.42</td>
<td>18.0</td>
<td>1.43 x 10^4</td>
<td>2.11 x 10^4</td>
</tr>
<tr>
<td>13</td>
<td>2.93</td>
<td>0.89</td>
<td>0.78</td>
<td>0.61</td>
<td>38.3</td>
<td>0.31</td>
<td>23.4</td>
<td>1.52 x 10^4</td>
<td>2.15 x 10^4</td>
</tr>
<tr>
<td>14</td>
<td>2.94</td>
<td>0.75</td>
<td>0.78</td>
<td>0.58</td>
<td>48.3</td>
<td>0.28</td>
<td>26.4</td>
<td>1.53 x 10^4</td>
<td>2.21 x 10^4</td>
</tr>
<tr>
<td>11</td>
<td>2.67</td>
<td>1.59</td>
<td>2.75</td>
<td>2.55</td>
<td>11.2</td>
<td>1.48</td>
<td>9.3</td>
<td>4.26 x 10^4</td>
<td>1.03 x 10^5</td>
</tr>
<tr>
<td>8</td>
<td>2.63</td>
<td>1.38</td>
<td>2.85</td>
<td>2.65</td>
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<td>1.11</td>
<td>8.9</td>
<td>4.15 x 10^4</td>
<td>1.00 x 10^5</td>
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<td>2.79</td>
<td>2.40</td>
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<td>15</td>
<td>2.86</td>
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<td>2.90</td>
<td>2.44</td>
<td>25.5</td>
<td>1.52</td>
<td>20.0</td>
<td>6.7 x 10^4</td>
<td>4.41 x 10^5</td>
</tr>
</tbody>
</table>

**Table 3.4** Effect of residence time on rate of polymerization and average molecular weights at low monomer concentration; \(T= 75 \, ^\circ\text{C}, \, P = 4000 \, \text{psig.}\)

At \([M]_{in}=0.78\) M, the \(R_p\) decreases with increasing \(\tau\). This trend can be explained using the homogeneous kinetics described by Equation 3.3. Since \([I]_{in}\) and \([M]_{in}\) are almost constant, both \([I]_{out}\) and \([M]_{out}\) decrease with increasing \(\tau\), thus resulting in a lower \(R_p\) at a higher \(\tau\).
In contrast to the rate, \( M_n \) does not decrease with increasing \( \tau \). From Equation 3.1 and 3.2, \( M_n \) is directly proportional to the rate of polymerization and inversely proportional to the rate of initiation. Both these rates decrease with increasing \( \tau \), resulting in a negligible combined effect on \( M_n \). The weight average molecular weight \( M_w \) shows a similar behavior as \( M_n \). In fact, the ratio \( M_w/M_n \) is almost constant, independent of \( \tau \).

These trends however, are not seen in the second set of experiments carried out at \([VF_2]_{in}\) of around 2.8 M. Runs 4 and 15 have a higher \( R_p \) than those carried out at a lower \( \tau \) (Runs 11 and 8), in spite of the lower values of \( [M]_{out} \) and \( [I]_{out} \). Additionally, the average molecular weights and the PDI do not follow the trends associated with classical homogeneous free radical kinetics. The PDI increases very little when \( \tau \) increases from 11 to 20 minutes. However, at \( \tau = 25 \) mins the PDI increases sharply to 6.6.

Figures 3.6a and 3.6b show the effect of residence time on the MWD at the low (0.78 M) and high (2.8 M) inlet monomer concentrations respectively. At the low monomer concentration, the effect of residence time on the MWD is negligible. The MWD curves shown in Figure 3.6a are almost coincidental. They are perfectly unimodal with a PDI of around 1.5 indicating that termination is primarily by combination. This behavior of the MWD with residence time is typical of homogeneous free radical kinetics as the lifetime of a radical from initiation to termination is of the order of milliseconds. This is orders of magnitude smaller than the average residence time. Therefore, the average residence time has no effect on the MWD.
Figure 3.6a Effect of residence time on the MWD at lower monomer concentration; T = 75; P = 4000 psig; [VF₂]₀ = 0.78 M

Figure 3.6b Effect of residence time on MWD at higher monomer concentration; T = 75 °C; P = 4000 psig; [VF₂]₀ = 2.8 M
At the higher monomer concentration, the MWDs are bimodal and the PDIs are greater. Moreover, at a residence time of 25 minutes, there is a significant shift in the second mode of the MWD to higher molecular weights. This results in a sharp increase in the PDI to 6.6.

§ 3.3.3 Homogeneous Rate Model

The mechanism of polymerization ofVF$_2$ in scCO$_2$ is that of a heterogeneous precipitation polymerization. However, in Section 3.3.2, it was shown that homogeneous kinetics simulated the trend in the number average molecular weight and the rate well. It is believed that that the lifetime of a polymer (PVDF) chain from initiation to termination is typically of the order of milliseconds. Consequently, a polymer chain terminates before it can precipitate. Therefore, all the reactions can be assumed to take place in the homogeneous phase, resulting in polymerization kinetics similar to that of homogeneous free radical polymerizations.

A homogeneous free radical polymerization typically consists of radical initiation, chain propagation, and chain termination steps. These are represented by the first four reactions in Figure 2.5. The steady state rate of polymerization, $R_p$ based on these reaction steps is given by

$$R_p = K_p [M]_{out} \cdot \lambda = \alpha \cdot [M]_{out} \cdot [I]_{out}^{1/2}$$

where $\lambda$ is the total concentration of radical species, given by $\lambda = \sum_{n=1}^{\infty} P_n^*$. The apparent rate constant, $\alpha$ is given by

$$\alpha = K_p \left( f \cdot K_d / K_s \right)^{1/2}.$$
This equation is identical to Equation 3.3 and $\alpha$ is the same as $K_{app}$. 

Figure 3.7 shows a parity plot of the experimental $R_p$ and that predicted by Equation 3.5. The monomer concentration, $[M]_{out}$ was measured experimentally, while $[I]_{out}$ was calculated from the inlet concentration and the decomposition rate constant, $K_d$ as previously described. The two parameters, $\alpha(75 \degree C)$, and $E_a(\alpha)$, the activation energy for $\alpha$, were determined using nonlinear regression as described by Charpentier et.al.\textsuperscript{7}. The resulting values were $3.02 \times 10^{-3} \text{ (L}^{0.5}\text{/mole}^{0.5}\text{.s)}$ and $84.3$ kJ/mole. From the value of $\alpha$ and from the values of $f$ and $K_d$ given in Table 2.4, a value of $K_p/K_t^{0.5}$ of $0.12$ (L/mol.s) was calculated using Equation 3.6. The minimized sum of squared errors is $5.51 \times 10^{-8}$ (mol/L.s) for 44 data points.

![Parity plot showing fit of experimental data for $R_p$ to that predicted by Equation 3.3. $\alpha(75 \degree C) = 3.02 \times 10^{-3} \text{(L}^{0.5}\text{/mole}^{0.5}\text{.s)}$; $E(\alpha) = 84.3$ kJ/mole.](image)

**Figure 3.7**
The parity plot shows a systematic error between the two \( R_p \) values. At low rates, the model generally under predicts the experimental rate. At higher rates, the model over predicts the experimental rates.

Charpentier et.al.\(^{50}\) showed that the \( R_p \) deviates from a first order dependency with respect to \( [M]_{out} \) at high values of \( R_p \). Clearly, this implies an inhibition, which is prominent at the higher rates. Since the rates are higher at higher monomer concentrations, this inhibition appears to be dependent on the monomer concentration.

A homogeneous kinetic model that incorporated an inhibition step was developed previously by Charpentier et.al.\(^{50}\) to predict the polymerization rates. This model was based on the kinetic scheme presented in Figure 2.5. The last step in the scheme, inhibition, is unusual. Two possibilities were considered: inhibition by a feed contaminant and inhibition by the monomer itself. No experimental evidence was ever found to support the contaminant hypothesis. Therefore, the following is based on the assumption that the VF\(_2\) monomer can terminate a growing chain without producing a radical that can reinitiate chain growth. On this basis, the last reaction in Figure 2.5 becomes

\[
P_n^* + M \xrightarrow{K_0} P_n + \text{inactive monomer radical}
\]

The rate of polymerization, \( R_p \), based on this model is given by\(^{50}\)

\[
\frac{R_p}{[M]_{out}} = \alpha \cdot \left( \frac{[I]^{1/2}_{out}}{\delta + \frac{\beta^2}{2[I]^{1/2}_{out}}} \right)
\]

(3.4)

where, \( \alpha = K_p \left( \frac{f \cdot K_d}{K_t} \right)^{1/2} \), \( \delta = \left( \frac{K_d/4 \cdot K_t}{f \cdot K_d/K_t} \right)^{1/2} \) and \( \beta = \delta [M]_{out} \).
Figure 3.8 presents a parity plot comparing the experimentally determined \( R_p \) to those predicted by Equation 3.4. This represents an update of the original model to include new data. The experimental data, which consisted of all the data reported earlier\(^7\) and those presented in Section 3.2, is exactly the same as that presented in Figure 3.7. The four kinetic parameters \( \alpha, \delta \) at 75 °C and the respective activation energies \( E_a(\alpha), E_a(\delta) \) were determined using nonlinear regression as described earlier. The resulting values were \( \alpha(75 \, ^\circ\text{C}) = 4.76 \times 10^{-3} (\text{L}^{0.5}/\text{mol}^{0.5}\cdot\text{s}) \), \( E_a(\alpha) = 121.3 \, \text{kJ/mole} \), \( \delta(75 \, ^\circ\text{C}) = 6.88 \times 10^{-3} (\text{L/mol})^{0.5} \), and \( E_a(\delta) = 60.8 \, \text{kJ/mol} \).
The experimental data appears to fit the model very well. The scatter seen at the higher rates is random. Additionally, the minimized sum of squared errors is \(3.03 \times 10^{-8}\) (mol/L.s) which is about half of that obtained for the model without the inhibition.

Table 3.5 shows a comparison of the updated kinetic parameters with those presented in Table 2.5. The \(\alpha\) and \(\delta\) values at 75 °C are similar but there are significant differences in the values of \(E_a(\alpha)\) and \(E_a(\delta)\), especially the latter. It is evident from Figure 3.8 that most of the data points are at 75 °C. Moreover, data used for the earlier analysis did not include any experiments at 85 °C. Therefore, it is not surprising that the present values of \(E_a(\alpha)\) and \(E_a(\delta)\) do not agree with those obtained earlier. On balance, the values of \(\alpha, \delta, K_p/K_t^{0.5}\) at 75 °C appear to be reasonably accurate, but more data points at the other temperatures would be required to obtain accurate values of the respective activation energies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>New Parameters</th>
<th>Parameters from Table 2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha) (at 75°C) (\times 10^{-3}) (L(^{0.5})/mol(^{0.5}).s)</td>
<td>5.0</td>
<td>4.8</td>
</tr>
<tr>
<td>(\delta) (at 75°C) (\times 10^{-3}) (L/mol(^{0.5}))</td>
<td>7.1</td>
<td>6.9</td>
</tr>
<tr>
<td>(E_a(\alpha)), kJ/mole</td>
<td>144</td>
<td>121</td>
</tr>
<tr>
<td>(E_a(\delta)), kJ/mole</td>
<td>143</td>
<td>61</td>
</tr>
</tbody>
</table>

**Table 3.5** Comparison of parameter values. New parameter values were obtained after updating earlier model to include new data.
The monomer inhibition model discussed above predicts the rates reasonably well. However, there is no evidence in the literature that supports inhibition by chain transfer to monomer. Therefore, at this point, the source of the inhibition is not clear.

§ 3.3.4 Thermal Characterization of PVDF

The melting behavior of the PVDF synthesized in \textit{scCO}_2 was investigated by DSC. The crystallization and melting results are presented in Table 3.6. Figure 3.9 shows two sample second heat scans. The melting temperatures are within the range of values reported in literature\textsuperscript{21}, i.e.; \(-150 \degree \text{C} – 175 \degree \text{C}\), and are close to the melting point of commercial PVDF - Solef, \(T_m=175 \degree \text{C}\). Samples 1 and 9 had a double melting peak in the second heat scan, giving rise to two melting points. This behavior has been reported earlier for PVDF synthesized in \textit{scCO}_2\textsuperscript{6}. However, two melting points were not seen for any commercial PVDF samples. The double melting point does not appear to result from bimodal MWDs because Sample\#1 has a perfectly unimodal MWD. Moreover, the other samples in Table 3.6 that have a bimodal MWD, do not show a double melting point.

