# POLYMERIZATION OF NORBORNENE AND A FLUORINATED ACRYLATE IN SUPERCRITICAL CARBON DIOXIDE

# THESIS

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# DEDICATION

To Xiaowei Zhang, without whom this would have not been possible.

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#### I. SUMMARY

The ring-opening metathesis polymerization (ROMP) of norbornene has been effected in supercritical carbon dioxide (SC  $CO_2$ ). The microstructure of the polynorbornene series was characterized by <sup>1</sup>H-NMR. It has been shown that the polynorbornenes made in SC  $CO_2$  are similar to their counterparts prepared in a traditional organic solvent- tetrahydrofuran (THF) in molecular weight, molecular weight distribution and thermal stability. With Grubbs catalyst, high *trans* content has been obtained in all the polynorbornenes and the *trans/cis* ratio can be adjusted by adding a certain amount of THF as co-solvent. However, with Schrock catalyst, high *cis* content was obtained. Temperature did not affect the *cis/trans* ratio in the final polymers but influenced the molecular weight and its distribution. Pressure did not result in significant differences in the microstructures of polynorbornenes made in SC  $CO_2$ .

Also, a chain transfer agent for the the ROMP process, the diacetate of *cis*-2butene-1,4-diol, has been prepared and employed in the ROMP of 1,5-Cyclooctadiene (COD). It has been demonstrated that, just like a typical chain transfer agent in chain polymerization, this diacetate performed effectively during the ROMP of COD and can be used to control the molecular weight and molecular weight distribution of the final producta precursor to the hydroxyl telechelic polybutadiene (HTPBD), which is of commercial importance.

Meanwhile, hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)-phenyl]-2-propyl acrylate (HFMPPPA), a monomer previously synthesized by the Polymer Research Group at Southwest Texas State University, was homopolymerized in bulk, toluene and SC CO<sub>2</sub>. Its copolymerization with methyl acrylate (MA) and 1H,1H-perfluorooctyl acrylate (FOA) in toluene and SC CO<sub>2</sub> has also been performed. All these homopolymers and copolymers were characterized by standard characterization techniques, such as nuclear magnetic

resonance spectroscopy (NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). It was found that the thermal properties, molecular weight and molecular weight distribution of these homo- and copolymer series prepared in SC CO<sub>2</sub> were comparable to those polymers made in toluene, indicating that the use of organic solvent in the synthesis of these homo- and copolymers can be eliminated or greatly reduced. Particularly, as evidenced by elemental analysis results and compared with their counterparts synthesized in toluene, the composition of those copolymers prepared in SC CO<sub>2</sub> almost entirely depended on the initial feed ratio of the two monomers involved in the copolymerization. This implied that SC CO<sub>2</sub> could influence the reactivity ratios of the two involved monomers.

## **II. INTRODUCTION**

#### 2.1 Supercritical Carbon Dioxide (SC CO<sub>2</sub>)

# 2.1.1 Properties and Advantages of Supercritical CO<sub>2</sub>

A supercritical fluid (SCF) is a substance above its critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ). Unlike the compression of a gas, which normally causes a phase separation and the appearance of a separate liquid phase, compression of a SCF results only in an increase in the density of the SCF and not in the formation of a second liquid phase.<sup>[1]</sup> As a result of the dependence of SCF density on pressure, a continuum of densities ranging from vapor-like to liquid-like can be obtained by varying the pressure while holding the temperature constant. At conditions near the critical point of the SCF, small changes in the pressure or temperature of the fluid result in large changes in density and other important physical properties of the fluid, such as viscosity, dielectric constant and solvent strength. The ability to systematically control and vary the solvent properties of SCFs provides an opportunity to investigate solvent effects on chemical reactions, without worries about the problems associated with changes in specific solute-solvent interactions that can arise when the chemical composition of the solvent is varied.

Just as other supercritical fluids, SC  $CO_2$  is characterized by three unique properties: 1) it can have gas-like diffusivities, which has important implications for reaction kinetics; 2) it has liquid-like densities that allow the solvation of many compounds; and 3) its densities can be altered with small changes in temperature or pressure without altering its composition.<sup>[2]</sup>

Supercritical  $CO_2$  possesses many properties that have made it become the most extensively studied supercritical fluid for polymerization reactions. First of all,  $CO_2$  is naturally occurring and abundant. It can also be produced in large quantities as a byproduct in ammonia, hydrogen and ethanol plants and in electrical power generation stations that burn fossil fuels. Second,  $CO_2$  has an easily accessible critical point with a  $T_c$  (critical temperature) of 31.1 °C and a  $P_c$  (critical pressure) of 73.8 bar (*i.e.* 1070 psi). Third, because  $CO_2$  is an ambient gas, the polymers can be isolated from the reaction media by simple depressurization, resulting in a dry polymer product. This feature eliminates energy-intensive drying procedures required in traditional polymer manufacturing to remove solvent and represents potential cost and energy savings for  $CO_2$ -based systems. And fourth and last, increasing concern regarding the dissemination of volatile organic compounds (VOCs), chlorofluorocarbons (CFCs) and aqueous waste streams into the environment has prompted the chemical industry to conform to more environmentally sound practices in the manufacture and processing of products. Indeed, on January 1st 1996, the Montreal Protocol will curtail the production and importation of CFCs despite their extensive use by many in the chemical industry as a solvent, diluent and/or blowing agent.<sup>[1]</sup> At present,  $CO_2$  offers an environmentally benign solvent choice and the possibility of developing new polymerization methods with near-zero waste production.

Supercritical  $CO_2$  has indeed been shown to be a promising solvent in which polymerization reactions can be effected. The 1960's experienced the initial breakthrough in the use of compressed  $CO_2$  as a continuous phase for polymerization,<sup>[2]</sup> especially in cationic and free radical precipitation polymerizations, followed by very little activity in the 1970s and 1980s. The 1990s, however, have seen an explosion of research in the area. The next breakthrough in the use of  $CO_2$  as a polymerization medium was realized when siloxanes and amorphous fluoropolymers were identified as polymeric materials which had high solubility in SC  $CO_2$  at easily attainable temperatures (< 100 °C) and pressures (< 350 bar). This realization opened up new areas of research in  $CO_2$ , mainly homogeneous polymerization as well as dispersion and emulsion polymerization.

## 2.1.2 Characteristics of Polymerizations in Supercritical CO<sub>2</sub>

Many factors need to be taken into consideration when supercritical  $CO_2$  is used in polymer synthesis.<sup>[2]</sup> First of all, solubility plays a very important role in the preparation of polymers in SC  $CO_2$ . While  $CO_2$  is a good solvent for most nonpolar and some polar molecules of low molar mass, it is a poor solvent for most high molar mass polymers

under mild conditions (< 100 °C, < 350 bar). So far, the only polymers that show good solubility in  $CO_2$  under mild conditions are amorphous fluoropolymers and silicones.<sup>[3]</sup> Therefore, many polymerization reactions in SC  $CO_2$  are conducted under heterogeneous processes, either as precipitation, dispersion, or emulsion polymerizations, due to the inherent insolubility of most polymers in SC  $CO_2$ . Thus, important research in this field involves the synthesis of surfactants, a critical component of dispersion and emulsion polymerizations, as stabilizers in SC  $CO_2$ .<sup>[2]</sup>

The fractionation of polymers is another important area affected by polymer solubility in SC CO<sub>2</sub> <sup>[2]</sup>. Careful and controlled lowering of the density of a polymer solution allows precipitation of the highest molecular weight polymer fraction. Another important feature of polymerization in SC CO<sub>2</sub> is the plasticization of the resulting products by SC CO<sub>2</sub>, which results in the lowering of the polymer's glass transition temperature (Tg). This plasticization offers many important advantages such as the removal of residual monomer from the polymer, incorporation of additives, formation of foams and polymer swelling. In addition, the highly plasticized state of the polymer can result in increased polymerization rates due to the enhanced diffusion of monomer into the polymer. The plasticization of polymers with SC CO<sub>2</sub> can also be used to lower the melt and solution viscosities and affect polymer morphology with supercritical drying and foaming.

## 2.1.3 The Disadvantages of Supercritical CO<sub>2</sub><sup>[4]</sup>

One of the most significant disadvantages of SC  $CO_2$  is that because it is relatively nonpolar it can not dissolve a wide variety of high molecular weight polymers and compounds, the most notable being the class of polymers called poly(ether ketones) (PEKs) and polycarbonates.

A further complication in the use of SC  $CO_2$  as a reaction medium is the need for special equipment to accommodate the elevated temperatures and pressures. Although the pressure and temperature demands are not as extreme as many other chemical processes in industry, a separate set of equipment must be used.

Moreover, it is usually very difficult to affect a condensation polymerization in SC  $CO_2$ . The main difficulty associated with this process is how to remove the by-products

while maintaining supercritical temperatures and pressures throughout the reaction. More basic scientific and engineering research must be done to minimize or eliminate these problems involved in the use of SC  $CO_2$  although some progress has been made in this area.

# 2.2 Ring Opening Metathesis Polymerization

# 2.2.1 Metathesis

The word "metathesis" is derived from the Greek. In chemistry, it refers to the interchange of atoms between two molecules. In olefin chemistry, it describes the interchange of carbon atoms between a pair of double bonds as shown in Figure 1.<sup>[5]</sup>



(Intermediate) Figure 1. Olefin Metathesis Reaction

Synthesis of polymers by olefin metathesis assumed its prominence in the 1970s, and is now recognized as a particularly convenient way to make polymers containing precisely spaced carbon-carbon double bonds in the backbone of the polymer. In general, olefin metathesis polymerization reactions fall into two groups:

Ring-opening metathesis polymerization is commonly referred as to ROMP.
One of the propagation steps in the reaction is shown below in Figure 2.<sup>[6]</sup>



Figure 2. ROMP Reaction

2) Acyclic diene metathesis polymerization is commonly abbreviated as ADMET. It differs from ROMP in that a by-product alkene, usually ethylene, must be expelled to obtain high-molecular-weight polymers. Highly purified, cation-free tungsten,

obtain high-molecular-weight polymers. Highly purified, cation-free tungsten, molybdenum, or ruthenium catalysts are usually used. For example, ADMET polymerization of 1,9-decadiene yields the same product that is obtained by ROMP of cyclooctene as shown in Figure 3.<sup>[7]</sup>



Figure 3. ADMET Polymerization of 1,9-Decadiene

## 2.2.2 General Mechanism - The Metal-Carbene Mechanism

So far, various mechanisms have been suggested which included cyclobutane intermediates, tetramethylenemetal complexes, five-membered metalocycles, and transition metal carbene complexes. Although the actual mechanism may not yet be established definitively, a large amount of evidence accumulated during the past few years favors the metal-carbene mechanism first proposed by Chauvin *et al.* in 1970.<sup>[8]</sup>

A carbene is a divalent carbon atom which is extremely reactive and electrophilic. Based on the placement of the electrons on the carbene carbon, there are two types of carbenes. One is the singlet carbene and the other one is the triplet carbene as shown in Structure 1.<sup>[9]</sup>



Singlet Carbene(sp<sup>2</sup>-hybridized)



Triplet Carbene (Diradical)

Structure 1. Singlet and Triplet Carbenes

For singlet carbene, the carbene carbon is sp<sup>2</sup>-hybridized with an empty Pz orbital.