There are at least two possible explanations for these double melting points. First, there may be two populations of crystallites, each having a different melting point. This suggests two different loci of polymerization, thus giving rise to biphasic morphology. Second, there is a very low molecular weight fraction present and the crystallites from this fraction can melt and recrystallize very quickly giving rise to a double melting point. However, the GPC curves do not show any low molecular weight fraction specific to samples 1 and 9.
With the exception of Sample 1, the enthalpies and the melting points for the different samples are almost constant. The enthalpies for Sample#1 are around 10 J/g lower than that for other samples. The DSC for Sample 1 was carried out at a different facility of Atofina and a difference in instrument type and operation is the probable cause of this difference.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Crystallization Enthalphy (J/g)</th>
<th>Crystallization Temperature (°C)</th>
<th>Melting Enthalphy (J/g) (2nd scan)</th>
<th>Melting Temperature (°C) (2nd scan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49.9</td>
<td>140.2</td>
<td>51.9</td>
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</tr>
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<td>61.9</td>
<td>143.8</td>
<td>67.9</td>
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</tr>
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<td></td>
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<td>171.4</td>
</tr>
<tr>
<td>9</td>
<td>60.7</td>
<td>139.7</td>
<td>67.4</td>
<td>170.1</td>
</tr>
<tr>
<td>15</td>
<td>60.2</td>
<td>139.0</td>
<td>67.4</td>
<td>169.0</td>
</tr>
</tbody>
</table>

*Table 3.6*  
Thermal analysis of PVDF synthesized in scCO2
Figure 3.9a  DSC Scan; Sample # 6

Figure 3.9b  DSC Scan; Sample # 7
§ 3.3.5 Microstructural Analysis using NMR Spectroscopy:

Fluorine-19 Nuclear Magnetic Resonance (NMR) spectroscopy studies were performed on a few samples to study the microstructure of the PVDF synthesized in scCO$_2$. Figure 3.10 shows a F-19 NMR spectrum of PVDF synthesized in scCO$_2$ (run #8). The NMR spectra was analyzed using the peak assignments reported by Russo et. al. $^{30}$ The peak assignments are listed in Table 3.7. The assignment for the chain end unit represented by F differs slightly from the reported value$^{30}$ of 102.4 ppm because the initiator used in this case was different from that used by Russo et.al.$^{30}$. The NMR spectrum in Figure 3.10 was referenced by setting the main chain VF$_2$ peak (A), corresponding to normal head-tail addition of VF$_2$ units, to $-91.6$ ppm.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>F-19 Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACH$_2$-CF$_2$-CH$_2$-CF$_2$-CH$_2$-CF$_2$-CH$_2$</td>
<td>-91.6</td>
</tr>
<tr>
<td>ACH$_2$-CF$_2$-CH$_2$-CF$_2$-CH$_2$-CF$_2$-CF$_2$</td>
<td>-92.1</td>
</tr>
<tr>
<td>BC$_2$-CH$_2$-CH$_2$-CF$_2$-CH$_2$-CF$_2$-CH$_2$</td>
<td>-94.8</td>
</tr>
<tr>
<td>BC$_2$-CH$_2$-CH$_2$-CF$_2$-CH$_2$-CF$_2$-CF$_2$</td>
<td>-95.7</td>
</tr>
<tr>
<td>CCH$_2$-CF$_2$-CH$_2$-CF$_2$-CF$_2$-CF$_2$-CH$_2$</td>
<td>-113.6</td>
</tr>
<tr>
<td>ECH$_2$-CF$_2$-CH$_2$-CF$_2$-CF$_2$-CH$_2$-CF$_2$</td>
<td>-113.9</td>
</tr>
<tr>
<td>DCF$_2$-CH$_2$-CH$_2$-CF$_2$-CF$_2$-CF$_2$-CH$_2$</td>
<td>-115.6</td>
</tr>
<tr>
<td>DCF$_2$-CH$_2$-CH$_2$-CF$_2$-CF$_2$-CH$_2$-CF$_2$</td>
<td>-116</td>
</tr>
</tbody>
</table>

$^{30}$Table 3.7a F-19 NMR peak assignments : Main chain VF$_2$ units
<table>
<thead>
<tr>
<th>Assignment</th>
<th>F-19 Chemical Shift $\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td></td>
</tr>
<tr>
<td>In-CH$_2$-CF$_2$-CH$_2$-CF$_2$</td>
<td>-102.9$^*$</td>
</tr>
<tr>
<td>J</td>
<td>-92.1 (J)</td>
</tr>
<tr>
<td>G</td>
<td>-115.1 (G)</td>
</tr>
<tr>
<td>CH$_2$-CF$_3$-CH$_2$-CF$_2$H</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-117.3</td>
</tr>
<tr>
<td>CF$_2$-CH$_2$-CH$_2$-CF$_2$H</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>-107.3 (L)</td>
</tr>
<tr>
<td>L</td>
<td>-114.3 (M)</td>
</tr>
<tr>
<td>CH$_2$-CF$_2$-CF$_2$-CH$_3$</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.7b** F-19 NMR peak assignments: Chain end VF$_2$ units.$^{30}$ *Peak assignment different from that reported by Russo et.al.$^{30}$

**% Inverse addition**

Figure 3.10 shows that normal head to tail addition is the most prevalent form of monomer addition. Small peaks corresponding to inverse additions also are seen. The percentage of inverse additions was calculated as described by Russo et.al.$^{30}$. The calculations are presented in detail in Appendix C. The percentage inversion was about 5-5.5 %, which is within the expected range, 3.5-6 %.$^{41}$, of values.
The peak corresponding to F is the dominant chain end unit. This is obtained by the addition of the first monomer unit to the initiator. In Figure 3.10, the peak F is slightly shifted to −103 ppm. The shift is attributed to the fact that the initiator used in these studies, DEPDC was different from that used by Russo et al. The absence of a peak at around −130 ppm arising from the terminal group −CH₂-CF₂-CH=CF₂, suggests that termination is by combination. This is in agreement with the PDI values of around 1.5.
obtained in the low monomer concentration experiments. The absence of a peak at about 10 ppm also implies that either there is no chain transfer to monomer or that the radical produced by chain transfer to monomer cannot reinitiate polymerization. This is consistent with the “monomer inhibition” hypothesis discussed in Section 3.3.3.

The presence of a signal corresponding to –CF₂-CF₂-CH₃ (L,M) suggests that some other form of chain transfer occurs. This transfer could be to either the initiator or the polymer. There is no literature evidence for chain transfer to initiator. However, chain transfer to polymer has been reported. Moreover, the concentration of polymer in the CSTR at steady state is much higher than the concentration of initiator. For these reasons, we attribute the L and M signals to chain transfer to polymer.

§ 3.4 Discussion of Bimodal MWDs:

Homogeneous free radical kinetics based on the reactions of Figure 2.5 can reasonably predict the rates and in certain cases the trends in the number average molecular weight reasonably well. Conventional homogeneous kinetics cannot however account for the broad and bimodal MWDs. Broad and bimodal MWDs are typically obtained either by polymer blending, i.e. mixing of high and low molecular weight fractions. Polymer blending requires a multi step process where the low and high molecular weight fractions are synthesized independently and then mixed together. On the other hand, the polymerization technique discussed here is a continuous single step process. It has been shown that the broad PDI and the bimodality can contribute to improved flow characteristics and processing behavior. Hence, this method of producing a bimodal MWD is of significant commercial interest. However, in order to
synthesize polymer of desired properties, it is very important to understand the origin of the bimodal MWD, and to be able to control the relative amounts and molecular weights of the two fractions.

Three possible explanations; *viz.* long chain branching, imperfect mixing, and heterogeneous polymerization; for the bimodal MWDs and the high PDIs have been investigated.

1) **Imperfect mixing**

Zhang et al.\(^5^8\) have shown that imperfect mixing in a CSTR can lead to bimodal MWDs. However, Charpentier et al.\(^7\) showed that the speed and type of agitation did not affect the molecular weights and the \(R_p\) for the polymerization of VF\(_2\) in scCO\(_2\). This study was carried out at low (0.77 M) inlet monomer concentrations. The percentage of solids in the reactor at these inlet monomer concentrations is around 1% (gms/mL), which is very low. Moreover, the GPC results show that bimodal and broad MWDs were obtained only at higher monomer concentrations. These factors have caused us to examine the effect of mixing at higher inlet monomer concentrations.

Table 3.8 presents the effect of mixing on the molecular weights and the rate of polymerization at an inlet monomer concentration of 2.8 M. The first three experiments in Table 3.8 were carried out using a dispersimax agitator at different agitation rates. The rest were performed by changing the type and number of agitators. These changes included using either a downward-pumping or upward-pumping agitator and adding a second agitator at the point where the initiator, monomer and CO\(_2\) are fed into the system. The different types of agitators used are shown in Figure 3.11. The corresponding MWD curves are presented in Figure 3.12.
<table>
<thead>
<tr>
<th>Run #</th>
<th>Agitation Speed (rpm)</th>
<th>Type of Agitator</th>
<th>Rp  g/min. L</th>
<th>X %</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>1300</td>
<td>D</td>
<td>1.16</td>
<td>16.0</td>
<td>5.92x10^4</td>
<td>1.59x10^5</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>1800</td>
<td>D</td>
<td>1.26</td>
<td>17.4</td>
<td>5.20x10^4</td>
<td>1.45x10^5</td>
<td>2.8</td>
</tr>
<tr>
<td>17</td>
<td>2700</td>
<td>D</td>
<td>1.44</td>
<td>19.8</td>
<td>6.00x10^4</td>
<td>1.42x10^5</td>
<td>2.4</td>
</tr>
<tr>
<td>18</td>
<td>1800</td>
<td>UP</td>
<td>1.41</td>
<td>19.5</td>
<td>5.94x10^4</td>
<td>1.61x10^5</td>
<td>2.7</td>
</tr>
<tr>
<td>19</td>
<td>1800</td>
<td>D+DP</td>
<td>1.62</td>
<td>22.4</td>
<td>6.21x10^4</td>
<td>1.46x10^5</td>
<td>2.4</td>
</tr>
<tr>
<td>20</td>
<td>1800</td>
<td>2 DP</td>
<td>1.47</td>
<td>20.3</td>
<td>6.21x10^4</td>
<td>1.59x10^5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**Table 3.8**  Effect of mixing on the rates and molecular weights. T=75 °C; P=4000 psig; τ=20 min; [M]_in=2.8 M; [I]_in= 2.8 mM; [I]_out=1.27 M; D = Dispersimax agitator, UP = Upward pumping agitator, DP = Downward pumping agitator.

![Dispersimax, Run #16,4,17](image1)

![Upward pumping, Run #18](image2)

![Dispersimax + downward-pumping, Run #19](image3)

![2 Downward-pumping, Run #20](image4)

**Figure 3.11**  Mixing studies - types of agitators used.
The conversion and rate results indicate that the mixing obtained using a dispersimax agitator at 1800 rpm is not optimum. Both the conversion and $R_p$ increase on increasing the speed of agitation and the number of agitators. Additionally, the upward pumping agitator appears to result in better mixing than the dispersimax agitator. These observations are in contrast to the mixing studies at the low inlet monomer concentration. This suggests that the inhibition in $R_p$ at the high monomer concentrations may be a result of imperfect mixing and not inhibition by the monomer.

The average molecular weights vary with the mixing conditions. However, there is no significant increase in either the molecular weights or the PDIs. Additionally, the MWDs, for the different agitation experiments, shown in Figure 3.12 are all bimodal and

![Figure 3.12](image) Effect of agitation on the MWD. $T=75\,^\circ C$; $P=4000$ psig; $\tau=20$ min; $[M]_{in}=2.8$ M; $[I]_{in}=2.8$ mM; $[I]_{out}=1.27$ M; D = Dispersimax agitator, DP = Downward pumping agitator.
very similar. This indicates that imperfect mixing is not the cause for the broad and bimodal MWDs.

2) Long chain branching

Long chain branches can be formed either by chain transfer to polymer or by terminal double bond polymerization. It has been established that branching can occur via chain transfer to polymer in polymers containing VF₂ units. Highly branched polymer chains may result in a high molecular weight fraction, which could be the cause of the second mode in the MWD. A homogeneous kinetic model (presented in chapter IV) that accounts for long chain branching has been developed in order to explore this possibility.

3) Heterogeneous Polymerization

As a polymer chain grows in length, the growing radical end may get trapped in the center with the rest of the polymer chain coiling around it. These active polymer chains precipitate once they reach a critical length, resulting in the formation of a polymer phase containing growing polymer chains. The monomer VF₂, partitions between the continuous CO₂ phase and the CO₂ swollen polymer phase. Polymerization might continue inside the precipitated polymer particles. The higher molecular weight mode might result from the polymerization in the polymer phase.

Monomer Partitioning Studies: In order to further investigate the possibility of polymerization in two phases, equilibrium partition coefficient studies are being performed in our laboratory. This research involves studying the effect of pressure,
temperature, and monomer concentration on the partition coefficient, $K_c$. The partition coefficient is defined as the monomer concentration in the CO$_2$ swollen polymer phase divided by the monomer concentration in the fluid phase:

$$K_c = \frac{[VF_2]_{\text{polymer}}}{[VF_2]_{\text{fluid}}}$$

It has been shown$^{59, 60}$ that $K_c$ decreases with increasing pressures and decreasing temperatures, at otherwise constant conditions. This implies that there is less VF$_2$ in the polymer phase at higher pressures and at lower temperatures. In fact, at the conditions of the polymerization reactions (T=75 °C, P=4000 psig), the partition coefficient is almost zero, implying that there is very little VF$_2$ in the polymer phase under equilibrium conditions. Since the monomer concentration directly affects the rate of polymerization, it can be concluded that the rate of polymerization at these conditions is negligible. Clearly, this is not consistent with the behavior seen in most of the polymerization experiments. Moreover, Figure 3.4 shows that a high molecular weight tail develops at the highest pressures resulting in a sharp increase in the PDI. Molecular weight distribution and partitioning studies to determine the effect of temperature also show the same inconsistency. MWD studies showed a decrease in bimodality and PDI at higher temperatures in contrast to the partitioning studies, which suggested a higher monomer concentration in the polymer phase at higher temperatures.

It is still uncertain whether simple heterogeneous polymerization is the source of the bimodal distribution. A more detailed study to include partitioning of the initiator - DEPDC, characterization of the effect of mass transport and equilibrium properties between species in the polymer and scCO$_2$ phases is required to understand the kinetics of heterogeneous polymerization.
§ 4.1 Long Chain Branching

Poly(vinylidene fluoride) with PDIs greater than 2 was obtained in most of the polymerization experiments discussed in Chapter 3. Such broad distributions are not common for polymerizations assumed to follow homogeneous free radical kinetics. It has been shown that long chain branching can lead to broadening of the MWDs. Therefore, long chain branching seemed to be a likely explanation for the broad MWDs.

Long chain branching is known to occur in free radical polymerizations through chain transfer to polymer or through terminal double bond polymerization. Terminal double bonds are formed either by chain transfer to monomer (VF$_2$) or by termination by disproportionation. There is no evidence in the literature for chain transfer to VF$_2$ or for termination of PVDF chains by disproportionation. Additionally, PDI values of around 1.5 at low monomer concentrations suggest that termination is by combination only. This is further verified by the NMR results, which did not show any signal corresponding to unsaturated chain ends. Hence, it can be concluded that chain transfer to polymer is the primary source of long chain branches. This transfer reaction occurs when a very reactive radical abstracts a proton from a dead polymer chain, as shown in Figure 4.1.

In these reactions, the live chain is terminated and the dead chain is reinitiated to form a polymer with a trifunctional branch point. Propagation at the trifunctional point leads to the formation of a branch. Repeated chain transfer to branched dead polymer chains can lead to chains with multiple branches. Additionally, combination of two
branched polymer species can lead to highly branched polymer units. These chains could be the source of the broad and bimodal MWDs shown in chapter III.

![Figure 4.1](image.png)

Figure 4.1  Long-chain branching in free radical polymerization of VF2

Nuclear magnetic resonance studies showed the presence of –CF2-CH3 end groups. However, no signal corresponding to –CH2-CF2H end groups shown in Figure 4.1 was seen. This suggests that the ratio of the probability that a growing radical terminates by chain transfer to polymer to the probability that it propagates by adding another monomer is much greater for a growing chain with a –CF2-CH2 end than that for a chain with a –CH2-CF2 end.

A number of methods to calculate the MWD and average molecular weights in free radical polymerization with long chain branching in batch reactors have been discussed in the literature.61-65 Most of these techniques are numerical, and require some assumptions regarding the polymerization mechanism.