For the triplet carbene, however, it is actually a diradical. Whether a free carbene exists in the ground state as a singlet or as a triplet depends on the nature of the substituents that are attached to carbon. When the substituents are alkyl or H, the triplet state is usually the ground state. A singlet ground state occurs, on the other hand, when the substituents are heteroatoms such as N, O, S, or the halogens.<sup>[9]</sup>

The propagating species involved in ROMP, which is a metal-carbene complex (*i.e.*, metal-alkylidene complex), is formed through the donation of electrons between the transition metal center and the carbene carbon as shown in Figure 4.



Occupied d Orbitals Figure 4. Formation of Metal-Alkylidene Complex

Based on the extent of the electron donation, there are generally two types of metal carbene complexes: Schrock complexes and Fischer complexes.<sup>[10]</sup>

In Schrock carbene complexes, the carbene carbon is nucleophilic due to the extensive electron transfer from the metal to the carbene carbon. However, in Fischer carbene complexes, the carbene carbon remains electrophilic. But it is still not clear whether the metal carbenes in the well defined catalysts, such as the Grubbs catalyst and Schrock catalyst, can be classified into Schrock carbene complexes or Fischer carbene complexes.

So during the ROMP process, the propagating species is a metal carbene formed in some way from the catalyst/substrate system and the propagation is assumed to proceed *via* a transient metallocyclobutane species and a metal carbene is regenerated at every stage. The idea that a metal carbene species might be involved in olefin metathesis was first proposed by Herisson and Chauvin on the basis of the initial products of cross-metathesis of cyclic and acyclic olefins.<sup>[8]</sup> The fact that metal carbenes such as  $Ph_2C=W(CO)_5$  can be

used as single-component initiators of olefin metathesis is reassuring, and recent identification of both initiating and propagating metal carbenes by <sup>1</sup>H and <sup>13</sup>C NMR may be regarded as providing the final proof of the metal carbene mechanism.<sup>[11]</sup>

# 2.2.3 Side Reactions<sup>[12]</sup>

The principle side reactions that can take place during olefin metathesis are alkylation, isomerization (especially double bond shift reactions), cyclization, and addition across the double bond. These side reactions can generally be avoided by taking one or more of the following measures:<sup>[13]</sup>

1) Choose a solvent which suppresses alkylation reactions; halogenated solvents, such as dichlorobenzene and methylene chloride, are preferred.

2) Use bases to suppress cationic side reactions; alkali metal hydroxide can be added to the supported catalysts and tertiary amines or other polar additives can also be added to catalyst systems in solution.

3) Carefully select the order of mixing of catalyst, co-catalysts, and substrates; this applies especially when oxygen is used as cocatalyst.

4) Use as low a reaction temperature as possible.

# 2.2.4 Main Features of ROMP of Cyclic Olefins<sup>[12]</sup>

Ring-opening metathesis polymerization of cycloalkenes, initiated by metathesis catalysts, shows the following main features:

1) The product generally consists of two distinct parts: a high molecular weight fraction often having a molecular weight in excess of  $10^5$  g/mol, and a low molecular weight fraction containing a series of cyclic oligomers.

2) If the initial monomer concentration exceeds a certain value, high polymer is formed and equilibrium between monomer, cyclic oligomers, and high polymer is eventually established.

3) If the initial monomer concentration, i.e.,  $[M]_0$ , exceeds the value required to produce a high polymer, the concentration of the oligomers at equilibrium is approximate constant. Hence the greater value of  $[M]_0$ , the greater the proportion of high polymer at

equilibrium. When  $[M]_0$  is below the critical value, no high polymer is formed and the only products are cyclic oligomers.

#### 2.2.5 Catalyst Systems

Catalyst Systems for olefin metathesis almost invariably contain a transition metal compound. Based on their compositions and initiation characteristics, the catalyst systems used in ROMP can be classified into the following two groups: traditional catalysts and the so-called well defined catalysts.

## 2.2.5.1 Traditional Catalysts<sup>[14]</sup>

Traditional catalysts are generally the compounds of Mo, W, Re, Ir, *etc*. Such catalysts are sometimes effective by themselves, but more commonly their activities can be enhanced by the incorporation of a second compound known as the cocatalyst, and sometimes even by a third compound termed a promoter. Many traditional catalyst systems are based on the chlorides, oxides, or oxychlorides of Mo, W, Re, Ru, Os, and Ir. Typical cocatalyst are EtAlCl<sub>2</sub> and R<sub>4</sub>Sn (R=Ph, Me, Bu, *etc.*), while promoters often contain oxygen, *e.g.* O<sub>2</sub>, EtOH, PhOH. A typical ROMP using the above described catalyst systems is shown in Figure 5.



## 1-Methyl-1, 5-Cyclooctadiene

Figure 5. ROMP Initiated by Traditional Catalyst

Thus the traditional catalysts usually contain an alkyl or allyl group in one of the components, from which a carbene ligand can readily be generated, or those having no preformed carbene nor an alkyl group in any components. In the latter case a metal carbene can be formed only by interaction of the substrate olefin itself with the transition metal center as shown in Figure 6.<sup>[15]</sup>



Figure 6. ROMP of Norbornene Initiated by Traditional Catalyst

Like Ziegler-Natta catalysts, the activity of a given traditional catalyst system is dependent on a number of physical factors including:<sup>[16]</sup>

1) the proportions of the components (there is frequently a maximum reactivity at some particular compositions);

2) pretreatment procedures, especially for the catalysts supported on some substrates such as  $Al_2O_3$  and  $SiO_2$ ;

3) the order in which the components are mixed.

However, there are also some disadvantages associated with these traditional catalysts such as: <sup>[17]</sup>

1) Controlling the stereochemistry of polymers is very difficult.

2) The metal centers in all catalysts are in their high oxidation states, which result in very limited tolerance to polar functional groups.

# 2.2.5.2 Well Defined Catalysts

The well defined catalysts, such as Grubbs catalyst and Schrock catalyst, usually consist of an actual metal carbene as shown in Structure 2.



Grubbs Catalyst

Schrock Catalyst



The main advantages from these so-called well defined catalysts are as follows:

1) effective control over many features of the metathesis polymerization, including molecular weight, molecular weight distribution, *cis-trans* content, *etc*. For example, Schrock catalyst has given rise to an almost all *cis*, isotactic polymer as shown below in Figure 7. <sup>[18]</sup>



Figure 7. ROMP Initiated by Schrock Catalyst

2) remarkable tolerance to many polar functional groups, including Bronsted acids and secondary amines. This allows the preparation of novel, highly functionalized polymers with predictable molecular weights. For example, by using a proper chain transfer agent (CTA), the Grubbs catalyst can initiate the preparation of hydroxyl telechelic polybutadiene, *i.e.*, HTPBD as shown in Figure 8 below. <sup>[19]</sup> Such telechelic polymers are potentially useful precursors for subsequent polymerizations, chain extension, and block copolymers.



HTPBD

Figure 8. ROMP of COD with Chain Transfer Agent

3) Living ROMP is possible. For example, by stepwise addition of two kinds of different cyclic olefins, Grubbs catalyst has resulted in the formation of a diblock copolymer as shown in Figure 9.<sup>[20]</sup>



Figure 9. Diblock Copolymer *via* Living ROMP Unlike the traditional catalyst systems, the activity of a well defined system is

almost exclusively determined by its own characteristics. Here, the ruthenium-based carbene complexes will be taken as an example to illustrate the factors that affect their reactivity.

Their metathesis reactivity depends mainly on the surrounding phosphine ligands and alkylidene moiety.

1) The size and basicity of phosphine ligands.<sup>[21]</sup>



**Grubbs** Catalyst

Modified Grubbs Catalyst

Structure 3. Structures of Grubbs and Modified Grubbs Catalysts

Compared with original Grubbs catalyst in in Structure 3, the modified catalyst in Structure 3 leads to better control over the molecular weight and its distribution, an indicative of a well-controlled polymerization. The precise steric and electronic effects of the  $Cy_2PCH_2SiMe_3$  phosphine ligand on the metathesis process are difficult to clarify due to the interplay of these two effects. However, the slightly lower basicity of the phosphorous in  $Cy_2PCH_2SiMe_3$  may lead to its more facile dissociation from the ruthenium center, thereby allowing monomer to bind, which is a prerequisite for initiation. In addition, the smaller size of  $Cy_2PCH_2SiMe_3$  compared with  $PCy_3$  is also likely to be a significant factor; the former has one of its phosphine substituents attached through a primary carbon center compared with three secondary carbons for  $PCy_3$ . Also, the C-Si bond is longer compared with C-C bond, which can alleviate the steric effect of the trimethylsilyl substituent.

2) The influence of the alkylidene moiety.<sup>[22]</sup>

Diazoalkanes have proved to be an efficient carbene source in the preparation of novel alkylidene complexes (*i.e.*, carbene complexes) of the following general type as

shown in Structure 4.



Structure 4. Novel Alkylidene Complexes for ROMP

A general synthesis of these novel alkylidene complexes is shown below in Figure 10.



Figure 10. Synthesis of Alkylidene Complexes

In this way, the alkylidene moiety in the well defined catalyst can be easily changed. A different alkylidene moiety can result in different reactivity in the ROMP of cyclic olefins, such as the two different alkylidene moieties shown in Structure 5.



Structure 5. Parent and Modified Alkyldiene Complexes

Compared with the parent complexes where R is Me, Et, n-Bu, *etc.*,, this newly produced complex (where R is CH=CPh<sub>2</sub>) display greater metathesis activity due to faster initiation and produce nearly monodisperse polynorbornene in a living fashion. The possible reason may be the conjugative effects in CH=CPh<sub>2</sub> (vinyl substituent), which might lower the ground state energy of the starting alkylidene *vs*. the presumed metallocyclobutane intermediates. As a result, the vinylalkylidene complex,which contains a highly conjugated alkylidene ligand, is a much poorer initiator. However, the reasons for the unexpected high reactivity of the phenyl-substituted carbene such as the one in the Grubbs catalyst relative to all others examined to date are still under investigation.