The effect of long chain branching on the MWD for a CSTR was examined almost 50 years ago66 for the case of termination by disproportionation. This work showed that the MWDs obtained were perfectly unimodal. However, some assumptions were made regarding the distribution of the primary chains, which may not be appropriate. Other studies61, 64, 66, 67 have shown that chain transfer to polymer coupled
with termination by disproportionation does not lead to a bimodal MWD. However, there do 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. This question was investigated in this research.

§ 4.2 Branching Model

A mathematical model that incorporates chain transfer to polymer and assumes termination by combination has been developed to determine whether bimodal MWDs can be obtained through this mechanism, and to determine whether this mechanism can account for the large PDIs found in the experiments described in Chapter 3. This model was based on the reactions shown below. The inhibition step discussed in §3.3.3 was not included because of the possibility that the observed deviation in $R_p$, from first order with respect to the monomer, was due to agitation rather than the inhibition reaction.

\[
I \xrightarrow{k_i} 2 fR^* \quad \text{(Decomposition)}
\]

\[
R^* + M \xrightarrow{k_i} P_1^* \quad \text{(Initiation)}
\]

\[
P_n^* + M \xrightarrow{k_p} P_{n+1}^* \quad \text{(Propagation)}
\]

\[
P_n^* + P_m \xrightarrow{mK_p} P_m^* + P_n \quad \text{(Chain Transfer to polymer)}
\]

\[
P_n^* + P_m \xrightarrow{k_c} P_{n+m} \quad \text{(Termination by Combination)}
\]

**Figure 4.2** Reaction scheme for modeling the MWD
The MWD model is based on the following assumptions:

1. The steady state approximation is valid. This assumption implies that the radical lifetime is very small compared to the residence time, hence the radical outflow is negligible. 2. All reactions occur in the fluid phase – (i.e.) the rates of any reaction occurring in the solid phase are negligible compared to the rates in the fluid phase. 3. The rate constants for propagation and termination are independent of chain length. 4. Since the hydrogen in the transfer to polymer step can be extracted from any one of the units of the dead polymer, the rate constant is proportional to its chain length. Shielding of the inner portion of the molecules, which is possible in the case of very large molecules is neglected.

§ 4.3 Results and Discussion:

§ 4.3.1 Rate of Polymerization ($R_p$).

For the above scheme, $R_p$ is not affected by chain transfer to polymer as long as a monomer adds to every radical that is formed on the polymer backbone. This implies that $R_p$ is the same as that obtained in classical free radical polymerizations.

§ 4.3.2 Average Molecular Weights

The weight ($\overline{M}_w$) and number ($\overline{M}_n$) average molecular weights were calculated for the above kinetic scheme in an ideal CSTR using the method of moments. The balance equations were written for the active radical species, $P_n^*$, and the dead polymer species, $P_n$ for all $n$. Thus, two sets of equations, each comprising of an infinite number of equations are obtained. These sets of infinite equations are reduced to two equations.
using transforms. The average molecular weights $\overline{M}_n$ and $\overline{M}_w$, were obtained from the zeroth ($\mu_0$), first ($\mu_1$) and second ($\mu_2$) moments calculated from the transformed equations. The calculations are shown in detail in Appendix D.

**Number average molecular weight.**

The number average molecular weight calculated from the model is given by,

$$\overline{M}_n = \frac{\mu_1}{\tau K_p \lambda^2} m$$  \hspace{1cm} (4.1)

where, $\tau$ is the residence time; $m$ is the monomer molar mass; $\lambda$ is the total active radical concentration given by $\lambda = \sqrt{\frac{f K_d [I]_{out}}{K_{ic}}}$; $\mu_1$ is the first moment of the dead polymer distribution given by

$$\mu_1 = [M]_n - [M]_{out} = [M]_n - \frac{[M]_{in} - 2 f K_d \tau [I]_{out}}{1 + \tau K_p \lambda}.$$  \hspace{1cm} (4.2)

Equation 4.1 can also be rewritten in the form of equation 3.1, to give

$$\overline{M}_n = \frac{R_p}{K_{ic} \lambda^2} m$$  \hspace{1cm} (4.3)

where, $R_p = \frac{[M]_{in} - [M]_{out}}{\tau}$.

It can be seen that $K_{ip}$ does not appear in equation 4.3. Additionally, since $R_p$ is independent of $K_{ip}$, it can be concluded that chain transfer to polymer has no effect on $\overline{M}_n$. Because the $R_p$ predicted by the model is not accurate, the $\overline{M}_n$ was calculated from the experimental rate using a modified form of equation 4.3 given by

$$\overline{M}_n = \frac{R_p (measured)}{K_{ic} \lambda^2} = \frac{R_p (measured)}{f K_d [I]_{out}}$$  \hspace{1cm} (4.4)
A parity plot of the $\overline{M}_n$ obtained from the GPC and the $\overline{M}_n$ predicted by equation 4.4 is presented in Figure 4.3. This plot shows only 39 of the 44 data points shown in Figures 3.7, and 3.8 as molecular weight data was not available for the remaining 5 points.

![Parity plot showing fit of experimental (GPC) data to $\overline{M}_n$ predicted by Equation 4.5.](image)

**Figure 4.3** Parity plot showing fit of experimental (GPC) data to $\overline{M}_n$ predicted by Equation 4.5.

The best fit, through the origin, for the data points has a slope of 2.2. The data shows a random scatter except for two data points with the highest measured values of $\overline{M}_n$ (around 65000). These were experiments carried out at the highest pressure (run #9 at 4400 psig), and at the highest residence time at the higher inlet monomer concentration of 2.8 M (run #15 at $\tau = 25$ mins.). These experiments were difficult to conduct because
of difficulty in removing the polymer. Additionally, these experiments resulted in polymer with very high PDIs.

A slope of 2.2 for the best fit line implies that, on an average the measured $\overline{M_n}$ is around twice that predicted using the model. This is rather surprising because $\overline{M_n}$ was calculated from the experimentally measured rates with the assumption that termination was by combination only. Any other means of termination would result in a further decrease in $\overline{M_n}$. The calculation also relied on the values of $f$ and $K_d$, which had been measured experimentally in separate experiments. This suggests that either: 1) there is some phenomenon that is not accounted for in this model that results in a higher $\overline{M_n}$ than the predicted value, or; 2) there is an error in the value of $fK_dI$ that was used, or; 3) there is a systematic error in the experimental values of $\overline{M_n}$ obtained from the GPC. Let us look at the later two possibilities.

The initiator concentration, $I$ is calculated from $I_0$, $K_d$, and $\tau$. The inlet initiator concentration, $I_0$ and the average residence time, $\tau$ are either measured or calculated from measured quantities. Therefore, any error in the value of $fK_dI$ could only be due to either $f$ and/or $K_d$. Based on previous studies, it appears that the value of $K_d$ is accurate since the measured values in scCO$_2$ compared very well to those measured in conventional solvents at atmospheric pressure. Therefore, it appears that the value of $f=0.6$, that was used in these calculations may be too high. This could be because $f=0.6$ corresponds to the initiator efficiency in pure CO$_2$, in the absence of VF$_2$ and polymer. This value represented the efficiency of the reaction between ethoxy radicals and galvinoxyl in the presence of CO$_2$. The efficiency of the reaction between these
radicals and \( \text{VF}_2 \) monomer in the presence of \( \text{CO}_2 \) and PVDF may not be the same. In fact for a value of \( f = 0.27 \) \((0.6 \div 2.2)\) the best fit line in the parity plot of Figure 4.3 would have a slope of exactly one indicating a very good agreement between the predicted and measured values of \( \overline{M}_n \).

**Number average molecular weight calculations from NMR.**

Five \( \overline{M}_n \) measurements using NMR were carried out to explore the possibility of an error in the experimental data obtained from the GPC. The number average molecular weight, \( \overline{M}_n \) is given by the average chain length times the monomer molar mass. The average chain length can be obtained from NMR using

\[
\text{Average Chain Length} = \frac{\text{Total Area corresponding to monomer units}}{\text{Area corresponding to end groups}/N} \tag{4.5}
\]

where, \( N \) is the average number of end groups per molecule.

The NMR peak assignments for PVDF were discussed in chapter III. The numerator in Equation 4.5 is given by the sum of the areas of all the peaks while the denominator is given by the sum of areas corresponding to the end groups. The number average molecular weight, \( \overline{M}_n \) was calculated for five experiments assuming linear polymer chains (i.e.) \( N=2 \). These calculations are shown in detail in Appendix C. This technique of determining \( \overline{M}_n \) probably is not accurate for very high molecular weight samples because the area corresponding to the end groups is very small compared to the area of the monomer units. Therefore, we used this technique only for samples expected to have a low to medium number average molecular weight. A reconstructed parity plot of Figure 4.3 is shown in Figure 4.4.
There is a significant difference in the $\bar{M}_n$ measured using GPC and that calculated using NMR data. However, the $\bar{M}_n$ calculated from the NMR data appear to agree with the model predictions reasonably well. The assumption that the chains are linear, (i.e.) $N=2$, is very critical to the $\bar{M}_n$ calculations. For example, if the average number of branches per molecule is 2, then $N=4$ and the $\bar{M}_n$ calculated from the NMR spectra would agree reasonably well with that calculated from the GPC results. However, estimates of the average number of branches per polymer molecule (see §4.3.3, following) do not support an average number of branches as high as 2.

Figure 4.4 Parity plot of measured $\bar{M}_n$ (GPC and NMR) versus predicted values (using Equation 4.5).
**Weight average molecular weight**

The weight average molecular weight, \( \bar{M}_w \) is given by

\[
\bar{M}_w = \frac{\mu_2}{\mu_1} m
\]  

(4.6)

From Appendix D, the second moment \( \mu_2 \) is given by

\[
\mu_2 = -\frac{p_1 \pm \sqrt{p_1^2 - 4p_2}}{2} \quad \text{if} \quad K_{tp} \neq 0
\]

(4.7a)

and \( \mu_2 = 2\tau \lambda d(K_{tc}a\lambda + [M]_out K_p) + \mu_1 \) if \( K_{tp} = 0 \)

(4.7b)

where, \( p_1 = \frac{2a}{b} + \frac{[M]_out K_p}{bK_{tc}\lambda} - \frac{1}{2\tau K_{tc}b^2\lambda^2} \) and \( p_2 = \frac{a^2}{b^2} + \frac{[M]_out K_p a}{b^2 K_{tc}\lambda} + \frac{\mu_1}{2\tau K_{tc}b^2\lambda^2} \).

The constants, \( a \), and \( b \) in the above equation are given by

\[
a = \frac{[M]_out K_p + 2K_{tc}\lambda}{\mu_1 K_{tp} + 2K_{tc}\lambda} \quad \text{and} \quad b = \frac{K_{tp}}{\mu_1 K_{tp} + 2K_{tc}\lambda}.
\]

Equation 4.7a gives two values of \( \mu_2 \). However, only the value corresponding to

\[
\mu_2 = -\frac{p_1 - \sqrt{p_1^2 - 4p_2}}{2}
\]

is considered since the other value results in a discontinuity in the value of \( \mu_2 \) at \( K_{tp} = 0 \). This can be seen by calculating \( \mu_2 \) from Equation 4.7a, in the limit \( K_{tp} \to 0 \) and comparing it with that obtained from Equation 4.7b. The mathematics is shown in detail in Appendix D.

Since, \( \mu_1 \) is independent of \( K_{tp} \), the dependence of \( \mu_2 \) on \( K_{tp} \) determines the dependence of \( \bar{M}_w \) on \( K_{tp} \). Algebraic manipulation of equations 4.6 and 4.7 showed that

\( \bar{M}_w \) is dependent only on the following parameters: \( \frac{K_{tp}}{K_p}, \frac{K_p}{\sqrt{K_t}} \) and \( fK_p \).
Figure 4.5 shows a plot of the effect of chain transfer to polymer on $\bar{M}_w$ calculated using Equations 4.6 and 4.7, for one particular set of experimental conditions. In these calculations, the ratio $K_p / \sqrt{K_p}$ determined from the rate model (Figure 3.8), and the initiator efficiency, $f$, and the initiator decomposition constant, $K_d$ determined in earlier studies (Table 2.4) were used.

Figure 4.5 shows that $\bar{M}_w$ increases with increasing $K_p / K_p$, with the rate of increase becoming greater at higher values of $K_p / K_p$. Beyond a particular value of $K_p / K_p$ (in this case around 0.0045), the calculated value of $\bar{M}_w$ becomes imaginary, as the expression under the square root in equation (4.7 a) becomes negative.

![Figure 4.5](image_url)

**Figure 4.5** Effect of chain transfer to polymer on $\bar{M}_w$. $K_p / \sqrt{K_p} = 0.19$ (L/mol.s)$^{0.5}$; $K_d = 0.00103$ s$^{-1}$; $f = 0.6$; $[M]_w = 3$ M; $[I]_w = 0.003$ M; $\tau = 15$ mins; $T = 75^\circ C$. 

65
**Poly Disperisty Index (PDI)**

The PDI is given by the ratio $\frac{\bar{M}_w}{\bar{M}_n}$. From Equations 4.3 and 4.6, the PDI is given by $\frac{1}{\tau K_t \lambda^2}$. Figure 4.6 shows the predicted and measured PDIs for the experiments in Table 3.1, which show the effect of varying the inlet monomer concentration at otherwise constant conditions. The predicted values were calculated for two values of the initiator efficiency, $f$, viz. 0.6 and 0.27 (0.6÷2.2). The parameter, $\alpha$ calculated from the rate model (Figure 3.8) was used to calculate the corresponding values of $\frac{K_p}{\sqrt{K_t}}$. The ratio $K_p/K_p$ was calculated from the data point at an inlet monomer concentration of 3.5 M; the same value was used at the other concentrations.

![Figure 4.6](image_url)

**Figure 4.6** Effect of inlet monomer concentration on PDI. $K_d = 1.03 \times 10^{-3}$ s$^{-1}$;
(a) $f = 0.6$, $K_x/\sqrt{K_t} = 0.19$ (L/mol.s)$^{0.5}$, $K_p/K_p = 2.6027 \times 10^{-3}$;
(b) $f = 0.27$, $K_x/\sqrt{K_t} = 0.28$ (L/mol.s)$^{0.5}$, $K_p/K_p = 1.1844 \times 10^{-3}$

All other reaction conditions are presented in Table 3.1
Figure 4.7 shows the predicted and measured PDIs for the experiments in Table 3.4, which show the effect of varying residence time for two different monomer concentrations at otherwise constant conditions. The kinetic parameters shown in Figure 4.6 were used to calculate the predicted values of the PDIs.