#### 2.2.6 Cyclic Olefins Used In ROMP

It is well known that ring-opening polymerization of 3-, 4-, 8-, and largermembered ring compounds are thermodynamically favorable and will proceed if a mechanism is available as shown in Figure 11.



Figure 11. ROMP of Cyclooctene

For 5-, 6-, and 7-membered rings, the situation is more critical and the sign of  $\Delta G^0$  for the polymerization may be sensitive to a number of physical factors such as monomer concentration, temperature, and pressure, and to chemical factors such as the nature of substituents and their positions in the ring.<sup>[23]</sup> For example, cyclopentene can undergo ROMP under some circumstances as shown below in Figure 12.



Figure 12. ROMP of Cyclopentene However, the following monosubstituted cyclopentene can not undergo ROMP

under the same conditions.<sup>[24]</sup>



Figure 13. ROMP of Substituted Cyclopentene

When bridging groups are present, *i.e.*, when the compound is bicyclic, the  $\Delta G^0$  for the opening of a particular ring may be more negative as a result of increased strain energy in the bicyclic monomer as shown below in Figure 14.<sup>[23]</sup>



Figure 14. ROMP of Norbornene

It must be remembered that for addition polymerization reactions of any kind, of which ring-opening polymerization is a particular case, the boundary between polymerizability and non-polymerizability is very distinct corresponding to  $\Delta G^0$ . Thus, one may observe a sharp temperature, known as the ceiling temperature, above which polymerization will not occur at a given monomer concentration. Conversely, at a given temperature there is a certain equilibrium monomer concentration below which polymerization will not occur. Substituents generally have an unfavorable effect on  $\Delta G^0$  in any ring-opening polymerization, either making  $\Delta G^0$  less negative or changing the sign from negative to positive.

Thus, when attempting the ring-opening polymerization of any new monomer it should be remembered that the most favorable thermodynamic conditions for polymerization of cycloalkenes are high monomer concentration (which makes  $\Delta$ S less negative), low temperature (if  $\Delta$ H is negative), and high pressure (if  $\Delta$ V, *i.e.*, the volume change, is negative). Meanwhile, the rate of polymerization appears to be a function of the metal carbene reactivity rather that of ring strain in the cycloalkene.<sup>[25]</sup>

## 2.2.7 Why ROMP in Supercritical CO<sub>2</sub>?

Although ring-opening metathesis polymerizations (ROMP) of cyclic olefins, dienes and unsaturated polymers have been extensively explored and studied during the past two decades,<sup>[19]</sup> almost all these reactions were carried out in traditional organic solvents, such as tetrahydrofuran (THF) and methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>). Until 1996, the ring-opening metathesis polymerization (ROMP) of bicyclo[2,2,1]-hept-2-ene (norbornene) in SC CO<sub>2</sub> catalyzed by Ru(H<sub>2</sub>O)<sub>6</sub>(TOS)<sub>2</sub> (TOS=p-toluenesulfonate) was reported by DeSimone, which was believed to be the first example of a ring-opening metathesis polymerization in SC CO<sub>2</sub>.<sup>[15]</sup> The catalyst used was insoluble in SC CO<sub>2</sub> but could be solubilized by the addition of methanol.

It was assumed that two types of propagating species were involved in the ROMP of norbornene: a *cis*-propagating species ( $P_c$ ) and a *trans*-propagating species ( $P_t$ ) as shown in Structure 6. <sup>[15]</sup>



Structure 6. Propagating Species in ROMP of Norbornene

A profound effect on the polymer microstructure was found with increasing methanol content. The presence of methanol decreased the *cis*-vinylene content in the resulting polymer. Presumably the addition of a polar co-solvent favors the *trans*-propagating species at the metal center and allows for control of the polymer microstructure.

Higher activities for the ROMP of norbornene observed with ruthenium and molybdenum carbene catalysts were reported by Grubbs and Schrock, respectively.<sup>[2]</sup> While the Ru catalyst appeared insoluble in SC CO<sub>2</sub>, the Mo catalyst was partially soluble.

The Ru catalyst gave about 25% *cis* content with no apparent dependence on  $CO_2$  density while the Mo catalyst gave 66% *cis* content at a reaction density of 0.57 g/mL and 82% *cis* at 0.72 g/mL. The Ru carbene catalyst was also used to polymerize *cis*-cyclooctene. The polymers produced in SC  $CO_2$  were similar in molecular weight and microstructure to those produced by conventional means in dichloromethane. In general, the ring opening metathesis polymerization in SC  $CO_2$  is still a new research area to be explored.

#### 2.2.8 Research Proposal-Part I

The first goal of this thesis was to affect the ROMP of a cyclic olefin, *i.e.*, norbornene in this case, in SC CO<sub>2</sub> and to investigate the factors that may affect the microstructure, *i.e.*, the *cis/trans* ratio, of the final products, such as temperature, pressure, polarity of the co-solvent, *etc*.

Various analytical methods such as differential scanning calorimetry (DSC), thermogravimetic analysis (TGA), gel permeation chromatography (GPC) and dynamic mechanical thermal analysis (DMTA) were used to characterize the products. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) and <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) were a powerful analytical tool to investigate the microstructure (*i.e. cis/trans* ratio) of the products. Furthermore, the difference in microstructure of the final polymer products can also be confirmed by DSC /TGA data.

# 2.3 Free Radical Polymerization of Fluorinated Acrylates in Supercritical CO<sub>2</sub>

Free radical polymerizations can be classified as either homogeneous or heterogeneous reactions. In a homogeneous polymerization, all components, including monomers, initiators, and polymers, are soluble throughout the reaction. A heterogeneous polymerization contains at least one insoluble component at some point during the reaction.

The four most widely studied heterogeneous processes (*i.e.*, precipitation, suspension, dispersion, and emulsion) can be clearly distinguished on the basis of the initial state of the polymerization mixture, the kinetics of polymerization, the mechanism of particle formation, and the shape and size of the final polymer particles. Some research

efforts have been made on the initiation and propagation kinetics of free radical polymerizations in SC CO<sub>2</sub>. The earliest work in this area used ultraviolet spectroscopy to study the thermal decomposition rate and the initiation efficiency of 2, 2'- azobis(isobutyronitrile) (AIBN) in CO<sub>2</sub>.<sup>[26]</sup> More recent work has evaluated the free radical propagation kinetics of styrene and methyl methacrylate in CO<sub>2</sub> using the pulsed laser polymerization (PLP) technique.<sup>[27]</sup> Another study compared the kinetics of the homogeneous polymerization of 1H,1H-perfluoropentyl acrylate in SC CO<sub>2</sub> to those in conventional solvents such as Freon-113.<sup>[28]</sup> Indeed, these kinetic studies have verified that CO<sub>2</sub> is an excellent medium in which to conduct free-radical polymerization.

# 2.3.1 Precipitation Polymerization in Supercritical CO<sub>2</sub>

A topic of many early studies in SC  $CO_2$  was the free radical polymerization of industrially important vinyl monomers. Although many common vinyl monomers exhibit high solubility in  $CO_2$ , most of the corresponding polymers are insoluble.

In 1968, a French patent issued to the Sumitomo Chemical Company disclosed the polymerization of several vinyl monomers in  $CO_2$ .<sup>[1]</sup> The US version of this patent was issued in 1970, when Fukui and co-workers published results for the free radical precipitation polymerization of several hydrocarbon monomers in liquid and SC  $CO_2$ .<sup>[2]</sup> As examples of this method, they demonstrated the preparation of various homopolymers including polyvinyl chloride (PVC), polystyrene (PS), polyacrylonitrile (PAN), polyacrylic acid (PAA), and polyvinyl acetate (PVAc).

More recently, precipitation polymerization of semicrystalline fluoropolymers in  $CO_2$  have been explored by DeSimone's group at UNC (University of North Carolina at Chapel Hill). In the study of the precipitation polymerization of acrylic acid in SC  $CO_2$ , they found that reaction pressures did not produce any effect on the product molecular weight, molecular weight distribution, particle size or morphology.<sup>[29]</sup>

## 2.3.2 Dispersion Polymerization in Supercritical CO<sub>2</sub>

In dispersion polymerization, the monomer is soluble in the continuous phase; however, the resultant polymer is insoluble and forms the precipitated polymer particles. Unlike a simple precipitation process, the particles become stabilized as a colloid by the presence of added interfacially active agent (surfactant or stabilizer). This results in the formation of very high molecular weight polymer at high rates of polymerization and produces micrometer-sized, spherical particles with a narrow size distribution.

Most recently, DeSimone reported a polymerization method that uses SC CO<sub>2</sub> as a medium for the free radical dispersion polymerization of olefinic monomers. One key to a successful dispersion polymerization is the surfactant. Since traditional surfactants for dispersion polymerization were designed for use in an aqueous or organic continuous phase and are completely insoluble in SC CO<sub>2</sub>, an exciting area of research is the design and synthesis of novel surfactants specifically to SC CO<sub>2</sub>.

It is proposed that for polymeric surfactants the steric stabilization is effective in solvents with low dielectric constants. Therefore steric stabilization, rather than electrostatic stabilization, provides the stabilization mechanism for  $CO_2$ -based systems.<sup>[2]</sup> The polymeric stabilizer is a macromolecule that preferentially exists at the polymer-solvent interface and prevents aggregation of particles by coating the surface of each particle and imparting long-range repulsion between them. These long-range repulsion must be great enough to compensate for the long-range van der Waals attraction of the particles. This complex phenomenon depends not only on the amount and molecular weight of the adsorbed stabilizer, but also on its conformation, which is affected by the nature of the solvent.

When steric stabilization acts effectively in a heterogeneous system, the stabilizing molecule attaches to the surface of the polymer particle by either chemical grafting or physical adsorption. Amphiphilic materials such as block and graft copolymers, which have one component that is soluble in the continuous phase and another component, the anchor, that prefers to reside in the polymer phase, offer the highest probability for physical adsorption.

The other route to stabilization includes the chemical grafting of the stabilizer to the particle surface, either through chain transfer to stabilizer or by using a functional stabilizer that can serve as an initiator, monomer, or terminating agent. In this case, the chemically grafted stabilizer cannot physically desorb from the particle surface, and as a result, grafted stabilizers impart better colloidal stability than physically adsorbed stabilizers.