![Poly Dispersity Index (PDI) vs Residence Time](image)

**Figure 4.7** Effect of Residence Time on PDI: $K_d = 1.03 \times 10^{-3}$ s$^{-1}$;  
(a) $f = 0.6$, $K_e \sqrt[4]{K_p} = 0.19$ (L/mol.s)$^{0.5}$, $K_{pP}/K_p = 2.6027 \times 10^{-3}$;  
(b) $f = 0.27$, $K_e \sqrt[4]{K_p} = 0.28$ (L/mol.s)$^{0.5}$, $K_{pP}/K_p = 1.1844 \times 10^{-3}$  
All other reaction conditions are presented in Table 3.4

It can be seen from Figures 4.6 and 4.7 that the model that includes chain transfer to polymer predicts the PDI reasonably well. Although the model could not reach a PDI of 6.6 as shown in Figure 4.7, it predicts the abrupt increase seen in the experimental PDI as the inlet monomer concentration is increased, and as the average residence time is increased at higher monomer concentration. This abrupt increase is seen only when both
chain transfer to polymer and termination by combination are present. Model predictions obtained when termination was assumed to be by disproportionation or in the absence of chain transfer to polymer did not show such an abrupt increase. Additionally, the predicted PDIs for the two different values of the initiator efficiency $f$, are the same. This is because the parameter $K_{tp}/K_p$ was recalculated using the data point at $[M]_{in}$ of 3.5 M for the corresponding $f$ value. It is surprising that the ratio of the two $K_{tp}/K_p$ values is same as the ratio of the corresponding initiator efficiencies.

The model predicts an imaginary value of $\bar{M}_w$, (and hence the PDI) for values of $\tau$ greater than 25 mins. (at $[M]_{in}$=2.8 M), and for $[M]_{in}$ greater than 3.5 M (at $\tau \sim 20$ mins.). This point at which the model predicts an imaginary value is termed the gel point. Gelation refers to the formation of an infinite network in which polymer molecules have been cross-linked to each other to form a macroscopic molecule. 68, 69 This is associated with a drastic physical change in the polymer and a sharp increase in viscosity. In free radical polymerizations, gelation requires a linking reaction such as termination by combination63, 64 and cannot occur in the presence of chain transfer to polymer alone. This is consistent with the model predictions.

Experiments were attempted at a monomer concentration greater than 3.5 M and at a residence time greater than 25 minutes (with $[M]_{in} = 2.9$ M) to confirm the formation of gels. The other reaction conditions for these experiments are given in Table 4.1. These experiments could not be completed and no data could be obtained because it was impossible to move the polymer continuously out of the reactor. In fact, at an inlet monomer concentration of 6 M, a hard, solid mass of polymer that was not soluble in any
solvent was obtained. This supports the theory that gelation occurs at these high monomer concentrations.

Table 4.1 shows a comparison between experimental and simulated PDI for reaction conditions on either side of the gel point. Beyond the gel point, experiments could not be conducted successfully and the simulation gave imaginary values for the PDI. This shows that the model appears to predict the gel point well.

<table>
<thead>
<tr>
<th>Experimental</th>
<th></th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ (mins)</td>
<td>[M]₀ (M)</td>
<td>PDI</td>
</tr>
<tr>
<td>25.5</td>
<td>2.9</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2.9</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0.78</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.1</td>
<td>3.5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>4.1</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.5</td>
<td>6.08</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 4.1 Comparison of experimental and simulated PDIs on either side of the gel point. X denotes experiments could not be conducted successfully. T=75 °C, P=4000 psig.

§ 4.3.3 Average number of branches:

In order to calculate the number average number of branches, \( \overline{B_n} \) a more detailed form of the kinetic scheme, shown in Figure 4.8, was used. The reactions are the same as those shown in Figure 4.2. However, the average number of branches is accounted for in this version.
\[ I \xrightarrow{K_i} 2fR^* \]  \hspace{1cm} \text{(Decomposition)}

\[ R^* + M \xrightarrow{K_n} P_{1,0}^* \]  \hspace{1cm} \text{(Initiation)}

\[ P_{n,b}^* + M \xrightarrow{K_p} P_{n+1,b}^* \]  \hspace{1cm} \text{(Propagation)}

\[ P_{n,b}^* + P_{m,c} \xrightarrow{mK_p} P_{m,c+1}^* + P_{n,b} \]  \hspace{1cm} \text{(Chain Transfer to polymer)}

\[ P_{n,b}^* + P_{m,c}^* \xrightarrow{K_t} P_{n+m,b+c} \]  \hspace{1cm} \text{(Termination by Combination)}

**Figure 4.8** Kinetic scheme to calculate average number of branches per polymer molecule. The first subscript denotes the number of monomer units; the second subscript denotes the number of branches.

The average number of branches per molecule, $\overline{B}_n$, was calculated by a technique similar to that used to calculate the $\overline{M}_n$. The mathematics are shown in Appendix E. The average number of branches per polymer molecule is given by

\[
\overline{B}_n = \frac{K_p\mu_1}{\sqrt{fK_d I \cdot K_t}} \tag{4.8}
\]

Table 4.1 shows the $\overline{B}_n$ calculated from Equation 4.8 for the experiments in Table 3.1.

<table>
<thead>
<tr>
<th>Run #</th>
<th>[M]$_{in}$</th>
<th>$\overline{B}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.78</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>1.68</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>2.79</td>
<td>0.26</td>
</tr>
<tr>
<td>5</td>
<td>3.53</td>
<td>0.34</td>
</tr>
</tbody>
</table>

**Table 4.2** Average number of branches as a function of the inlet monomer concentration. Other reaction conditions given in Table 3.1.
Currently, there are no measured values with which the predicted values can be compared. However, these predictions compare reasonably well with measurements on a VF$_2$/hexafluoropropylene/tetrafluoroethylene (72/18/10) polymer synthesized at a similar temperature.$^{56}$

§ 4.3.4 Complete MWD:

The current model predicts the broadening of the MWD reasonably well. However, the entire MWD is required in order to determine whether a bimodal distribution can result from the reactions of Figure 4.2. An analytical solution for the entire MWD could not be obtained because of the mathematical complexity arising from the presence of both chain transfer to polymer and termination by combination. A recursive algorithm to calculate $P_n^*$, $P_n$ from $P_{n-1}^*$, $P_{n-1}$ respectively, has been developed. This method to construct the entire MWD is presented in detail in Appendix F. The weight fraction of polymer of chain length $n$ is given by

$$X_w = \sum nP_n$$

where, $\sum nP_n$ is equal to the first moment, $\mu_1$. Since $\mu_1$ is independent of $n$, a plot of $nP_n$ versus $n$ gives the shape of the MWD curve. Figure 4.9 shows the MWD curve obtained for two values of $K_{tp}/K_p$, the chain transfer constant. The calculations were performed up to a chain length of 7000 monomer units. The other parameters in Figure 4.9 were chosen to lie in the range where the GPC results showed bimodal distributions.

Although the MWD is broader at the higher value of the chain transfer constant, the distribution is perfectly unimodal. Simulations at higher monomer concentrations and
chain transfer constants also gave perfectly unimodal distributions. From these calculations, it appears that chain transfer to polymer is not the source of the bimodal distributions. They must result from a phenomenon that is not accounted for in the model.

Figure 4.9  Effect of chain transfer to polymer on the MWD. $K_{tp}/K_p =0.001$, $K_{tp}/K_p =0.01$. $K_p (L/mol.s)^{0.5}$, $K_d =0.00103$ s$^{-1}$, $f =0.6$, $[M]_n =3$ M; $[I]_n =0.003$ M; $\tau =20$ mins; T=75°C.
CHAPTER 5      ALTERNATE INITIATOR STUDIES

The polymerization studies discussed in the earlier chapters all involved DEPDC as the polymerization initiator, which is active at a temperature of around 75 °C. There has been considerable interest, especially for scCO₂ polymerizations, in alternate initiator systems that could be useful at lower temperatures. This chapter presents some preliminary work done to develop low temperature initiators for polymerizations in scCO₂. Though such a new initiator system is potentially beneficial for free radical polymerizations in general, this study has focused on VF₂ polymerizations.

§ 5.1 Need for alternate low temperature initiators

There are two main advantages of operating at lower temperatures:

1) Lower costs: Properties of CO₂ such as density, solvency, and dielectric constant typically increase with increasing pressure and decreasing temperature (Figures 1.1 –1.3). Hence at lower temperatures, a lower pressure is required in order to maintain constant solvent properties. For example, the density of scCO₂ at 75 °C and 4000 psig is 0.74 g/ml. At 40 °C, the pressure required to operate at this same density is 1900 psig. Thus, operating at lower temperature may permit operation at lower pressures. Lower pressures significantly reduce the energy required for recompression and recycle of CO₂ and the unreacted monomer- VF₂. Moreover, equipment costs also are lower for a low temperature-pressure system.

2) Potential for higher molecular weights: The molecular weights (\(\bar{M}_n\)) of the polymers produced using DEPDC are lower than generally desired. Only at higher
monomer concentrations are the desired molecular weights obtained. However, there are a number of difficulties associated with this approach. First, the polymerization reaction is exothermic and a higher monomer concentration results in more heat evolved per unit volume per unit time. The temperature control in such a situation becomes increasingly difficult. Second, high monomer concentrations may mean operating near the gel point, thus producing some gelled polymer, which may not be tolerable.

An alternative to higher monomer concentrations is lower temperatures. Studies of the effect of temperature (Section 3.3.2) showed that the molecular weight is higher at lower temperatures. This is true not only for VF$_2$ polymerizations, but for most free radical polymerizations. The above arguments favor operating at temperatures around 35°C.

It is not feasible to use DEPDC at temperatures close to 35°C. This can be explained using classical free radical kinetics. For a sequence of reactions involving initiation, propagation, and chain termination equation 3.1 can be rewritten as

$$
\bar{M}_n = \frac{K_r[M]}{n.fK_d[I]^{0.5}} \cdot m 
$$

(5.1)

where, n equals 1 if termination is by combination and 2 if termination is by disproportionation; $K_r$ is the apparent rate constant of the rate of polymerization given by

$$
K_r = \frac{K_p}{\sqrt{K_i}} \cdot \sqrt{K_d} \cdot f \cdot K_d
$$

and $I$ and $[M]$ are the initiator and monomer concentrations respectively. An apparent rate constant for $\bar{M}_n$, $K_{\bar{M}_n}$, can be defined from Equation 5.1 as

$$
K_{\bar{M}_n} = \frac{K_r}{K_d}.
$$
The rate constants defined above are all dependent on temperature. In equation 5.1 the temperature dependence arises primarily from the kinetic constants \( K_r \) and \( K_d \).

For conventional free radical polymerizations, \( E_a(K_r/\sqrt{K_t}) \) the activation energy of \( K_r/\sqrt{K_t} \) is in the range of 10-40 kJ/mole\(^6\), and \( E_a(K_d) \) the activation energy of \( K_d \) for DEPDC was determined to be 132 kJ/mole\(^5\). The values of \( E_a(K_r) \), the activation energy of \( K_r \), and \( E_a(K_{M/n}) \), the activation energy for \( K_{M/n} \), calculated using these values, are in the range of \(-51\) to \(-21\) kJ/mole and \(71\) to \(111\) kJ/mole respectively. A negative value for \( E_a(K_{M/n}) \) indicates that \( M_n \) increases with decreasing temperature. However, a high positive value for \( E_a(K_r) \) indicates that the rate of polymerization drops significantly with temperature. This is evident from Figure 5.1, a plot of the ratio of the rate and \( M_n \) at any temperature to the rate and \( M_n \) obtained using DEPDC at 75 °C, for two different initiators. The values of initiator and monomer concentrations were assumed to be the same when calculating the ratios for the two initiators.

The first initiator considered was DEPDC itself. For DEPDC, at 35 °C the rate is \(1/50\text{th}\) of that at 75 °C. Again, for DEPDC, \( M_n \) at 35 °C would be around 15 times the \( M_n \) at 75 °C. The above ratios then were calculated for a hypothetical low temperature initiator with about the same \( E_a(K_d) \) as DEPDC, and a \( K_d \) at 35 °C equal to that of DEPDC at 75 °C. The numbers from Figure 5.1 indicate that at 35 °C, \( M_n \) is increased by around 30 % and the rate is about \(1/8\text{th}\) of that obtained when using DEPDC at 75 °C. Though the decrease in rate is not desirable, it is much more favorable than that seen in the case of DEPDC at 35 °C.
Two particular initiator systems, viz. a redox initiation system of benzoyl Peroxide (BPO) with N, N-dimethyl aniline (DMA) and a fluorinated initiator have been investigated in an attempt to match or exceed the behavior of the hypothetical initiator discussed above.
§ 5.2 Redox Initiation Studies

§ 5.2.1 BPO Decomposition Mechanism

Benzoyl peroxide by itself has been used as an initiator for VF2 polymerizations at around 90°C. It has been shown that the presence of DMA can accelerate the rate of BPO decomposition by at least three orders of magnitude. The decomposition of BPO in the presence of DMA is believed to be a second order reaction that occurs by the nucleophillic attack of the DMA on the peroxide linkage in BPO as shown in Figure 5.2.

![BPO Decomposition Mechanism Diagram](image)

Figure 5.2 Scheme for Reaction of Benzoyl Peroxide with N,N-Dimethylaniline.

§ 5.2.2 Experimental

Polymerization of VF2 was attempted using BPO and DMA (diluted with Freon 113) as the initiator system. A solvent was required to dissolve the BPO as it is a solid at room temperature. Experiments were carried out using either toluene or tetrahydrofuran (THF) as the solvent to dissolve the initiator. The reaction conditions for these
experiments are presented in Table 5.1. A detailed description of the polymerization system, experimental procedure and initiator preparation is presented in Appendix G.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temperature °C</th>
<th>Pressure psig</th>
<th>Solvent to dissolve BPO</th>
<th>[BPO] mM</th>
<th>[DMA] (in Freon113) mM</th>
<th>τ (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>2450</td>
<td>Toluene</td>
<td>3.08</td>
<td>7.88</td>
<td>20.5</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>2450</td>
<td>Toluene</td>
<td>4.09</td>
<td>7.09</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>2450</td>
<td>THF</td>
<td>0.09</td>
<td>3.94</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 5.1 Experimental conditions: Redox polymerization studies. Continuous reactor, [VF2]₀=0.78 M.