In  $CO_2$ -based systems, the types of surfactants that have been used for steric

stabilization include  $CO_2$ -philic ( $CO_2$ -soluble) homopolymers, copolymers (statistical, block, or graft) containing a  $CO_2$ -philic component and a  $CO_2$ -phobic ( $CO_2$ -insoluble) anchoring component, and  $CO_2$ -philic reactive macromonomers. Meanwhile, several theories have been recently evaluated and/or developed to illustrate the stabilization offered by these surfactants in highly compressible supercritical media, including the traditional Napper theory for steric stabilization in colloidal systems and lattice fluid self-consistent field theory (LFSF) developed by Peck and Johnston. LFSF allows traditional colloidal stabilization theory to be extended to supercritical fluid continuous phases.<sup>[30]</sup>

The stabilizer initially used for the dispersion polymerization of methyl methacrylate (MMA) in a  $CO_2$  continuous phase was polyperfluorooctyl acrylate (PFOA) as shown in Figure 15.

$$\begin{array}{c} \overbrace{(CH_{2} - CH)_{n}} \\ \overbrace{(CH_{2} - CH)_{n}} \\ \overbrace{(CH_{2} - CH)_{n}} \\ \downarrow \\ \overbrace{(CH_{2} - CH)_{n}} \\ \overbrace{(CH_{2} - CH)_{n}} \\ \overbrace{(CF_{2})_{0}} \\ \overbrace{(CF_{3} - CH)_{n}} \\ \hline{(CF_{2})_{0}} \\ \overbrace{(CF_{3} - CH)_{n}} \\ \hline{(CF_{3} - CH)_{n}} \\ \hline \hline{(CF_{3} - CH)_{n}$$

# Figure 15. Structure of PFOA

It is thought that the lipophilic acrylic backbone of this polymer adsorbs, either by physical means or by chemical grafting, onto the acrylic colloidal particle and provides a surface anchor for the  $CO_2$ -philic ( $CO_2$ -soluble) fluorocarbon stabilizing moieties. These fluorocarbon segments extend the PFOA chain into the continuous phase, thereby preventing flocculation of the particles probably by a steric stabilization mechanism.<sup>[31]</sup>

Generally, there are two kinds of polymeric surfactants widely used for dispersion polymerization in SC CO<sub>2</sub>. One is the homo- or copolymers of FOA and the other is the PDMS (polydimethylsiloxane)-based copolymers. The structures of these polymeric surfactants commonly used in supercritical CO<sub>2</sub> are shown in Figure 16. <sup>[2]</sup>



Figure 16. Structures of Surfactants Used in Supercritical CO<sub>2</sub>

### 2.3.3 Suspension Polymerization in Supercritical CO

Suspension polymerization is essentially a bulk polymerization in droplets. In a typical suspension polymerization, neither the monomer nor the initiator are soluble in the continuous phase. The resulting polymer is also insoluble in the continuous phase, which simply acts as a dispersant and heat-dissipation agent during the polymerization. <sup>[2]</sup>

However, as a result of the high solubility of many common monomers and organic initiators in SC CO<sub>2</sub>, suspension polymerization in SC CO<sub>2</sub> are not common.

#### 2.3.4 Emulsion Polymerization in Supercritical CO<sub>2</sub>

7

Emulsion polymerization involves the polymerization of monomers in the form of emulsion. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs, in the kind of initiators employed, and in the dependence of polymer molecular weight on reaction conditions.<sup>[32]</sup>

In emulsion polymerization the monomer has very low solubility in the continuous phase. Most common monomers studied so far have been found to be quite soluble in  $CO_2$  at moderate conditions, and thus few examples exist of  $CO_2$ -based emulsion polymerizations.<sup>[2]</sup>

Beckman has investigated the water-in-oil or "inverse" emulsion polymerization of acrylamide in SC CO<sub>2</sub> (AIBN, 65 °C, 352 bar, 1h).<sup>[33]</sup> An amide functionalized perfluoropolyether surfactant was used to promote latex formation and the latex was observed to be more stable in the presence of the surfactant.

Since water and  $CO_2$  has very low miscibility, more studies in the field of inverse emulsion polymerization in SC  $CO_2$  are expected with the recent discoveries of surfactants which have the ability to form microemulsions of water and water soluble molecules in  $CO_2$ as evidenced by DeSimone, Beckman and Johnston.<sup>[2]</sup>

A quite different approach was taken by Quadir *et al.*, who investigated the emulsion polymerization of MMA in hybrid  $CO_2$ /water mixture. In these studies the emulsion was formed in the aqueous phase and not in the  $CO_2$  layer.<sup>[33]</sup>
#### 2.3.5 Fluorine-Containing Polyacrylates

Initiated by the discovery of Teflon<sup>®</sup> at the DuPont Jackson Laboratory in 1938, fluoropolymers have been in commercial use for over half a century and have found wide applications in nonstick coatings for cookware, carpets, textiles, electronic devices, *etc*. <sup>[34]</sup> Since fluorine has the highest electronegativity of any elements and the C-F bond has a great deal of polar character, incorporation of C-F bonds into materials leads to a variety of attributes, such as low polarizability of C-F bond, low surface tension, low index of refraction, low dielectric constant, chemical inertness and good thermal stability. <sup>[35]</sup>

Meanwhile, polymers prepared from acrylates and methacrylates have been long recognized for their optical clarity and stability upon aging under severe conditions. Polyacrylates, whether linear or cross-linked, are excellent adhesives and are easily fabricated into many different components and shapes.

The inclusion of a substantial number of fluorine atoms into polyacrylates results in a broader resistance to physical and chemical attack than their hydrocarbon counterparts, provided such an introduction does not compromise their characteristic properties. Griffith and co-workers at the Naval Research Lab have done extensive research work in this area. Several hydrophobic polyacrylates (derived from hexafluoro-2-alkoxy-2-propyl-substitued arenes) having water contact angles of 90-91° have been prepared and characterized.<sup>[34]</sup> Because these fluorine-containing polymers have low critical surface energies and water absorption, they have found wide applications as coating materials in wet environments. Hexafluoro-2-phenyl-2-propxy-containing polyacrylates have also been suggested for medical applications, such as dental materials and artificial joints.<sup>[37]</sup>

The Polymer Research Group at Southwest Texas State University has also made some research efforts in this area. Both hexafluoro-2-(4-fluorophenyl)-2-propyl acrylate and methacrylate have been observed to form homopolymers and copolymers with hydroxyethyl and hydroxypropyl methacrylate.<sup>[38]</sup> In addition, Martinez *et al.* reported the synthesis of homo- and copolyacrylates made from hexafluoro-2-phenyl-2-propyl acrylate (HFPPA) monomer and methyl acrylate both in SC CO<sub>2</sub> and organic solvent-1,3bis(trifluoromethyl) benzene. It has been demonstrated that the properties of the polyacrylates prepared by free radical polymerization in SC CO<sub>2</sub> compared favorably to polyacrylates made in 1,3-bis(trifluoromethyl) benzene.<sup>[4]</sup> Moreover, Cassidy, Fitch and co-workers reported the synthesis and characterization of homo- and copolyacrylates derived from commercially available 1,3-bis(hexafluoro-2-hydroxy-2-propyl) benzene (1,3-HFAB).<sup>[39]</sup> Both bulk polymerization and solution polymerization in toluene have been successfully effected. It has been shown that a large water contact angle was obtained for these fluorinated polyacrylates, suggesting a preferential orientation of trifluoromethyl groups on the surface of the polymer films. The weight loss of these polyacrylates occurred in a single step and they decomposed completely with a negligible quantity of char yield.

#### 2.3.6 Research Proposal-Part II

The second goal of this thesis was to synthesize a series of homopolymers and copolymers of a fluorinated acrylate derived from the commercially available 1,3-bis(hexafluoro-2-hydroxy-2-propyl) benzene (1,3-HFAB) *via* free radical polymerization with AIBN as the initiator in SC CO<sub>2</sub> for the purpose of eliminating volatile organic solvent and developing laboratory techniques for this type of polymerization.

The polymer series that were synthesized included homo- and copolymers of hexafluoro-2-[3-(hexafluoro-2-methoxy-2-proply)-phenyl]-2-propyl acrylate (HFMPPPA), methyl acrylate (MA) and 1H,1H-perfluorooctyl acrylate (FOA) respectively. These polymers would be characterized by traditional methods such as NMR, TGA, DSC, GPC and elemental analysis.

The main goal of this project is to ascertain: 1) whether the polymers prepared in SC CO<sub>2</sub> were comparable to their counterparts synthesized *via* bulk and solution polymerization; and 2) whether the addition of FOA during the copolymerization in SC CO<sub>2</sub> solubilized the resultant polymers.

## **III. EXPERIMENTAL**

#### 3.1 General

Bicyclo[2.2.1]hept-2-ene (norbornene, 99%), 1,5-cyclooctadiene (COD, 99%), acetic anhydride (99%), triethylamine (98%), methylene chloride (ACS reagent), chloroform (ACS reagent), calcium hydride (90-95%), toluene (anhydrous), tetrahydrofuran (THF, GR), methanol (ACS reagent), dimethyl sulfoxide (DMSO, ACS reagent) and dimethyl formamide (DMF, 99.9%) were purchased from Aldrich. *Cis*-2-butene-1,4-diol (94.5% *cis*) was obtained from Sigma. Both Grubbs catalyst and Schrock catalyst were purchased from Strem Chemical Inc. AIBN (2,2'-azobisisobutyronitrile), obtained from Kodak Laboratory Chemicals, was recrystallized three times from a mixture of chloroform and methanol (1:9) and then dried *in vacuo*. Chromatography grade liquid carbon dioxide was obtained from Praxair and used as received. All other materials were used as received unless specified.

#### 3.2 Preparation of Chain Transfer Agent AcOCH<sub>2</sub>CH=CHCH<sub>2</sub>OAc

Acetic anhydride (25 mL, 27 g, 0.26 mol, 2.5 equiv.) was added dropwise to a stirring methylene chloride/chloroform (*c.a.* 100 mL, 1:1 v/v) solution of *cis*-2-butene-1,4-diol (9.3 g, 0.10 mol, 1 equiv.) and triethylamine (26.8 g, 37 mL, 0.26 mol, 2.5 equiv.) at 0 °C over *c.a.* 1 hour. The solution was allowed to slowly warm to room temperature and then was heated to reflux at *c.a.* 55 °C overnight. The reaction was followed by thin layer chromatography (TLC) until the reaction mixture turned orange and all starting material was gone.

The orange solution was washed with deionized water (3 x 75 mL) and concentrated under reduced pressure. The resultant orange oil was distilled under vacuum and the middle fraction was collected at *c.a.* 76 °C. The distillate was stirred over calcium

hydride at room temperature, overnight and under vacuum. This was then redistilled under reduced pressure (as above c.a. 76 °C) and collected in a flask which was sealed under argon gas. The product was characterized by NMR.

#### **3.3 Monomer Purification**

#### 3.3.1 Purification of Methyl Acrylate (MA)

The MA monomer, inhibited with 100 ppm of monomethyl ether hydroquinone (MEHQ), was purchased from Aldrich Chemical Supply Company. The inhibitor was removed *via* distillation under vacuum and stored under argon in a refrigerator.

#### 3.3.2 Purification of 1H,1H-Perfluorooctyl Acrylate (FOA)

The FOA monomer, inhibited with 100 ppm MEHQ, was purchased from Lancaster Chemical Supply Company. The inhibitor was removed by pouring the liquid into a column packed with Aldrich MEHQ inhibitor remover. The purified FOA was collected in a small flask fitted with a septum and stored under argon in a refrigerator

#### 3.4 Polymer Synthesis

# 3.4.1 Polymerization of 1,5-Cyclooctadiene (COD) with Grubbs Catalyst and Chain Transfer Agent (CTA)

#### 3.4.1.1 Neat Reaction

A three-neck, 50 mL, round-bottom flask equipped with a magnetic stirrer, was charged with COD (4.0 g, 4.5 mL, 37 mmol, 4300 equiv.), Grubbs catalyst (0.007 g, 8 mmol, 1 equiv.) and CTA (0.138 g, 800 mmol, 100 equiv.). The reaction was kept under a slow purge of argon, the stirrer was started and the flask was immersed in an oil bath at c.a. 50°C. The dark red-orange reaction mixture was stirred for c.a. 19 hours. The resultant light orange reaction mixture was allowed to cool to room temperature and was poured into c.a. 20 mL of methanol. The polymer that precipitated became white and the methanol solution turned yellow. The methanol was decanted, and the methanol wash (3 x 10 mL) was repeated for three times. the product was redissolved in 2 mL of chloroform, reprecipitated with 20 mL of methanol and washed with methanol (3 x 10 mL). Finally, the

precipitate was put under high vacuum, at room temperature and held overnight for future analysis and characterization.

#### 3.4.1.2 Polymerizations in Supercritical CO<sub>2</sub>

Polymerizations were carried out in a high pressure view cell equipped with sapphire window (to observe reaction progress) and a magnetic stirrer. Typically, the monomer (COD), Grubbs catalyst and CTA were added to the view cell which was then sealed. An Isco D Series automatic syringe pump was used to deliver the necessary amount of CO<sub>2</sub> (usually 12 mL at 3000 psi and 19.2 °C) into the reaction cell. The reaction temperature was set from 35 °C to 70 °C and the pressure was kept at 5000 psi. The reaction mixture was stirred for *c.a.* 16 hours. At the end of the reaction time, the CO<sub>2</sub> was slowly vented, the polymeric product was removed from the reactor and purified with the same procedures described above for further analysis.

#### 3.4.2 ROMP of Norbornene in Supercritical CO

Polymerizations were performed in the high pressure view cell described above. Usually, the monomer-norbornene (0.23 g, 25 mmol, 200 equiv.), Grubbs catalyst/Schrock catalyst (0.12 mmol, 1 equiv.), as well as co-solvent (if necessary) were charged into the view cell which was then sealed. An Isco D series automatic syringe pump was used to pressurize the required amount of  $CO_2$  (usually 12 mL at 3000 psi and 19.2 °C) into the reactor.

The reaction was kept at the desired temperature and pressure for about 4 hours. At the end of the reaction the  $CO_2$  was slowly vented, the polymer removed from the cell, dissolved in THF, precipitated with methanol, put under high vacuum at room temperature and kept overnight for further characterization and analysis.

# 3.4.3 <u>Synthesis of Poly(Hexafluoro-2-[3-(hexfluoro-2-methoxy-2-propyl)-phenyl]-2-</u> proply acrylate) (HFMPPPA) in Supercritical CO<sub>2</sub>

The monomer-to-initiator ratio was changed according to Table 1.

Polymer Number	Monomer /Initiator (mol)	Mass of HFMPPPA (g)	Mass of AIBN (g)	Reaction Conditions
1a	50:1	0.569	0.004	Bulk
1 b	50:1	0.285	0.002	Solution
1 c	50:1	0.285	0.002	SC CO <sub>2</sub> , 60 °C
1d	50:1	0.285	0.002	SC CO <sub>2</sub> , 80 °C
1 e	100:1	0.569	0.002	SC CO <sub>2</sub> , 80 °C
1f	200:1	0.569	0.001	SC CO <sub>2</sub> , 80 °C

Table 1. Homopolymerization of HFMPPPA

In a typical reaction, a clean, high-pressure reaction vessel was charged with 0.004 g (0.024 mmol, 1 equiv.) of AIBN. Next, 0.57 g (1.2 mmol, 50 equiv.) of HFMPPPA was added to the cell and the cell was sealed. Then, about 12 mL of CO<sub>2</sub> (about 10 g) at 3000 psi and 19.2 °C were transferred to the front of the cell and allowed to stir for 10 min. Then the back of the vessel was pressurized with CO<sub>2</sub> to a pressure of 3000 psi and vented if necessary. The cell was then placed in a water bath and heated to 80 °C. The reaction mixture was allowed to react for about 24 hours at 80 °C, after which the back of the vessel was vented, then the front of the vessel was slowly vented. The resultant polymers were dissolved in a minimal amount of THF and precipitated in methanol. The solvent methanol was evaporated leaving the polymer to be dried under vacuum overnight.

#### 3.4.4 Bulk Polymerization of HFMPPPA

In a typical experiment, both 0.57 g (1.2 mmol, 50 equiv.) of HFMPPPA and 0.004 g (0.024 mmol, 1 equiv.) of AIBN were dissolved in 4 mL of THF in a 25 mL, round-bottom flask. The THF was evaporated at room temperature and the mixture was vacuum dried overnight. Next, the mixture was placed in an oil bath whose temperature was maintained at 80 °C. The reaction proceeded for about 24 hours. The polymer was dissolved in THF as needed and precipitated into methanol. Then, the white powder was isolated by filtration and dried under vacuum overnight at room temperature.

#### 3.4.5 Solution Polymerization of HFMPPPA

In a typical homopolymerization, HFMPPPA (0.28 g, 0.6 mmol, 50 equiv.) and AIBN (0.002 g, 0.012 mmol, 1 equiv.) dissolved in toluene (1.0 mL) were placed in a 25 mL, round-bottom flask fitted with a condenser. The polymerization flask was kept under argon at 80 °C for about 24 hours. The solution was then cooled to room temperature and precipitated into methanol. The product was isolated by filtration and dried under vacuum overnight to yield the polyfluoroacrylate as white powder. The same procedure was used for the solution copolymerizations of HFMPPPA with MA or FOA, with the only exception being that in this case about 8.5 mL of toluene was employed.

#### 3.4.6 Copolymerization of HFMPPPA with MA in Supercritical CO, and Toluene

The experimental procedures for these copolymerizations were the same as those for the synthesis of PolyHFMPPPA, except that the MA monomer was added in accordance with Table 2. The monomer-to-initiator ratio was kept constant at about 50:1.

Polymer Number	HFMPPPA/MA in the feed (mol%)	Mass of HFMPPPA (g)	Mass of MA (g)
2a	75/25	0.448	0.027
2 b	50/50	0.717	0.129
2 c	25/75	0.299	0.161

Table 2. Copolymerization of HFMPPPA with MA

#### 3.4.7 Copolymerization of HFMPPPA with FOA in Supercritical CO, and Toluene

The experimental procedures for the copolymerizations were the same as those for the synthesis of polyHFMPPPA and the monomer-to-initiator ratio was kept constant at about 50:1, except that the FOA monomer was added according to Table 3.

Polymer Number	HFMPPPA / FOA in the feed (mol %)	Mass of HFMPPPA (g)	Mass of FOA (g)
3a	75/25	0.448	0.142
3 b	50/50	0.299	0.284
3 c	25/75	0.239	0.681

Table 3. Dispersion Copolymerization of HFMPPPA with FOA

#### 3.5 Characterization

#### 3.5.1 Gel Permeation Chromatography (GPC) Analysis

GPC analyses in THF were obtained on a system utilizing Waters 600 pump and Waters 600 Controller. The molecular weight and polydispersity were reported versus monodisperse polystyrene standards. Samples were prepared by dissolving about 5 mg of polymer in 1 mL of THF (HPLC Grade). The solutions were filtered using a 0.45 micron PTFE syringe filter and 50 microliters of each solution were injected into the GPC system consisting of a Waters 2410 refractive index detector and a Waters 2487 dual wavelength UV absorbance detector. The molecular weight calculations were based on the calibration made of narrow disperse polystyrene ranging in molecular weight from 1.01x10<sup>6</sup> g/mol to 1,320 g/mol. The actual calculations were completed with the software Millennium<sup>32</sup>.

#### 3.5.2 Nuclear Magnetic Resonance (NMR) Analysis

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Varian 400 MHz NMR spectrometer with deuterated chloroform or acetone as solvent. Chemical shifts in proton NMR were reported in ppm downfield from tetramethylsilane (TMS) and <sup>13</sup>C spectra were referenced to CHCl<sub>2</sub>.

#### 3.5.3 Thermogravimetric Analysis (TGA)

TGA data were collected on a Rheometric Scientific TGA 1000 thermal analyzer at the test conditions of 20 °C/min in argon atmosphere with about 10 mg of sample. The

decomposition temperature (T<sub>d</sub>) is taken as the temperature at which 10% mass loss takes place.

#### 3.5.4 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA data were collected on a Rheometric Scientific DMTA IV analyzer with single cantilever bending mode for all the samples over a temperature range of -100 °C to 250 °C with applied force conditions of 0.01%, 1 H<sub>z</sub>, 5 °C/min.

#### 3.5.5 FT-IR Analysis

IR spectra of samples were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer, using KBr pellets and films.

### 3.5.6 Differential Scanning Calorimetry (DSC) Analysis

DSC analyses were performed on a Rheometric Scientific differential scanning calorimeter with about 10 mg of sample at the heating rate of 10 °C/min in argon. The glass transition temperature  $(T_g)$  is determined by using a two point cursor method and the inflection point is taken as the T<sub>g</sub>.

#### 3.5.7 Elemental Analysis

Elemental analyses on polymer samples were carried out by Desert Analytics (Tucson, AZ, USA) and the contents of C, H, and F were reported.