§ 5.2.3 Results and Discussion

Polymerization experiments using the redox initiator system were carried out at 50 °C and 2450 psig. A BPO solution in toluene and DMA in Freon 113 was used as the initiating system for the first two runs. The VF₂ conversion was monitored for run#2 using a gas chromatograph. The data (Appendix G) showed that we were indeed getting some VF₂ conversion. However, no polymer was collected in any of the filters during any of these two runs. There may be significant chain transfer to toluene resulting in the formation of very low molecular weight oligomers that remain dissolved in the CO₂.

A search for a new solvent for BPO showed that BPO is not soluble to a sufficient extent in many fluorinated solvents. Tetrahydrofuran (THF) was found to dissolve the BPO reasonably well. Additionally, chain transfer to THF is less likely than that to toluene. An experiment was carried out using BPO in THF and DMA in Freon 113 as the initiator. Once again, no polymer was collected. Unless a fluorinated solvent can be
found to dissolve BPO, the BPO-DMA system is not a feasible initiator system for the polymerization of VF$_2$.

§ 5.3 Fluorinated Initiator Studies

Polymerizations of VF$_2$ using a fluorinated initiator made from hexafluoropropyleneoxide dimer (HFPO) - Bis(perfluor-2 propoxypropionyl) peroxide (BPPP) have been investigated. It has been reported in the literature that fluorinated acyl peroxides have activation enthalpies 5-8 kcal/mol lower than non-fluorinated analogs. Molecular orbital calculations have also revealed that fluorination leads to weakening of the peroxy O-O bond, as well as the C-C bond between the fluoroalkyl chain and the carbonyl carbon. The weakening of the O-O linkage makes these fluorinated initiators active at low temperatures.

![Structure of Bis(perfluor-2 propoxypropionyl) peroxide (BPPP)](image)

The rate constant for decomposition of BPPP in scCO$_2$ at 35 °C is about 2.8 × 10$^{-4}$ s$^{-1}$. Although, this is around 1/4$^{th}$ of that of DEPDC at 75 °C, it is around two orders of magnitude greater than that of DEPDC at 35 °C. Hence, it could fit the description of the hypothetical initiator discussed in §5.1. Kipp et al. have carried out feasibility studies on VF$_2$ polymerization using a number of initiators. Their studies showed that BPPP was indeed able to polymerize VF$_2$ to a significant extent at 25 °C. In fact the
conversion obtained using an initiator concentration of $2.6 \times 10^{-4}$ M and a monomer concentration of 6.1 M was as high as 85%. However, no comparisons of yields and molecular weights with those obtained with DEPDC, were done. Moreover, the time scale of the polymerization reactions was around 15 hours, which is very high compared to the average residence times used in the CSTR studies.

§ 5.3.1 Experimental

Polymerizations in a batch system were carried out at around 30 °C, 4000 psig, and reaction times of around 2 hours. The yields and molecular weights were compared to those obtained with using DEPDC at a higher temperature. The initiator synthesis, polymerization system and procedure are described in detail in Appendix H.

§ 5.3.2 Results and Discussion :

Preliminary results from the batch polymerizations with fluorinated initiators are presented in Table 5.2. Experiment # 1 was carried out using DEPDC and the rest were performed using BPPP. The BPPP initiator gives reasonable yields at much lower temperatures than DEPDC. The molecular weights also appear to be higher, as desired. At high temperatures, (e.g., Run # 2) the molecular weights with HFPO dimer were very low, and below the calibration limit of the GPC. Additionally, at very low initiator concentrations, the polymer sample was not very soluble and resulted in plugging the columns of the GPC, suggesting very high molecular weight. No specific trend could be seen in the conversions and molecular weights with the reaction conditions except that the conversion appears to increase with pressure (Runs # 6-8).
Table 5.2  Batch Polymerization results; Time of Reaction = 2 hours.  * Using DEPDC as the initiator; BPPP was the initiator for all other runs.

It should be noted that the mixing in the batch cell was performed using two tiny magnetically stirred bars. Once the polymerization began, these bars were completely covered with polymer and they stopped stirring, thus amounting to no mixing at all. Therefore, the above results should be used only to form a qualitative picture of the behavior of BPPP in comparison to that when using DEPDC. Additionally, although the BPPP synthesis was performed as described in literature, the BPPP initiator was very difficult to synthesize. The yields obtained were only about 5%, which is much lower than reported values of around 50 %. The reason for the low yields and the effect of byproducts or unreacted components on the polymerization is not clear.
Because of the above-mentioned problems associated with the BPPP initiator, polymerizations using another fluorinated initiator, perfluorobutrylperoxide (PBP) have been carried out. Moreover, a much better stirring mechanism was developed for carrying out these polymerizations. These studies are not a part of the present research.
§ 6.1 Conclusions

Continuous polymerizations of VF₂ have been carried out to study the effect of reaction parameters such as temperature, pressure, inlet monomer concentration and residence time on the rate of polymerization and on the MWD. Rate of polymerization studies suggested inhibition in the rates at higher ([M]_{in} > 2 \text{ M}) monomer concentrations. A dispersimax agitator operated at 1800 rpm was used for these studies. A homogeneous rate model that incorporates inhibition by the monomer predicted the rates reasonably well. However, there is no literature evidence for inhibition by monomer. Mixing studies carried out at low inlet monomer concentration, [M]_{in} = 0.77 \text{ M}, showed that the type and speed of agitation had no effect on the rates. However, at high monomer concentration, [M]_n = 2.8 \text{ M}, the mixing was inadequate and the rate increased with increasing the speed and number of agitators. Therefore, it is still not clear whether the inhibition seen in the rates is because of either imperfect mixing or the presence of an inhibitor.

Gel Permeation Chromatography (GPC) results showed that a unimodal MWD is obtained at lower inlet monomer concentration ([M]_{in} \text{ ca. 0.77 to 1.5 M}). The MWD broadens and a second mode appears at higher monomer concentration. Very high PDI values were obtained in three experiments carried out at either the highest pressure (4400 psig), or the highest residence time (25 mins.), or the highest inlet monomer concentration (3.5 M). Nuclear Magnetic Resonance (NMR) results suggested that chain termination is by combination. Additionally, they suggest the presence of chain transfer to polymer.
Three different possibilities, viz. imperfect mixing, long chain branching and heterogeneous polymerizations, were explored to explain the source of the broad and bimodal MWDs. Mixing studies showed that the type and speed of agitation did not have any significant effect on the molecular weights and the shape of the MWD. Therefore, imperfect mixing is not a cause for the broad and bimodal MWDs.

Chain transfer to polymer leads to the formation of long chain branches. A model that incorporated chain transfer to polymer and assumed termination by combination was developed. This model predicted the variation of the PDI with the residence time and the inlet monomer concentration reasonably well. The model also suggested that the sharp increase in the PDI that was observed experimentally was due to the onset of gelation. With this model, the predicted MWD curves were perfectly unimodal. This suggests that chain transfer to polymer can account for the broad MWDs and not for the bimodal MWDs.

The $\bar{M}_n$ predicted by the model were about half those measured using the GPC results, if the values of $f$ and $K_d$ measured by Charpentier et.al.\textsuperscript{7} were used. This disparity in $\bar{M}_n$ was attributed to an error in the value of the initiator efficiency, $f$ that was used in the calculations. However, the $\bar{M}_n$ calculated using F-19 NMR spectra did not agree with the GPC values.

It appears that heterogeneous polymerization in two phases is the source of the bimodal MWDs. However, monomer partitioning studies\textsuperscript{59, 60} showed that the equilibrium monomer concentration in the polymer phase is almost negligible at the polymerization conditions. A more detailed study to include partitioning of the initiator - DEPDC, characterization of the effect of mass transport and equilibrium properties...
between species in the polymer and scCO$_2$ phases would be required to understand the kinetics of heterogeneous polymerization.

Low temperature initiator studies showed that the redox system of BPO and DMA was not successful in polymerizing VF$_2$. However, the fluorinated initiator BPPP produced high molecular weight polymer with reasonable yields at lower temperature.

§ 6.2 Recommendations

Polymerization experiments should be carried out at high monomer concentrations (ca.2.0-3.0 M) and at better mixing conditions, i.e., using dual agitators at 2700 rpm, to determine whether the inhibition in $R_p$, is a result of imperfect mixing or some other inhibition mechanism such as inhibition by monomer. A heterogeneous model that accounts for polymerization inside the precipitated polymer particles should be developed to determine whether heterogeneous polymerization is the source of the bimodal distributions. Initiator partitioning studies should be carried out to determine the amount of initiator in the polymer phase. The pressure effect should be incorporated into the heterogeneous model using the partitioning studies. Fluorinated initiator studies should be extended to polymerizations in the continuous system in order to estimate kinetic parameters at the lower temperatures.
REFERENCES


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APPENDICES
APPENDIX A   MONOMER CONVERSIONS FROM THE GC

The monomer conversion and polymerization rates were determined by both GC analysis and by measuring the weight of polymer collected per unit time. Figure A.1 shows a typical GC trace (Run # 17 in §3.3.2) of the filtered effluent stream from a polymerization run, showing a clear separation of the CO$_2$ and VF$_2$ peaks.

![GC trace of an effluent stream showing the separation of CO$_2$ and VF$_2$ peaks.](image)

**Figure A.1**  GC trace of an effluent stream showing the separation of CO$_2$ and VF$_2$ peaks.

**GC Calibration**

Figure A.2 shows the calibration curve used to determine VF$_2$ concentration in the effluent stream during a polymerization run of known inlet concentrations. From Figure A.2, the ratio of volumetric flow rates is given by
\[
(VF_2/CO_2)_{\text{flow rates}} = \frac{1}{0.7512} \times (VF_2/CO_2)_{\text{peak areas}}
\]  
(A.1)

**Figure A.2**  Calibration curve from the GC using the areas of the CO\textsubscript{2} and VF\textsubscript{2} peaks for varying CO\textsubscript{2} and VF\textsubscript{2} flow rates.

Calibration was performed by sampling a stream of known amounts of CO\textsubscript{2} and VF\textsubscript{2} coming directly from the syringe pumps. The syringe pumps were maintained in a constant flow mode at the same temperatures, (i.e.) CO\textsubscript{2} pumps at 10 °C and VF\textsubscript{2} pumps at 0 °C, as those during the polymerization runs. The pressure of the system was maintained using a backpressure regulator (BPR).

**Computing the monomer conversion.**

The monomer conversion, \( X \) is given by

\[
X = \frac{m_{in}^{VF2} - m_{out}^{VF2}}{m_{in}^{VF2}}
\]  
(A.2)
where, \( \dot{m} \) is the mass flow rate; the subscripts in and out refer to reactor inlet and outlet streams and the superscript refers to the component (in this case VF\(_2\)).

Equation A.1 can be rewritten in terms of the ratio of mass flow ratios of an effluent stream from a polymerization reaction to give

\[
\frac{\dot{m}_{VF_2}^{\text{out}}}{\dot{m}_{CO_2}^{\text{out}}} = \gamma_{CO_2}^{VF_2} \cdot \frac{1}{0.7512} \left( \frac{VF_2/CO_2}{\text{effluent peak areas}} \right) \tag{A.3}
\]

where, \( \rho \) is the density of the respective component at the conditions of the syringe pumps. Carbon dioxide is inert and does not react during the polymerization. Therefore, at steady state the outlet mass flow rate for CO\(_2\) is same as the inlet mass flow rate. From Substituting for the outlet mass flow rate of VF\(_2\) from Equation A.3 into Equation A.2, we get

\[
X = 1 - \frac{1}{0.7512} \frac{\dot{m}_{in}^{CO_2} \gamma_{CO_2}^{VF_2}}{\dot{m}_{in}^{VF_2} \gamma_{VF_2}^{CO_2}} \left( \frac{VF_2/CO_2}{\text{effluent peak areas}} \right) \tag{A.4}
\]

Equation A.4, can be simplified in terms of the volumetric flow rates to give

\[
X = 1 - \frac{1}{0.7512} \left( \frac{VF_2/CO_2}{\text{effluent peak areas}} \right) \left( \frac{CO_2/VF_2}{\text{pump flow rates}} \right) \tag{A.5}
\]

where, the VF\(_2\) and CO\(_2\) pump flow rates are the volumetric flow rates at which the syringe pumps, operating in a constant flow mode, are set during a polymerization run.
APPENDIX B  MWD RESULTS FROM ATOFINA

GPC analysis for a few experiments discussed in Chapter 3 was also carried out by Atofina, Philadelphia. This analysis was carried out on a Waters-Alliance 150C system operating at 95 °C using HPLC grade dimethylsulfoxide (DMSO) as the eluent. 250 µL of a 3g/L sample of PVDF in DMSO was used for the analysis. The GPC was calibrated using eight polymethylmethacrylate (PMMA) standards. All reported MWDs and average molecular weights are with respect to PMMA.

Table B.1 shows a comparison of the average molecular weights obtained from the GPC analysis carried out at Solvay Research, Belgium and at Atofina, Philadelphia. The number average molecular weights from the two different sources appear to agree reasonably well. The difference between the values obtained from the two sources is consistent and varies from about 3 to 7 kg/mole. This difference could be because the values from Atofina are relative to PMMA whereas those obtained from Solvay are corrected to absolute quantities.

In contrast to the number average molecular weights, the weight average molecular weights from the two sources differ significantly. Although, they do not show a consistent difference, it does appear that with the exception of run #9, the $\overline{M}_w$ obtained from Atofina are higher than those obtained from Solvay. This is because Atofina carried out the analysis at 95 °C, which is much greater than that used by Solvay (45 °C). It is usually easier to dissolve the high molecular weight fractions at a higher temperature. Additionally, unlike the number average molecular weight, the weight average molecular weight is very sensitive to the presence of even small amounts of very high molecular
weight fractions. The above factors put together could thus contribute to significantly higher weight average molecular weights at higher operating temperatures for GPC analysis.

<table>
<thead>
<tr>
<th>Run #</th>
<th>SOLVAY (absolute MWs)</th>
<th>ATOFINA (MWs relative to PMMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n \times 10^4$</td>
<td>$M_w \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>5.65</td>
<td>14.47</td>
</tr>
<tr>
<td>5</td>
<td>7.85</td>
<td>44.26</td>
</tr>
<tr>
<td>6</td>
<td>4.46</td>
<td>16.96</td>
</tr>
<tr>
<td>7</td>
<td>4.49</td>
<td>11.3</td>
</tr>
<tr>
<td>8</td>
<td>4.15</td>
<td>10.01</td>
</tr>
<tr>
<td>9</td>
<td>6.86</td>
<td>70.27</td>
</tr>
<tr>
<td>10</td>
<td>3.22</td>
<td>5.75</td>
</tr>
<tr>
<td>11</td>
<td>4.26</td>
<td>10.34</td>
</tr>
<tr>
<td>15</td>
<td>6.7</td>
<td>11.86</td>
</tr>
</tbody>
</table>

**Table B.1** Comparison of number and weight average molecular weights obtained from Atofina and Solvay.

Molecular weight distributions obtained from both Solvay and Atofina were similar in terms of the shape of the distribution. Additionally, they were in agreement with respect to the modality (i.e.) whether the MWD curve is bimodal or unimodal, of the distributions.
The percentage of reverse additions and the number average molecular weight, were calculated using NMR spectra were obtained for 4 different polymer samples. The % inverse additions was evaluated from the peak areas using the following expression:

\[
\text{Inversion (\%) } = \frac{\left[ \frac{1}{2} (C + D + D') + E + L \right]}{100 \times \text{total area corresponding to monomer groups}}
\]  

(C.1)

where, total area refers to the sum of areas of all peaks obtained by integrating the NMR spectra and the letters refer to the areas of the corresponding peaks.