## **IV. RESULTS AND DISCUSSIONS**

# 4.1 Chain Transfer Agent (CTA) in Supercritical CO

The diacetate of *cis*-2-butene-1,4-diol has been proven to be an efficient chain transfer agent (CTA) during the ROMP of 1,5-cyclooctadiene (COD) <sup>[16]</sup> and as a result, a precursor to the commercially important hydroxyl telechelic polybutadiene (HTPBD) can be produced in toluene. With adequate stirring and control of reaction temperature these polymerizations can be also performed in the absence of solvent and on a large scale with similar results. However, whether or not this chain transfer agent works in SC CO<sub>2</sub> is not known.

# 4.1.1 Synthesis of CTA

The chain transfer agent used was prepared according to the reported procedures<sup>[16]</sup> and the reaction scheme is shown below in Figure 17.



Figure 17. Synthesis of the Diacetate-Chain Transfer Agent

The diacetate was then purified, characterized with <sup>1</sup>H-NMR and the NMR spectra of the starting material and the product were shown in Figure 18.

Starting Material: Cis-2-butene-1,4-diol



Thus, according to the <sup>1</sup>H-NMR spectra above, the conversion of hydroxyl groups in the 1,4-diol to acetate groups was complete and successful.

# 4.1.2 ROMP of 1,5-Cyclooctadiene (COD) with CTA in Supercritical CO.

Generally, during the chain polymerization, of which ROMP of COD is just a particular case, chain transfer is usually unavoidable. As a result, lower molecular weight polymer products and relatively broad molecular weight distribution are expected. Figure

19 is a schematic representation of the ROMP process of COD with CTA:



Figure 19. ROMP of COD with CTA in Supercritical  $CO_2$ 

The resultant acetate-functionalized polybutadienes made in different conditions were characterized with <sup>1</sup>H-NMR and their spectra are shown below in Figure 20.



Figure 20. <sup>1</sup>H-NMR Spectra of Functionalized Polybutadienes

Table 4 below shows the polymerization results of COD with and without CTA in SC  $CO_2$ .

Entry	[M]/[I]/[CTA]	Mn	Mw	PDI
1	4300/1/100	3,600	21,700	6.0
2	4300/1/0	45,600	85,500	1.8

Table 4. ROMP of COD with and without CTA

Reaction Conditions: 5000 psi, 50 °C, c.a. 20 hours

As expected, in the presence of the CTA, the resultant polymer showed lower molecular weight and broader molecular weight distribution although the CTA did not affect the microstructure of the resultant polymers.

The effect of the CTA and temperature on the ROMP of COD was also evidenced by the variation of molecular weight and polydispersity index of the resultant polybutadienes. Since high temperature is more favorable to the chain transfer reaction, the higher the reaction temperature, the lower the molecular weight and broader molecular weight distribution are obtained. The effect of temperature is shown in the Table 5.

Table 5. Polymerizations of COD Employing CTA in Supercritical CO<sub>2</sub> at Different

Temperatures

Reaction Conditions	Mn	Mw	PDI
5000 psi, 35 °C	16K	55K	3.4
5000 psi, 50 °C	3.6K	21.7K	6.0
5000 psi, 70 °C	2.9K	27.2K	9.3
1 atm, 50 °C	3.0K	17.4K	5.8
	Reaction Conditions 5000 psi, 35 °C 5000 psi, 50 °C 5000 psi, 70 °C 1 atm, 50 °C	Reaction Conditions         Mn           5000 psi, 35 °C         16K           5000 psi, 50 °C         3.6K           5000 psi, 70 °C         2.9K           1 atm, 50 °C         3.0K	Reaction Conditions         Mn         Mw           5000 psi, 35 °C         16K         55K           5000 psi, 50 °C         3.6K         21.7K           5000 psi, 70 °C         2.9K         27.2K           1 atm, 50 °C         3.0K         17.4K

\* Neat Reaction

Meanwhile, since the polybutadienes made *via* the ROMP of COD with the CTA have carbonyl termini, this group should be detectable by IR and <sup>13</sup>C-NMR. However, the presence of the carbonyl group failed to be identified by <sup>13</sup>C-NMR due to the high

molecular weight of the polymers and the quarternary nature of the carbonyl carbon. The IR spectra of the products prepared in SC  $CO_2$  and in bulk are shown below in Figure 21 and Figure 22, respectively.



Figure 21. IR Spectrum of Polybutadiene via the ROMP of COD with CTA in



Figure 22. IR Spectrum of Polybutadiene via the ROMP of COD with CTA in Bulk

Comparison of these two IR spectra indicated that the characteristic absorption band of carbonyl group was clearly present at 1750 cm<sup>-1</sup>. This is another strong piece of evidence that the chain transfer agent worked well during the ROMP of COD in SC  $CO_2$ .

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#### 4.2 ROMP of Norbornene in Supercritical CO<sub>2</sub>

#### 4.2.1 Background

Until 1996, the first and only example of ROMP in SC CO<sub>2</sub> was reported by DeSimone.<sup>[15]</sup> In addition, it was also reported that both the Grubbs and Schrock catalysts could initiate the ROMP of norbornene in SC CO<sub>2</sub> to form the commercially important polymer-Norsorex.<sup>[6]</sup> However, the factors that may influence the microstructure, (*i.e.*, the *trans/cis* ratio in the resultant polynorbornenes), have yet to be fully explained. That is one of goals of this thesis.

It was postulated that during the ROMP of norbornene there were two types of possible propagating species involved in the ROMP process. One is the *cis* propagating species and the other one is the *trans* propagating species, which are shown below in Structure 7.



Structure 7. Possible Propagating Species in the ROMP of Norbornene Their relative ratio and reactivity determine the microstructure of the final polymeric products, *i.e.*, the *trans/cis* ratio of vinyl hydrogen along the backbone of the polymer. The reaction scheme is shown below in Figure 23.



Figure 23. ROMP of Norbornene in Supercritical CO<sub>2</sub> H<sub>t</sub>-Hydrogens are *trans*; H<sub>c</sub>-Hydorgens are *cis* 

<sup>1</sup>H-NMR has been proven to be a powerful tool to investigate the microstructure (i.e., the *trans/cis ratio*) of the polymer products made in SC CO<sub>2</sub>. Their <sup>1</sup>H-NMR spectra are shown below in Figure 24 with assigned characteristic peaks for  $H_t$  and  $H_c$  respectively.



Figure 24. <sup>1</sup>H-NMR Spectra of Polynorbornenes Made in Supercritical CO<sub>2</sub>

It was found that with Grubbs catalyst, high *trans* content was obtained in these polynorbornenes.

### 4.2.2 Microstructure of Polynorbornenes Prepared in Supercritical CO<sub>2</sub>

Many factors that may influence the microstructure of polynorbornenes prepared in SC CO<sub>2</sub>, such as co-solvent, the polarity of the reaction medium, temperature, pressure,

etc., have been explored in detail.

#### 4.2.2.1 Co-solvent Effect

Tetrahydrofuran (THF) is a polar solvent in which norbornene, the Grubbs catalyst and polynorbornene are completely soluble. It was found that the polarity of the reaction medium could affect the *cis/trans* ratio, (*i.e.*, the microstructure of the polymer). To some extent, the higher the polarity of the reaction medium, the higher the *trans/cis* ratio.The <sup>1</sup>H-NMR spectra of polynorbornene obtained in SC CO<sub>2</sub> as well as in SC CO<sub>2</sub> with a certain amount of THF (as co-solvent) at 5000 psi, 70 °C are shown below in Figure 25.



Figure 25. <sup>1</sup>H-NMR Spectra of Polynorbornenes in Supercritical CO<sub>2</sub> @ 5000 psi, 70 °C From the <sup>1</sup>H-NMR spectra in Figure 25 above, the *trans/cis* ratios of these

polynorbornenes were determined by integration of  $H_t$  and  $H_c$  signals and the results are listed in Table 6.

Entry	THF(wt/vol)	Mn	Mw	PDI	Trans/Cis
1	0	33,900	89,300	2.6	3.8:1
2	5%	39,000	83,000	2.1	5.1:1
3	10%	37,500	67,300	1.8	5.0:1
4	15%	50,500	91,000	1.8	5.6:1
5	20%	38,700	79.100	2.0	5.1:1
6*	100%	24,500	77,300	3.1	5.6:1

Table 6. Polymerizations of Norbornene in Supercritical CO<sub>2</sub> @ 5000 psi

Reaction Conditions: 70 °C, 4 hours @ c.a. [M]/[I]=200:1

\*Neat Reaction in THF

It can be seen that the co-solvent (THF) does influence the microstructure of the resultant polymeric products. With a little amount of THF, (*i.e.*, 5%), the *trans/cis* ratio was increased from 3.8:1 to about 5:1. After that point, the *trans/cis* ratio did not vary too much with the applied amount of THF. The reason for this change was presumably due to the fact that the polar medium may favor the *trans* propagating species and with 5% THF the whole reaction system has been saturated.

#### 4.2.2.2 Pressure Effect

As a supercritical fluid, the solvent power of SC  $CO_2$  can be adjusted by varying the applied pressure. The effect of pressure on microstructure, molecular weight and molecular weight distribution of the resultant polynorbornene was also investigated.

The <sup>1</sup>H-NMR spectra of polynorbornenes made in SC CO<sub>2</sub> and a certain amount of THF at 2500 psi are shown in Figure 26.



Figure 26. <sup>1</sup>H-NMR Spectra of Polynorbornenes in Supercritical CO<sub>2</sub> @ 2500 psi From the NMR spectra in Figure 26 above, the *trans/cis* ratios of the resulting polynorbornenes were calculated and the results are listed in Table 7.

Entry	THF (wt/vol.)	Mn	M <sub>W</sub>	PDI	Trans/Cis
1	0	10,300	25,400	2.5	3.2:1
2	5%	25,000	69,700	2.8	4.5:1
3	10%	31,800	58,700	1.8	4.7:1
4	15%	32,800	64,400	2.0	5.3:1
5	20%	45,700	87,800	1.9	5.3:1
6*	100%	24,500	77,300	3.1	5.6:1

Table 7. Polymerizations of Norbornene in Supercritical CO<sub>2</sub> @ 2500 psi

Reaction Conditions: 70 °C, 4 hours @ c.a. [M]/[I]=200:1

\*Neat Reaction, 1 atm

Compared with the results from Table 6, similar tendencies were obtained. A small amount of THF increased the *trans/cis* ratio. An interesting result from the comparison of these two tables was that the *trans/cis* ratio and the molecular weight distribution of the polynorbornenes made at 5000 psi and 2500 psi were similar to each other, *i.e.*, there is no significant dependence of molecular weight distribution and *trans/cis* ratios on pressure; although at higher pressures a slightly higher molecular weight was obtained. The possible reason could be attributed to the change of solvent power of SC CO<sub>2</sub> with pressure. In addition, a little THF can make the reaction medium polar enough to be a good solvent for the monomer, catalyst and product, which was confirmed by looking through the sapphire window during the reaction process.