The number average molecular weight, \( \overline{M}_n \) was calculated from the average chain length using the

\[
\overline{M}_n = \frac{\text{Total Area corresponding to monomer units}}{\text{Area corresponding to end groups}/N} \times m
\]  

(C.2)

where, \( m \) is the monomer molar mass; \( N \), the average number of chain ends per polymer chain is assumed equal to two. From the peak assignments shown in Table 3.7b, the end group areas equals the sum of areas corresponding to peaks F, G, K and L (or M).

Table C.1 lists the areas of the different peaks obtained by integrating the spectra of the four NMR samples. The percentage reverse additions and \( \overline{M}_n \) were then calculated using Equations C.1 and C.2. These are listed in Table C.2.
<table>
<thead>
<tr>
<th>Assignment (Russo et.al.)</th>
<th>$^{19}$F $\delta$ (ppm)</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>A+A’</td>
<td>$-91.6 + -92.1$</td>
<td>100 100 100 100</td>
</tr>
<tr>
<td>B+ B’</td>
<td>$-94.8 + -95.7$</td>
<td>5.223 5.141 4.862 4.969</td>
</tr>
<tr>
<td>C</td>
<td>$-113.6$</td>
<td>4 4.133 5.109 5.13</td>
</tr>
<tr>
<td>E</td>
<td>$-113.9$</td>
<td>1.8 1.512 0.53 0.66</td>
</tr>
<tr>
<td>D + D’</td>
<td>$-115.6 + -116$</td>
<td>4.884 4.536 5.317 5.422</td>
</tr>
<tr>
<td>F</td>
<td>$-102.9^*$</td>
<td>1.552 0.806 0.518 0.668</td>
</tr>
<tr>
<td>J</td>
<td>$-92.1$</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>G</td>
<td>$-115.1$</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>K</td>
<td>$-117.3$</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>L</td>
<td>$-107.3$</td>
<td>0.323 0 0.097 0.194</td>
</tr>
<tr>
<td>M</td>
<td>$-114.3$</td>
<td>0.323 0 0.097 0.194</td>
</tr>
</tbody>
</table>

**Table C.1** Areas corresponding to different peaks obtained by integrating the NMR spectrum. Peak assignments are listed in Table 3.7

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Mn (from NMR spectra)</th>
<th>Reverse additions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$8.06 \times 10^3$</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>$1.84 \times 10^4$</td>
<td>5.0</td>
</tr>
<tr>
<td>8</td>
<td>$2.43 \times 10^4$</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>$1.74 \times 10^4$</td>
<td>5.2</td>
</tr>
</tbody>
</table>

**Table C.2** Number average molecular weight and percentage reverse defects from NMR spectroscopy.
APPENDIX D AVERAGE MOLECULAR WEIGHTS

The kinetic model for predicting the average molecular weights and the MWD is based on the following kinetic scheme

\[ \begin{align*}
    I & \rightarrow^{K_s} 2fR^* \quad \text{(Initiation)} \\
    R^* + M & \rightarrow^{K_n} P_1^* \quad \text{(Adding of first monomer)} \\
    P_n^* + M & \rightarrow^{K_p} P_{n+1}^* \quad \text{(Propagation)} \\
    P_n^* + P_m & \rightarrow^{mK_p} P_m^* + P_n \quad \text{(Chain Transfer to polymer)} \\
    P_n^* + P_m & \rightarrow^{K_e} P_{n+m}^* \quad \text{(Termination by Combination)}
\end{align*} \]

**Figure D.1** Reaction scheme for modeling the MWD

**Method of moments**

The chain length distribution of the dead polymer can be described in part by the first three (i.e.) the zeroth \((\mu_0)\), first \((\mu_1)\), and second \((\mu_2)\), moments. These moments are defined as

\[ \begin{align*}
    \mu_0 &= \sum_{n=1}^{\infty} P_n, \quad \text{(D.1a)} \\
    \mu_1 &= \sum_{n=1}^{\infty} nP_n = w \quad \text{and} \quad \text{(D.1b)} \\
    \mu_2 &= \sum_{n=1}^{\infty} n^2P_n. \quad \text{(D.1c)}
\end{align*} \]

Further, the number and weight average molecular weights can be written in terms of the ratios of successive moments as given below.
\[
\overline{M}_n = \frac{\mu_1}{\mu_0} m \quad \text{and} \quad (D.2a)
\]
\[
\overline{M}_w = \frac{\mu_2}{\mu_1} m \quad (D.2b)
\]

where, \( m \) is the monomer molar mass. Next, we write expressions for the mass balance on different species in order to evaluate the various moments.

**Mass Balance Equations**

**Balance on the monomer, \( M \).**

A mass balance on the monomer \( M \) using the above kinetic scheme gives
\[
v_{in}[M]_{in} - v_{out}[M]_{out} = V (2 f K_d [I]_{out} - K_p [M]_{out} \sum_{n=1}^{\infty} P_n ). \quad (D.3)
\]

If the volumetric flow rates \( v_{in} = v_{out} = \tau V \), the above equation can be rewritten as
\[
[M]_{out} = [M]_{in} - \frac{2 f K_d \tau [I]_{out}}{1 + \tau K_p \lambda} \quad (D.4)
\]

The initiator decomposition generally follows first order kinetics. Using this we get,
\[
[I]_{out} = \frac{[I]_{in}}{1 + K_d \tau} \quad (D.5)
\]

**Balance on the active radical species.**

The radical outflow in a continuous reactor is negligible and hence it does not contribute to the balance equations. Additionally, no active radical species are formed during the propagation and termination steps. Therefore equating the rate of formation of radicals (initiation step) and the rate of termination of radicals (termination step) we get
\[
2 f K_d [I]_{out} = 2 K_t \left( \sum_{n=1}^{\infty} P_n \right)^2. \quad (D.6)
\]
This can also be written as \[ \lambda = \sqrt{\frac{fK_d[I]_{out}}{K_{tc}}} \] \hspace{1cm} (D.7)

Solving Equations D.5, D.7 and D.4 sequentially we can calculate the exit monomer and initiator concentrations and \( \lambda \) in terms of the inlet concentrations, reactor residence time and the different rate constants.

**Balance on active polymer chains \( P_n \)**

Neglecting the outflow of the active radical species (\( P_n \)) we get,

\[
V \left( \frac{2fK_d}{[I]_{out}} - P_1 \left[ M \right]_{out} K_p - K_{tp} P_1 \sum_{n=1}^{\infty} nP_n + K_{tp} P_1 \sum_{n=1}^{\infty} P_n - 2K_{tc} P_1 \sum_{n=1}^{\infty} P_n \right) = 0 \text{ if } n=1, \text{ and }
\]

\[
V \left( P_{n-1} \left[ M \right]_{out} K_p - P_n \left[ M \right]_{out} K_p - K_{tp} P_n \sum_{m=1}^{\infty} mP_m + K_{tp} P_n \sum_{m=1}^{\infty} P_m - 2K_{tc} P_n \sum_{m=1}^{\infty} P_m \right) = 0 \text{ if } n>1.
\]

Simplifying the above equations we get,

\[
P_1 \alpha = K_{tp} P_1 \lambda + 2fK_d[I]_{out} \text{ if } n=1 \text{ and } (D.8a)
\]

\[
P_n \alpha = nK_{tp} P_n \lambda + \left[ M \right]_{out} K_p P_{n-1} \text{ if } n>1 \text{ (D.8b)}
\]

where, \( \alpha = K_p \left[ M \right]_{out} + 2K_{tc} \lambda + K_{tp} w \), \( P_n \) and \( P_n \) are the concentrations of the active polymer chain and dead polymer chain of \( n \) monomer units respectively, and \( w = \left[ M \right]_{in} - \left[ M \right]_{out} \).

**Balance on dead polymer chains (\( P_n \))**

A balance on \( P_n \) gives

\[
v_{out} P_n = V \left( K_{tp} P_n \sum_{n=1}^{\infty} nP_n - K_{tp} P_n \sum_{n=1}^{\infty} P_n + K_p \sum_{i=1}^{n-1} P_i P_{n-i} \right) \text{ (D.9)}
\]

Simplifying, the above equation we get

\[
P_n \left( 1 + \tau nK_{tp} \lambda \right) = \tau P_n w K_{tp} + \tau K_{tc} \sum_{i=1}^{n-1} P_i P_{n-i} \text{ (D.10)}
\]

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If the chain length distribution of the dead polymer species is known, it is very easy to calculate the moments and the average molecular weights from the above equations. However, the combination term \( \sum_{i=1}^{n-1} P_i P_{n-i} \) in Equation D.10, makes it very difficult to solve Equations D.9 and D.10 simultaneously for every value of \( n \). Therefore, we use the discrete transform method to calculate the moments.

**Discrete Transformation method**

The generating function for the chain length distribution of the active and dead polymer species is defined as

\[
G(s) = \sum_{n=1}^{\infty} P_n s^n \quad \text{and} \quad D(s) = \sum_{n=1}^{\infty} P_n s^n .
\]

(D.11a)

(D.11b)

From Equations D.1 and D.11, the moments can be written in terms of the generating functions as given below:

\[
\mu_0 = \lim_{s \to 1} D(s) = \lim_{s \to 1} \mu_0(s), \quad \text{(D.12a)}
\]

\[
\mu_1 = \lim_{s \to 1} \frac{\partial D(s)}{\partial (\ln s)} = \lim_{s \to 1} \mu_1(s), \quad \text{(D.12b)}
\]

\[
\mu_2 = \lim_{s \to 1} \frac{\partial^2 D(s)}{\partial (\ln s)^2} = \lim_{s \to 1} \mu_2(s) \quad \text{and so on for the higher moments.} \quad \text{(D.12c)}
\]

Similarly, the limits for the moments of the active polymer chain length distribution can be written as,

\[
\lambda = \lim_{s \to 1} G(s) = \lim_{s \to 1} \lambda(s), \quad \text{(D.13a)}
\]
\[ \lambda_1 = Lt \frac{\partial G(s)}{\partial (\ln s)} = Lt \lambda_1(s), \quad \text{(D.13b)} \]

\[ \lambda_2 = Lt \frac{\partial^2 G(s)}{\partial^2 (\ln s)} = Lt \lambda_2(s) \quad \text{and so on for the higher moments.} \quad \text{(D.13c)} \]

**Transform Equations.**

Multiplying Equation D.8 by \( \tau s^n \), substituting for \( fK_d[I]_{out} \) from D.7 and summing for all values of \( n \), we get,

\[ \sum_{n=1}^{\infty} \tau s^n (D.8) \Rightarrow \tau \sum_{n=1}^{\infty} P_n \alpha s^n = \tau K_{ip} \lambda \sum_{n=1}^{\infty} nP_n s^n + \tau [M]_{out} K_p \sum_{n=1}^{\infty} P_{n-1} s^n + 2\tau K_{ic} \lambda^2 s. \]

\[ \Rightarrow \quad \tau G(s)[K_p [M]_{out} s - \alpha] + 2\tau K_{ic} \lambda^2 s + \tau K_{ip} \lambda \frac{D(s)}{\partial \ln s} = 0, \quad \text{(D.14)} \]

Multiplying D.9 by \( s^n \) and summing for all \( n \), we get

\[ \sum_{n=1}^{\infty} s^n (D.9) \Rightarrow \sum_{n=1}^{\infty} P_n s^n + \tau K_{ip} \lambda \frac{D(s)}{\partial \ln s} = \tau wK_{ip} \sum_{n=1}^{\infty} P_n s^n + \tau K_{ic} \sum_{n=1}^{\infty} \left( \sum_{i=1}^{n-1} P_i P_{n-i} s^n \right) s^n \]

\[ \Rightarrow D(s) + \tau K_{ip} \lambda \frac{\partial D(s)}{\partial \ln s} = \tau wK_{ip} G(s) + \tau K_{ic} G^2(s) \quad \text{(D.15)} \]

Taking Limit \( s \to 1 \) for D.15, we get

\[ \mu_0 + \tau K_{ip} \lambda w = \tau wK_{ip} \lambda + \tau K_{ic} \lambda^2 \]

\[ \Rightarrow \quad \mu_0 = \tau K_{ic} \lambda^2 \quad \text{(D.16)} \]

Differentiating D.14 and D.15 with respect to \( \ln(s) \), we get

\[ \frac{\partial (D.14)}{\partial \ln s} \Rightarrow \tau \lambda_1(s)[K_p [M]_{out} s - \alpha] + \tau \lambda(s) K_p [M]_{out} s + 2\tau K_{ic} \lambda^2 s + \tau K_{ip} \lambda \mu_1(s) = 0 \quad \text{(D.17)} \]

\[ \frac{\partial (D.15)}{\partial \ln s} \Rightarrow \mu_1(s) + \tau K_{ip} \lambda \mu_2(s) - \tau wK_{ip} \lambda_1(s) - 2\tau K_{ic} \lambda_1(s) \lambda(s) = 0 \quad \text{(D.18)} \]
Taking limits $s \to 1$ for D.17 and solving for $\lambda_1$, we get

$$\frac{\lambda_1}{\lambda} = a + b\mu_2,$$  \hspace{1cm} (D.19)

where, $a = \frac{K_p [M]_{out} + 2K_i \lambda}{wK_{ip} + K_i \lambda}$ and $b = \frac{K_{ip}}{wK_{ip} + K_i \lambda}$.

Taking limits $s \to 1$ for D.17 and D.18 and subtracting, we get,

$$\mu_1 = \frac{\tau \lambda (K_r \lambda + K_p [M]_{out})}{K_{ip} \lambda}$$  \hspace{1cm} (D.20)

Differentiating D.17 and D.18 again with respect to $\ln(s)$,

$$\frac{\partial(D.17)}{\partial \ln s} \Rightarrow \tau \lambda_2 (s) (K_p [M]_{out} s - \alpha) + 2\tau \lambda_1 (s) K_p [M]_{out} + \tau \lambda (s) K_p [M]_{out} s + 2\tau K_i \lambda^2 s + \tau K_{ip} \lambda_3 (s) = 0$$  \hspace{1cm} (D.21)

$$\frac{\partial(D.18)}{\partial \ln s} \Rightarrow \mu_2 (s) + \tau K_p \lambda_3 (s) - \tau wK_{ip} \lambda_2 (s) - 2\tau K_i \lambda (s) \lambda_2 (s) + \lambda_1 (s) \lambda_1 (s) = 0$$  \hspace{1cm} (D.22)

Taking limits $s \to 1$ for D.20 and D.21 and subtracting, we get

$$\mu_2 = 2\tau \lambda_1 (K_r \lambda_1 + K_p [M]_{out}) + \tau \lambda (K_p [M]_{out} + 2K_i \lambda)$$

$$\Rightarrow \mu_2 = \tau \lambda_1 (K_r \lambda_1 + 2K_p [M]_{out}) + \mu_1$$  \hspace{1cm} (D.23)

Substituting for $\lambda_1$ from D.19 into D.23, we get

$$\mu_2 = 2\tau a \lambda (K_r \lambda + K_p [M]_{out}) + \mu_1 \text{ if } K_{ip} = 0 \text{ and}$$  \hspace{1cm} (D.24a)

$$\mu_2^2 + \mu_2 p_1 + p_2 = 0 \text{ if } K_{ip} \neq 0$$  \hspace{1cm} (D.24b)

where, $p_1 = \frac{1}{b^2} \left(2ab + \frac{2K_p b [M]_{out}}{K_i \lambda} - \frac{1}{2\tau K_i \lambda^2}\right)$, $p_2 = \frac{1}{b^2} \left(a^2 + \frac{aK_p [M]_{out}}{\lambda K_i} + \frac{\mu_1}{2\tau K_i \lambda^2}\right)$.

Equation D.24b is a quadratic equation in $\mu_2$, which results in two possible values of $\mu_2$. 

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However, only one of these values is correct. In order to find the correct value let us calculate the value of \( \mu_2 \) obtained from D.25a in the limiting case of \( K_{tp} \to 0 \) and then compare it with that obtained from D.24a.

\[
\mu_2 = \frac{-p_i}{2} \left( 1 \pm \sqrt{1 - 4 \frac{p_2}{p_i^2}} \right) \tag{D.25b}
\]

In the limit \( K_{tp} \to 0, b \to 0 \). Therefore, \( \frac{p_2}{p_i^2} \to 0 \). Therefore, \( \frac{p_2}{p_i^2} = \frac{b^2}{\left( \frac{2}{a} + \frac{a \lambda K_p [M]_{out} + \mu_1}{\lambda K_{ic}^2} + \frac{2}{\pi K_{ic} \lambda^2} \right)} \to 0 \).

Expanding D.25b in a Taylor series and neglecting higher order terms, we get

\[
\mu_2 = \frac{-p_i}{2} \left( 1 \pm \left( 1 - \frac{4 p_2}{2 p_i^2} \right) \right). \tag{D.25a}
\]

Hence, the two values of \( \mu_2 \) in the limit \( K_{tp} \to 0 \) are,

\[
\mu_2^- = Lt\left(- \frac{p_2}{p_1}\right) = 2\pi a \lambda (K_{ic} \lambda a + K_p [M]_{out}) + \mu_1 \quad \text{and} \quad \mu_2^+ = Lt\left(- \frac{p_1 + 4 p_2}{p_i}\right) \to \infty.
\]

Thus \( \mu_2^+ \) results in a discontinuity at \( K_{tp} = 0 \), whereas \( \mu_2^- \) equals the value obtained from D.24a. From this it can be concluded that

\[
\mu_2 = -\frac{p_i}{2} \left( 1 - \sqrt{1 - \frac{4 p_2}{p_i^2}} \right) \quad \text{if} \quad K_{tp} \neq 0 \quad \text{and} \quad \mu_2 = 2\pi a \lambda (K_{ic} \lambda a + K_p [M]_{out}) + \mu_1 \quad \text{if} \quad K_{tp} = 0. \tag{D.26a, D.26b}
\]

The average molecular weights can now be calculated from the following equations:

\[
\overline{M_n} = \frac{\mu_1}{\tau K_{ic} \lambda^2} \quad \text{and} \quad \overline{M_w} = \frac{\mu_2}{\mu_1} \quad \text{where,} \quad \mu_1 = \frac{w = [M]_{in} - [M]_{out}}{\mu_2} \quad \text{and} \quad \mu_2 \quad \text{is given by Equation D.26.}
\]
APPENDIX E   AVERAGE NUMBER OF BRANCHES

The average number of branches per polymer chain was calculated using a more detailed form of the kinetic scheme described in Figure D.1. This scheme is shown below:

\[
\begin{align*}
I & \xrightarrow{K_i} 2fR^* \quad \text{(Initiation)} \\
R^* + M & \xrightarrow{K_{n,0}} P^*_{1,0} \quad \text{(Addition of first monomer unit)} \\
P^*_{n,b} + M & \xrightarrow{K_p} P^*_{n+1,b} \quad \text{(Propagation)} \\
P^*_{n,b} + P_{m,c} & \xrightarrow{mK_v} P^*_{m,c+1} + P_{n,b} \quad \text{(Chain Transfer to polymer)} \\
P^*_{n,b} + P_{m,c} & \xrightarrow{fK_t} P_{n+m,b+c} \quad \text{(Termination by Combination)}
\end{align*}
\]

Figure E.1  Kinetic scheme to calculate average number of branches

The second subscript (b or c) in the above kinetic scheme represents the number of branches in that particular polymer chain and it varies from 0 to \( n-1 \) for every value of n. The average number of branches, \( B_n \), is given by

\[
B_n = \frac{\sum_{n=1}^{\infty} \sum_{b=0}^{n-1} bP_{n,b}}{\sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b}}.
\]  \( \text{(E.1)} \)

The denominator in the above equation is the zeroth moment, \( \mu_0 \) defined in Appendix D and the numerator is the first moment for the branching distribution. Since, the zeroth moment is a summation of the dead polymer concentration for all n and b, it equals that given by Equation D.16,

\[ \mu_0 = \tau K_r \lambda^2. \]  \( \text{(E.2)} \)
Mass Balance Equations

The balance equations for the monomer, initiator and the total radical concentration are the same as those formulated in Appendix D. From Appendix D we get,

\[ [M]_{\text{out}} = \frac{[M]_{\text{in}} - 2fK_d \epsilon[I]_{\text{out}}}{1 + \tau K_p \lambda}, \quad [I]_{\text{out}} = \frac{[I]_{\text{in}}}{1 + K_d \tau}, \quad \lambda = \sqrt{fK_d [I]_{\text{out}} / K_t} \]  

(E.3)

where, \( \lambda \) equals the total concentration of active polymer radicals given by

\[ \lambda = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} P_{n,b} \].

Additionally the first moment of the chain length distribution of the dead polymer molecules is given by

\[ w = [M]_{\text{in}} - [M]_{\text{out}} = \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nP_{n,b} \]  

(E.4)

**Balance on active polymer chains** \( P_{n,b} \)

\[
V \left( 2fK_d [I]_{\text{out}} - P_{1,0} [M]_{\text{out}} K_p - K_{ip} P_{1,0} \sum_{m=1}^{\infty} \sum_{c=0}^{m-1} mP_{m,c} - 2K_{ic} P_{1,0} \sum_{m=1}^{\infty} \sum_{c=0}^{m-1} P_{m,c} \right) = 0 \quad \text{if, } n=1, b=0
\]

\[
V \left( P_{n-1,b} [M]_{\text{out}} K_p - P_{n,b} [M]_{\text{out}} K_p - K_{ip} P_{n,b} \sum_{m=1}^{\infty} \sum_{c=0}^{m-1} mP_{m,c} + K_{ic} nP_{n,b} \sum_{m=1}^{\infty} \sum_{c=0}^{m-1} P_{m,c} \right) = 0, \quad \text{if } n > 1, 0 \leq b < n.
\]

Rewriting the above equations we get,

\[ P_{1,0} \alpha = 2fK_d [I]_{\text{out}} \quad \text{for } n=1, b=0 \]  

(E.5a)

\[ P_{n,b} \alpha = [M]_{\text{out}} K_p P_{n-1,b} + K_{ip} nP_{n,b-1} \lambda \quad \text{for } n > 1, 0 \leq b < n. \]  

(E.5b)

**Balance on dead polymer chain** \((P_{n,b})\)

\[
v_0 P_{n,b} = V \left( K_{ip} P_{n,b} \sum_{m=0}^{\infty} \sum_{c=0}^{m-1} mP_{m,c} - K_{ip} nP_{n,b} \sum_{m=0}^{\infty} \sum_{c=0}^{m-1} P_{m,c} + K_{ic} \sum_{i=0}^{n-1} \sum_{j=0}^{b-1} P_{n-i,b-j} P_{i,j} \right)
\]

Simplifying the above equation, we get
\[
P_{n,b} (1 + \tau K_{ip} n \lambda) = \tau K_{ip} P_{n,b} w + \tau K_{rc} \sum_{j=0}^{b-1} \sum_{i=j}^{n-1} P_{n-i,b-j} P_{i,j}
\]

(E.6)

In order to calculate the first moment of the branching distribution, we use the discrete transformation method.

**Discrete Transformation Method**

The generating functions \(D(s,r)\) and \(G(s,r)\) are defined as follows:

\[
D(s,r) = \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b} s^n r^b
\]

and

\[
G(s,r) = \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b} s^n r^b.
\]

(E.7a, E.7b)

From E.1 and E.2, the average number of branches per molecule is given by

\[
\bar{B}_n = Lt \frac{\partial D(s,r)}{\partial \ln r} / \tau K_{ip} \lambda^2
\]

(E.8)

**Transform Equations**

Multiplying E.5 by \(\tau s^n r^b\) and summing for all \(n,b\) we get,

\[
\sum_{n=1}^{\infty} \sum_{b=0}^{n-1} (E.5) s^n r^b \Rightarrow \tau K_{ip} [M]_{out} \sum_{n=2}^{\infty} \sum_{b=0}^{n-1} P_{n-1,b} s^n r^b - \tau \alpha \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b} s^n r^b + 2 \tau f K_d [I]_{out} s + \tau K_{ip} \lambda \sum_{n=2}^{\infty} \sum_{b=0}^{n-1} n P_{n,b-1} s^n r^b = 0
\]

\[
\Rightarrow \tau K_{ip} [M]_{out} s G(s,r) - \tau \alpha G(s,r) + \tau K_{ip} \lambda r \sum_{n=1}^{\infty} \sum_{c=0}^{n-2} n P_{n,c} s^n r^c + 2 \tau f K_d [I]_{out} s = 0 \quad (E.9)
\]

Let \(D_1(s,r) = \sum_{n=1}^{\infty} \sum_{b=0}^{n-2} P_{n,b} s^n r^b\), therefore

\[
K_{ip} \lambda r \sum_{n=1}^{\infty} \sum_{c=0}^{n-2} n P_{n,c} s^n r^c = \frac{\partial D_1(s,r)}{\partial \ln s}.
\]

(E.10)
Note that $D_1(s,r)$ does not include the summation terms when $b=n-1$.

Substituting E.10 in E.9 we get,

$$\tau K_p \left[ M \right]_{out}, sG(s,r) - \tau \alpha G(s,r) + \tau K_{tp} \lambda r \frac{\partial D_1(s,r)}{\partial \ln s} + 2\tau f K_d \left[ I \right]_{out}, s = 0 \tag{E.11}$$

Multiplying E.6 by $s^n r^b$ and summing for all $n,b$ we get,

$$\sum_{n=1}^{\infty} \sum_{b=0}^{n-1} (E.6)s^n r^b \Rightarrow \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b} s^n r^b + \tau K_{tp} \lambda \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nP_{n,b} s^n r^b = \tau K_{tp} W \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} P_{n,b} s^n r^b$$

$$+ \tau K_{tc} \lambda \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} \left( \sum_{i=0}^{n-1} \sum_{j=0}^{b-n} P_{n-i,b-j} P_{i,j} \right)$$

$$\Rightarrow D(s,r) + \tau K_{tp} \lambda \frac{\partial D(s,r)}{\partial \ln s} = -\tau K_{tp} W G(s,r) - \tau K_{tc} \lambda G^2(s,r) = 0 \tag{E.12}$$

Differentiating Equations E.11 and E.12 with respect to $\ln(r)$:

$$\frac{\partial (E.11)}{\partial \ln r} \Rightarrow \tau \left( K_p [M]_{out} - \alpha \right) s \frac{\partial G(s,r)}{\partial \ln r} + \tau K_{tp} \lambda \left( r \frac{\partial^2 D_1(s,r)}{\partial (\ln r) \partial (\ln s)} + \frac{\partial D_1(s,r)}{\partial (\ln s)} \right) = 0 \tag{E.13}$$

$$\frac{\partial (E.12)}{\partial \ln r} \Rightarrow \frac{\partial D(s,r)}{\partial \ln r} + \tau K_{tp} \lambda \frac{\partial^2 D(s,r)}{\partial (\ln r) \partial (\ln s)} - \tau K_{tp} W \frac{\partial G(s,r)}{\partial \ln r} - 2\tau K_{tc} \lambda G(s,r) \frac{\partial G(s,r)}{\partial \ln r} = 0 \tag{E.14}$$

Now, $L_1 \left( r \frac{\partial^2 D_1(s,r)}{\partial (\ln r) \partial (\ln s)} + \frac{\partial D_1(s,r)}{\partial (\ln s)} \right) = \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nbP_{n,b} + \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nbP_{n,b} \tag{E.15}$

From the kinetic scheme, the termination is primarily by combination. However, termination also occurs by chain transfer to polymer in some cases, which leads to branch formation. Additionally, the rate of propagation is usually much larger than the rate of chain transfer to polymer. Therefore, the number of branches in a polymer molecule is much lower than the number of monomers. Hence, it can be assumed that the concentration of a polymer molecule when $b=n-1$, (i.e.) $P_{n,n-1}$ is negligible compared to the sum of all other concentrations. Rewriting E.15, we get
\[
\left. \begin{array}{c}
L_t \left( \frac{\partial^2 D(s, r)}{\partial \ln r \partial \ln s} + \frac{\partial D(s, r)}{\partial \ln s} \right) \right|_{r \to 1, s \to 1} = \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nbP_{n,b} + \sum_{n=1}^{\infty} \sum_{b=0}^{n-1} nbP_{n,b} \\
= L_t \left( r \frac{\partial^2 D(s, r)}{\partial \ln r \partial \ln s} + \frac{\partial D(s, r)}{\partial \ln s} \right)
\end{array} \right. \quad \text{ (E.16)}
\]