Moreover, the ROMP of norbornene initiated by the Grubbs catalyst in pure SC  $CO_2$  at some different pressures was also performed and the <sup>1</sup>H-NMR spectra of the resultant polynorbornenes are shown below in Figure 27.



Figure 27. <sup>1</sup>H-NMR Spectra of Polynorbornenes Made in Supercritical CO<sub>2</sub> at Different Pressures

From the NMR spectra in Figure 27, the *cis/trans* ratios of these polynorbornenes were calculated and listed in Table 8.

Entry	Pressure (psi)	Mn	Mw	PDI	Trans/Cis
1	5000	18K	33K	1.8	3.5:1
2	4500	18K	33K	1.8	3.0:1
3	4000	20K	37K	1.9	3.5:1
4	3500	27K	59K	2.2	3.3:1
5	3000	29K	57K	2.0	3.5:1
6	2500	20K	38K	1.9	3.2:1
7	2000	20K	37K	1.9	3.6:1
8	1500	27K	59K	2.2	3.2:1

Table 8. Polymerizations of Norbornene in Supercritical CO<sub>2</sub> at Different Pressures

Reaction Conditions: 50 °C, 4 hours @ c.a. [M]/[I]=200:1

It can be seen that reaction different pressures did not greatly influence the microstructure of polynorbornenes made in SC  $CO_2$ . In our experiments the pressure ranged from 1500 psi to 5000 psi. All the polynorbornenes made in SC  $CO_2$  have similar *trans*-to-*cis* ratios and comparable molecular weight and molecular weight distribution. Table 9 below shows the thermogravimetric analysis (TGA) result of polynorbornenes made in SC  $CO_2$ , SC  $CO_2$  with co-solvent (THF) and pure THF at different pressures.

Entry	Reaction Conditions	Td, <sup>o</sup> C
1	5000 psi	455
2	5000 psi + 5% THF	455
3	2500 psi	454
4	2500 psi + 5% THF	454
5	100% THF, 1 atm	457

Table 9. Thermal Stability of Polynorbornenes Prepared in Supercritical CO<sub>2</sub>

Td-the temperature at which 10% weight loss takes place in Ar.

It can be seen that with respect to their thermal decomposition temperature  $(T_d)$ ,

there is no difference in the thermal stability among these polynorborenes made at different pressures, as would be expected.

#### 4.2.2.3 Catalyst Effect

In addition to the Grubbs catalyst, other kinds of well defined catalyst can also be used in the ROMP process, such as the Schrock catalyst shown in Structure 8.





The Schrock catalyst is a molybdenum-based catalyst which usually results in high *cis* structure in the ROMP of norbornene in organic solvents, such as methylene chloride. The <sup>1</sup>H-NMR spectrum of polynorbornene obtained with this catalyst is shown below in Figure 28.



Reaction Conditions: 50 °C, 1 atm under Ar, *c.a.* 20 hours Figure 28. <sup>1</sup>H-NMR Spectrum of Polynorbornene Initiated by Schrock Catalyst As shown in Figure 28, a high *cis* content was obtained with a *trans/cis* ratio of 1:3.3. The <sup>1</sup>H-NMR spectrum of polynorbornene made in SC CO<sub>2</sub> with Schrock catalyst is also shown in Figure 29.



Figure 29. <sup>1</sup>H-NMR Spectrum of Polynorbornene Obtained with Schrock Catalyst in Supercritical CO<sub>2</sub>

Again, similar high *cis* content (*trans/cis* ratio=1:3.9) was found in the polymeric product prepared in SC CO<sub>2</sub> although the *trans/cis* ratio is even a little lower that that made in methylene chloride.

The <sup>1</sup>H-NMR spectra of polynorbornenes obtained in SC  $CO_2$  with Grubbs and Schrock catalysts respectively are shown below in Figure 30.



Figure 30. <sup>1</sup>H-NMR Spectra of Polynorbornenes Obtained with Schrock and Grubbs Catalysts in Supercritical CO<sub>2</sub> Reaction Condition: 3000 psi, 50 °C

It is very clear that the type of the well defined catalysts is a very important factor in determining the microstructure of the resultant polymer products. With Grubbs catalyst, usually high *trans* structures are obtained while the Schrock catalyst generally results in high *cis* content in the final product.

Table 10 below showed the thermal analysis (TGA) result of polynorbornenes made in SC  $CO_2$  with Grubbs and Schrock catalysts respectively.

Entry	Types of Catalyst	Reaction Conditions	Td, <sup>o</sup> C
1	Grubbs	5000 psi, 70 °C	455
2	Grubbs	2500 psi, 70 °C	454
3	Schrock	3000 psi, 50 °C	450

Table 10. TGA Results of Polynorbornenes Obtained with Different Catalysts

Although as evidenced by the NMR spectra in Figure 29, the types of catalysts did influence the *trans/cis* ratio of the final products, they did not affect the thermal stability of the polynorbornenes made in SC  $CO_2$ .

#### 4.2.2.4 Polarity of the Reaction Medium

The polarity of the reaction medium, in case of SC CO<sub>2</sub>, can be changed by adding a small amount of polarity modifiers (*i.e.*, polar solvents which are completely soluble in SC CO<sub>2</sub> over the entire pressure range of 1500 psi to 5000 psi). The modifiers used in this study were methanol, toluene, tetrahydrofuran (THF), N,N'-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

The effect of polarity modifiers on the microstructure of the final polymeric products was also studied and their <sup>1</sup>H-NMR spectra are shown in Figure 31.



Polarity Modifiers

From the NMR spectra in Figure 31, the microstructures of the resultant polynorbornenes made in SC  $CO_2$  with different polarity modifiers were determined and the results are listed in the Table 11.

Entry	Polarity Modifier	Amount (wt/vol)	Mw	PDI	Trans/Cis	
1			33K	1.8	3.5:1	
2*	Methanol	5%			3.8:1	
3	THF	10%	30K	1.8	5.2:1	
4	Toluene	10%	53K	2.0	5.5:1	
5	DMF	10%	37K	1.9	3.2:1	
6**	DMSO	10%	26K	2.3	3.4:1	

Table 11. *Trans/Cis* Ratios of Polynorbornenes Made in Supercritical CO<sub>2</sub> with Polarity Modifiers

Reaction Conditions: 5000 psi, 50 °C

\* Reaction Temperature is 70 °C

\*\* The yield is very low

All these polarity modifiers gave rise to similar *trans/cis* ratios as the one made in pure SC  $CO_2$ , except for THF and toluene which resulted in a relatively higher *trans* content. The reason for this is still under investigation.

#### 4.2.2.5 Temperature Effect

Temperature is another factor that may influence the ROMP of norbornene in SC  $CO_2$ . For addition polymerizations, of which ROMP is a particular case, there is always a ceiling temperature,  $T_c$ , at which the forward and reverse reactions are exactly balanced and the free energy change for the propagation reaction is zero. Tc can be affected by pressure, whose effect is given by the Clausius-Clapeyron equation below.<sup>[40]</sup>

$$\frac{d\ln T_C}{dP} = \frac{\Delta V}{\Delta H}$$

When the volume change,  $\Delta V$ , and heat change,  $\Delta H$ , accompanying polymerization are both negative, as is usually the case, T<sub>c</sub> is raised by an increase of pressure P. In other words,  $\Delta G$  is made more negative at a given temperature. So, during the ROMP process, high pressure is more favorable for the process. Meanwhile, since high temperatures can result in severe side reactions, the ROMP of norbornene is usually conducted at low reaction temperatures.

The <sup>1</sup>H-NMR spectra of polynorbornenes made at 50°C are shown in Figure 32.



Figure 32. <sup>1</sup>H-NMR Spectra of Polynorbornenes Made in Supercritical CO<sub>2</sub> and THF @ 5000 psi, 50 °C

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From the <sup>1</sup>H-NMR spectra and GPC data of polynorbornenes made in SC CO<sub>2</sub> with co-solvent (THF) at 50 °C and 70 °C respectively, the *trans/cis* ratios and molecular weights of these polynorbornenes were determined and the results are listed in Table 12.

	- 							
Entry	THF	THF Mw		P	PDI		Trans/Cis	
	(wt/vol)	50 °C	70 °C	50 °C	70 °C	50 °C	70°C	
1	0	33K	89K	1.8	2.6	3.5:1	3.8:1	
2	5%	32K	83K	1.8	2.1	5.3:1	5.1:1	
3	10%	***	67K	***	1.8	5.2:1	5.5:1	
4	15%	31K	91K	1.8	1.8	4.8:1	5.3:1	
5	20%	30K	79K	1.8	2.0	5.6:1	5.1:1	

Table 12. Polymerizations of Norbornene in Supercritical CO<sub>2</sub> at Different Reaction

Temperatures

Reaction Conditions: 5000 psi, 4 hours @ c.a. [M]/[I]=200:1

From the Table 12, it was found that reaction temperature did not affect the microstructure, *i.e.*, the *trans/cis* ratios, of the resultant polynorbornenes significantly. However, at higher temperatures, relatively higher molecular weights and slightly broader molecular weight distributions were obtained. The reason could be due to the increase in the solvent power of SC  $CO_2$  and the side reactions at high temperatures, which promoted the formation of higher molecular weight polymers with broader molecular weight distribution.

#### 4.2.2.6 DMTA Result

DMTA has also been performed on the polynorbornenes prepared in the organic solvent THF, SC  $CO_2$  as well as SC  $CO_2$  with THF respectively. Table 13 shows the glass transition temperature (Tg) of these polynorbornenes obtained by DMTA.

Entry	Reaction Conditions	Cis/Trans	Tg, °C
1	SC CO <sub>2</sub> , 5000 psi, 70 °C	1:3.8	46
2	SC CO <sub>2</sub> , 2500 psi, 70 °C	1:3.0	46
3	SC CO <sub>2</sub> +10% THF, 5000 psi	1:5.0	43
4	1 atm, THF	1:5.6	44

Table 13. Glass Transition Temperatures of Polynorbornenes

It is shown in Table 13 that the polynorbornenes obtained in SC  $CO_2$  are comparable to their counterparts made in the organic solvent-THF with respect to the glass transition temperature. Also, the *cis/trans* ratio did not significantly influence the glass transition temperatures of these high *trans*-contained polynorbornenes.