Adding E.13 and E.14, taking limit \( r \to 1 \) and \( s \to 1 \), and substituting E.16 in the resulting equation, we get

\[
\frac{L_t}{r \to 1} \frac{\partial D(s, r)}{\partial \ln r} = \tau K_{lp} \lambda L_t \frac{\partial D(s, r)}{\partial \ln s} \quad \text{where} \quad L_t \frac{\partial D(s, r)}{\partial \ln s} = w = \mu_i \quad \text{ (E.17)}
\]

Using Equation E.8 and E.17, we get the average number of branches per polymer molecule, \( \bar{B}_n \) is

\[
\bar{B}_n = \frac{K_{lp} w}{K_{lc} \lambda} = \frac{K_{lp} w}{\sqrt{K_{tc} f K_d I_{out}}} \quad \text{ (E.18)}
\]
Recursive method to calculate $P_n$

In Appendix D, a discrete transformation method was used to calculate the moments of the dead polymer chain length distribution. In order to calculate the entire distribution we need to first solve for the generating function $D(s)$. The entire distribution can then be obtained from $D(s)$ by inverse transformation techniques. The above method is mathematically very complex as it is very difficult to get an analytical solution for $D(s)$. Therefore, a better technique is to solve for the concentration from the difference equations for $P_n$ and $P_{n-1}$. From Appendix D, the difference equations are:

\[ P_1\alpha = K_{tp}P_1\lambda + 2fK_\alpha [I]_{out} \quad \text{if } n=1 , \quad (F.1a) \]

\[ P_n\alpha = nK_{tp}P_n\lambda + [M]_{out}K_pP_{n-1} \quad \text{if } n>1 \quad \text{and} \quad (F.1b) \]

\[ P_n(1+\tau nK_{tp}\lambda) = \tau P_n wK_{tp} + \tau K_{tc} \sum_{i=1}^{n-1} P_i P_{n-i} \quad \text{for all } n. \quad (F.2) \]

where, $\alpha = K_{tp}[M]_{out} + 2K_{tc}\lambda + K_{tp}w$. Expressions for $[M]_{out}, [I]_{out}, w, \lambda$ are given in Appendix D. The combination term, $\sum_{i=1}^{n-1} P_i P_{n-i}$ in F.2 makes it very difficult to obtain a general solution for $P_n$. Therefore, we seek a recursive solution for $P_n$.

Rewriting F.2 for $n=1$ we get,

\[ P_1(1+\tau K_{tp}\lambda) = \tau P_1 wK_{tp} \quad (F.3) \]

Equations F.1a and F.3 are two equations in two unknowns, $P_1$ and $P_i$. Solving for these unknowns we get
Substituting for $P_n$ from (F.2) into (F.1b) we get,

\[ P_1 = \frac{2fK_d [I]_{out} (1 + \tau K_p \lambda)}{\alpha + \tau K_p \lambda (\alpha - w K_p)} \quad \text{and} \quad (F.4) \]

\[ P_1 = \frac{(2fK_d [I]_{out} (w\tau K_p \lambda))}{\alpha + \tau K_p \lambda (\alpha - w K_p)} \quad (F.5) \]

\[ K_p P_{n-1} [M]_{out} \left(1 + n \tau K_p \lambda\right) + n \tau K_p \lambda K_{tc} \sum_{j=1}^{n-1} P_i P_{n-i} \]

\[ P_n = \frac{K_p P_{n-1} [M]_{out} \left(1 + n \tau K_p \lambda\right) + n \tau K_p \lambda K_{tc} \sum_{j=1}^{n-1} P_i P_{n-i}}{\alpha + \tau K_p \lambda n \left(K_p [M]_{out} + K_{tc} \lambda\right)} \quad \text{for } n>2 \quad (F.6) \]

The above equation gives $P_n$ in terms of $P_k$'s where $k<n$. Using (F.4) and (F.6), we can calculate $P_n$ for all $n$. The dead polymer chain length distribution $P_n$, can now be obtained from the distribution of the active polymer chains, (i.e.) from $P_n$, using Equation (F.2). A computer program (in ‘C’) was used to calculate $P_n$ using the above-mentioned recursive algorithm. The qualitative behavior of the molecular weight distribution can be obtained from $P_n$, by plotting $nP_n$ versus $n$. 

\[ P_1 = \frac{2fK_d [I]_{out} (1 + \tau K_p \lambda)}{\alpha + \tau K_p \lambda (\alpha - w K_p)} \quad \text{and} \quad (F.4) \]

\[ P_1 = \frac{(2fK_d [I]_{out} (w\tau K_p \lambda))}{\alpha + \tau K_p \lambda (\alpha - w K_p)} \quad (F.5) \]
Computer program to calculate the chain length distribution, $P_n$

/* To calculate the chain length distribution of the dead polymer ($P_n$) */
#include <stdio.h>
#include <math.h>

/* Maximum chain length until which the distribution (i.e.) $P_n$ is sought. */
#define MAX 7000
main() {
    /*Arrays to hold values of $P_n$ and $P_{ndot}$ */
    double Pn[MAX],Pndot[MAX];

    /*Defining all constants and variables involved. $M_0,I_0$ are inlet monomer, initiator concentrations. $M,I$ are outlet concentrations. */
    double alpha,Kp,f,Kd,M0,lambda,Ktp,w,Tau,I0,I,M,Ktc;
    int n,j;

    /*Sum is the summation of the combinatorial term ($\sigma P[i]P[n-i]$) */
    double sum;

    /*Initializing the variables and constants defined above. */
    sum=0;
    I0=0.003;
    M0=3.0;
    Kd=0.00103;
    f=0.6;
    Kp=1000000;
    Ktp=0.01*Kp;
    Ktc=55.4*Kp*Kp;
    Tau=1200;

    /*The concentration of polymer species of zero chain length is 0 */
    Pn[0]=0;
    Pndot[0]=0;
    I=I0/(1+(Kd*Tau));
    lambda=sqrt(2*f*Kd*I/Ktc);
    M=(M0-2*f*Kd*Tau*I)/(1+Tau*Kp*lambda);
    w=M0-M;
    alpha=Ktp*w+Kp*M+Ktc*lambda;

    /* Calculating $P_1$ and $P_{1dot}$ using Equations (F.4) and (F.5) */
    Pndot[1]=(2*f*Kd*I)*(1+2*Kp*I)/(alpha+2*Ktp*lambda);
    Pn[1]=Pndot[1]*w*Ktp*Tau/(1.0+(Tau*Ktp*lambda));
/* Calculating $P_n$ recursively */
for (n=2;n<MAX;n++) {

    for (j=1;j<n;j++) {
        sum=sum+Pndot[j]*Pndot[n-j];
    }

    /* Calculating $P_{ndot}$ using Equation F.6 */
Pndot[n]=(Pndot[n-1]*Kp*M*(1+n*Ktp*Tau*lamda)+(n*Ktp*Ktc*Tau*lamda*sum/2.0))/(Tau*Ktp*lamda*n*(M*Kp+lamda*Ktc)+alpha);

    /* Calculating $P_n$ using Equation F.2 */
Pn[n]=(Tau*Pndot[n]*w*Ktp+Tau*Ktc*sum/2.0)/(1.0+(Tau*Ktp*lamda*n));
    printf("  %d	%.20f	%.20f
",n,Pndot[n],Pn[n]);
    sum=0;
}

/* Output the values of $P_{ndot}$, $P_n$ for 0<n<7000 */
for (n=1;n<MAX;n++) {
    printf("  %d	%.20f	%.20f
",n,Pndot[n],Pn[n]);
}
APPENDIX G  REDOX INITIATION STUDIES

**Initiator preparation**

Dimethyl Aniline (DMA) and Benzoyl Peroxide (BPO) were obtained from Aldrich. Dimethyl Aniline, a liquid, was diluted with Freon® 113 to the required concentration. Benzoyl Peroxide, a solid at room temperature, was first recrystallized using Chloroform and then dissolved in an appropriate solvent. A number of solvents were tried to dissolve the BPO. These are listed in Table G.1. However, only Toluene and Tetrahydrofuran (THF) were able to dissolve the BPO reasonable well. Three experiments, two with toluene and one with THF were carried out to study the polymerization using the BPO+DMA initiator system.

<table>
<thead>
<tr>
<th>Solvents Tried</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freon 113</td>
<td>Insoluble</td>
</tr>
<tr>
<td>E-2 (DuPont’s perfluopolyether)</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Dichlorotetrafluoroethane</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Hexafluorobenzene</td>
<td>Insoluble</td>
</tr>
<tr>
<td>APF-215</td>
<td>Insoluble</td>
</tr>
<tr>
<td>APF-240</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Toluene</td>
<td>Soluble</td>
</tr>
<tr>
<td>THF</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

**Table G.1**  Solvents used to dissolve BPO

![Structures of APF-215 and APF-240](image)

perfluoro per hydro phenanthrene (APF-215)  perfluoro di isopropyl per hydro naphthalene (APF-240)

**Figure G.1**  Structures of APF-215 and APF-240
**Experimental Procedure**

The polymerization system was similar to that described in Chapter 3. The schematic for the polymerization system is shown in Figure G.2. An additional syringe pump was used to feed the DMA solution. The polymer withdrawal system consisted of only two filters, 1 steady state and 1 non-steady state.

![Redox Polymerization System](image)

A-CO2 cylinder; B- VF2 Cylinder; C- BPO Solution (in Toluene or THF); D-DMA Solution (in Freon 113); E,F,G,H – Syringe Pumps; I-Thermostated Autoclave; J-Chiller/Heater Unit; K-Effluent Cooler; L- Static Mixer; V-Valves; GC- Gas Chromatograph.

**Figure G.2** Redox Polymerization System

The polymerization procedure was identical to that using DEPDC as the initiator, except that the filtered reactor effluent stream is sampled even while operating at unsteady state conditions in order to monitor the VF$_2$ conversion as a function of the
residence time. Additionally, no back flushing with CO₂ was required as there was no pressure drop across the filters during the polymerization reaction.

**Gas Chromatograph data.**

Table G.2 shows the GC data obtained for the run #2 (Table 5.1) using toluene as the solvent for BPO. The scatter in the data appears to be more than normal. However, it can be concluded that some VF₂ conversion is occurring.

<table>
<thead>
<tr>
<th>No. of Residence Times</th>
<th>VF₂ Coversion (X %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>12.5</td>
</tr>
<tr>
<td>1.2</td>
<td>4.8</td>
</tr>
<tr>
<td>1.7</td>
<td>11.8</td>
</tr>
<tr>
<td>2.3</td>
<td>18.5</td>
</tr>
<tr>
<td>2.8</td>
<td>19.4</td>
</tr>
<tr>
<td>3.4</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>28.8</td>
</tr>
<tr>
<td>5</td>
<td>17.3</td>
</tr>
</tbody>
</table>

**Table G.2** GC data showing monomer conversion as a function of time onstream (number of residence times).
Initiator Synthesis

The initiator synthesis is represented by the following chemical reaction:

\[
2 \text{R-C-F} + 2\text{KOH} + \text{H}_2\text{O}_2 \xrightarrow{\text{condensation}} \text{R-C-O-O-C-R} + 2\text{KF} + 2\text{H}_2\text{O}
\]

Under vacuum, the HFPO dimer was first condensed into a round bottom flask, then cooled in liquid nitrogen, and weighed. The reaction was carried out in a three-neck flask that was equipped with an addition funnel, gas inlet and outlet adapters. The reactor was purged with argon and stirred continuously using a magnetic stir bar throughout the course of the reaction. A two-phase mixture of perfluorohexanes and water was added to the reaction vessel and cooled to \(-5^\circ\text{C}\). To this mixture 0.5 eq \(\text{H}_2\text{O}_2\) (as a 35 wt% solution), and 1 eq KOH (as a 5M solution) was added. The condensed HFPO dimer was then transferred to the addition funnel, and added drop wise so that the temperature never exceeded 0\(^\circ\text{C}\). When addition was complete, the reaction was allowed to continue for an additional 15 minutes. At this time, stirring was stopped to allow the phases to separate. The reaction mixture was transferred to a separating funnel and the heavier organic layer extracted. The organic layer was transferred to a precooled flask and dried over \(\text{MgSO}_4\), while the solution was kept in dry ice at -78\(^\circ\text{C}\). The solution was vacuum filtered, titrated and stored under an inert atmosphere at -78\(^\circ\text{C}\).

The initiator titration is carried out in the dark in order to minimize the formation of any interfering radicals. An Erlenmeyer flask was charged with 12.5ml glacial acetic acid, and 0.75 g \(\text{NaHCO}_3\). To this flask was added 2.0 ml saturated Sodium Iodide (NaI) solution and 2.0 ml initiator solution and the solution, now yellow to dark brown, was
stored in the dark for 15 min. This solution was then titrated to a clear endpoint using a Na₂S₂O₃ standard solution.

The concentration of the initiator solution was typically around 0.05 M. This corresponds to a yield of around 5% for the initiator synthesis. The reason for such a low yield is not known and repeated synthesis attempts failed to increase the initiator yield.

**Experimental Procedure.**

Polymerizations were carried out in an 80 mL high-pressure cell with sapphire windows on each end. A schematic of the experimental setup is shown in Figure G.1. The cell was first charged with CO₂ at 300 psig and then vented to remove air and other impurities. This was repeated two times. The vessel was then leak tested to the desired reaction pressure using CO₂, and vented down to 700 psig CO₂. A known volume of VF₂, based on the desired monomer charge, was then added to the reactor from a syringe pump. The vessel was then heated to the desired reaction temperature. Carbon dioxide was then added and the vessel allowed to stabilize at a pressure about 500 psig below the desired reaction pressure. The desired volume of initiator solution was added to a bypass loop in the presence of an Argon purge. The initiator was then added to the system by flowing CO₂ at the reaction pressure through the solution into the batch cell. The polymerization reaction was allowed to continue for two hours. Carbon dioxide was added during the reaction to compensate for the pressure drop occurring as a result of consumption of VF₂. At the end of the polymerization, the vessel was vented to remove CO₂ and excess monomer. In order to remove as much excess monomer as possible, CO₂
at 800 psig was charged into the vessel and vented again. The polymer was isolated as a dry powder and weighed.

Figure H.1  Schematic of batch polymerization system