#### 4.2.2.7 DSC Result

DSC analyses were also performed on the polynorbornenes made in SC CO<sub>2</sub> as well as in THF with two different catalysts, *i.e.*, the Grubbs catalyst and the Schrock catalyst. Since the Grubbs catalyst usually leads to high *trans* content while the Schrock catalyst usually gives rise to high *cis* content, it can be expected that the polynorbornenes obtained with these two different catalysts should have different glass transition temperatures (T<sub>g</sub>) due to their different microstructures. Table 14 shows the DSC results of these polymers.

Entry	Reaction Conditions	Cis/Trans	Tg, oC
1	In THF	1:5.6	42
2	In SC CO <sub>2</sub> , 5000 psi, 50 °C	1:3.5	44
3	In SC CO <sub>2</sub> + 15% THF, 5000 psi	1:5.6	41
4	In SC CO <sub>2</sub> , 3000 psi, 50 °C	1:3.5	45
5	In SC CO <sub>2</sub> , 3000 psi, 50 °C	3.9:1	60

 Table 14. Glass Transition Temperatures of Polynorbornenes with Different

 Microstructures

As can be seen in Table 14, microstructures did influence the glass transition of these polynorbornenes. For those high *trans*-contained polynorbornenes, the *cis/trans* ratios did not affect their  $T_g$  very much. Meanwhile, as expected, for those polynorbornenes made by the Schrock catalyst and Grubbs catalyst respectively, due to their completely different microstructures, they show different glass transition temperatures. The high *cis*-contained polynorbornene has a higher  $T_g$  than their counterparts with high *trans*-contained microstructures.

# 4.3 Polymerization of HFMPPPA in Supercritical CO,

#### 4.3.1 Homopolymerization of HFMPPPA

Homopolymerization of hexafluoro-2-[3-(hexfluoro-2-methoxy-2-propyl)-phenyl]-2-proply acrylate) (HFMPPPA) was conducted in bulk, toluene and SC  $CO_{2}$ . The reaction involved is schematically illustrated in Figure 33.



Figure 33. Homopolymerization Scheme of HFMPPPA

The obtained homopolymers were characterized by GPC and TGA. The result was listed in Table 15.

Polymer Number	Reaction Conditions	[M]/[I]	Mn	Mw	PDI	Td,⁰C
1a	In Bulk	50:1	22.3K	36.7K	1.64	309
1 b	In Toluene	50:1	4.3K	5.0K	1.16	334
1 c	In SC CO <sub>2</sub>	50:1	***	***	***	***
1d	In SC CO <sub>2</sub>	50:1	***	***	***	***

Table 15 Homopolymerizations of HFMPPPA

As shown in the Table 15, higher molecular weights were obtained in the bulk polymerization. This is a common phenomenon in free radical polymerization probably due to the fact that the gel effect, usually referred to as the Trommsdorff effect, occurs in bulk or concentrated solution polymerizations when the medium viscosity becomes very high, or in solution polymerizations when the polymer precipitates.<sup>[41]</sup> As a result, higher molecular weights result from the decrease in termination rate.
The homopolymers prepared in toluene were comparable to their counterparts made in SC  $CO_2$  regarding molecular weight and its distribution with monomer-to-initiator ratio at 100:1 or 200:1, as shown in Table 16.

Polymer Number	Reaction Conditions	[M]/[I]	Mn	Mw	PDI	T <sub>d</sub> , ℃
1b	In Toluene	50:1	4.3K	5,0K	1.16	334
1 e	In SC CO <sub>2</sub>	100:1	8.0K	13.2K	1.64	***
1f	In SC CO <sub>2</sub>	100:1	6.7K	8.1K	1.22	155

Table 16. Effect of Monomer-to-Initiator Ratio

However, the yield for the homopolymers made in SC CO<sub>2</sub> was very low and no solid particles can be obtained when the monomer-to-initiator ratio was kept at about 50:1 and 100:1. Also, as shown in Table 16, the homopolymer of HFMPPPA in SC CO<sub>2</sub> has a very low T<sub>d</sub>. The reason for this is probably due to the very low conversion of this reaction. As a result, a large number of oligomers was formed instead, which led to the very low T<sub>d</sub>.

Actually, when the monomer-to-initiator ratio was set at 50:1, no polymer was formed in SC  $CO_2$ , as evidenced by their <sup>1</sup>H-NMR spectra in Figure 34.



Figure 34. <sup>1</sup>H-NMR Spectra of PolyHFMPPPA Synthesized in Supercritical CO<sub>2</sub>

However, in bulk or solution polymerizations where only a small amount of toluene was employed as the reaction medium (the monomer concentration was about 20%, wt%), solid polymer was precipitated out of methanol and the reaction was evidenced by their <sup>1</sup>H-NMR spectra in Figure 35.



Figure 35. <sup>1</sup>H-NMR Spectra of PolyHFMPPPA Made in Bulk

From the <sup>1</sup>H-NMR spectrum in Figure 35, it can be seen that the bulk polymerization was almost complete. Also, as evidenced by their <sup>1</sup>H-NMR spectra below in Figure 36, when the monomer-to-initiator ratio was increased from 50:1 to 100:1 and 200:1, polymerization took place and when the monomer-to-initiator ratio reached 200:1, solid polymer was precipitated out of methanol, although the yield was still very low.



PolyHFMPPPA @ [M]/[I]=200:1 in SC CO<sub>2</sub>

Figure 36. <sup>1</sup>H-NMR Spectra of PolyHFMPPPA Prepared in Supercritical CO<sub>2</sub> with

# Different Monomer-to-Initiator Ratios

It is very clear that all these products were a mixture of polymer and oligomers, which was partly demonstrated by their thermal analysis result (TGA) as shown in Table 15 above. The reasons could presumably due to: 1) the solubility of AIBN in SC  $CO_2$  is very low (Therefore, it could not initiate the polymerization of HFMPPPA because the monomer HFMPPPA is very soluble in SC  $CO_2$ ), and/or 2) the reactivity of HFMPPPA is very low.

The low reactivity of HFMPPPA could be partly verified by the observation that when the monomer-to-initiator ratio was set at 50:1 and about 8.5 mL of toluene was used (comparable to 12 mL of SC CO<sub>2</sub> at 3000 psi), almost no solid precipitated out of methanol (*i.e.*, the yield was very low).

## 4.3.2 Copolymerization of HFMPPPA with MA

Copolymerization of HFMPPPA with MA was also performed in bulk, toluene and SC  $CO_2$  with different HFMPPPA-to-MA ratios. Figure 37 is the schematic representation of this kind of copolymerization.



Figure 37. Copolymerization of HFMPPPA with MA

Again, the resultant copolymers were characterized by GPC, NMR and TGA and the results are listed in Table 17.

Polymer Number	Reaction Conditions	[HFMPPPA] / [MA] (mol)	Mn	$M_W$	PDI	T <sub>d</sub> ,°C	Yield,%
2b	In Bulk	1:1	26K	65.8K	2.53	341	59.3
2 b	In Toluene	1:1	5.4K	7.1K	1.31	324	***
<b>2</b> b	In SC CO <sub>2</sub>	1:1	7.6K	10.2K	1.34	306	30.7
2a	In Toluene	3:1	4.3K	5.9K	1.37	316	***
2a	In SC CO <sub>2</sub>	3:1	6.9K	8.6K	1.26	***	***
2 c	In Toluene	1:3	9.7K	12.1K	1.25	325	***
2 c	In SC CO <sub>2</sub>	1:3	6.1K	9.8K	1.62	308	36.5

Table 17. Copolymers of HFMPPPA and MA

As can be seen, bulk copolymerization gave rise to the highest molecular weights and the broadest molecular weight distributions. The copolymers made in SC  $CO_2$  were comparable to their counterparts prepared in toluene, which was demonstrated by their <sup>1</sup>H-NMR spectra below in Figure 38.



Figure 38. <sup>1</sup>H-NMR Spectra of Copolymers of HFMPPPA and MA However, in many cases, the copolymers made in SC CO<sub>2</sub> had slightly higher

molecular weights than those synthesized in toluene. The reason could possibly be attributed to the low dielectric constant of  $CO_2$  relative to toluene and very high initiator efficiencies resulting from negligible cage effects in SC  $CO_2$  as SC  $CO_2$  has a very low viscosity (at least an order of magnitude lower than the viscosity of conventional organic solvents). The high initiation efficiency of AIBN in SC  $CO_2$  has already been reported by DeSimone.<sup>[26]</sup>

In addition, the decomposition temperatures of the copolymers made in SC  $CO_2$  were a little lower than those prepared in toluene and the reason is not clear.

Furthermore, compared with the homopolymers of HFMPPPA as listed in Table 18, at the same monomer-to-initiator ratio of 50:1, when an equivalent amount of methyl acrylate (MA) was added, both the yield and molecular weight of the copolymer products increased.

Polymer Number	[HFMPPPA] /[MA] (mol)	Reaction Conditions	M <sub>n</sub>	$M_W$	PDI	Yield,%
1 <b>d</b>	1:0	SC CO <sub>2</sub>	***	***	***	***
2b-1	1:1	Bulk	26K	65.8K	2.53	59.3
2b-2	1:1	Toluene	5.4K	7.1K	1.31	***
2b-3	1:1	SC CO <sub>2</sub>	7.6K	10.2K	1.34	30.7

Table 18. The Effect of MA on the Polymerization of HFMPPPA

the monomer-to-initiator ratio was kept at 50:1

This could be attributed to the relatively higher reactivity of MA compared with HFMPPPA, which helped the polymerization of HFMPPPA. However, when more HFMPPPA was used (such as the [HFMPPPA]/[MA]=3:1 case), both the conversion and the yield of the resultant copolymer, especially the one made in SC CO<sub>2</sub>, were very low, as shown in its <sup>1</sup>H-NMR spectrum below in Figure 39.



## 4.3.3 Copolymerization of HFMPPPA with FOA

Precipitation copolymerization of HFMPPPA with FOA was conducted in toluene and a possible dispersion copolymerization of HFMPPPA with FOA was performed in SC  $CO_2$  as well. The reaction scheme is shown in Figure 40.



Since all these copolymers were not soluble in conventional organic solvents, such as acetone, chloroform and THF, the obtained copolymers were characterized only by TGA and the results are listed in Table 19.

Polymer Number	Reaction Conditions	[HFMPPPA] /[FOA] (mol)	T <sub>d</sub> , °C
3a	In Toluene	3:1	300
3a	In SC CO <sub>2</sub>	3:1	***
3b	In Toluene	1:1	321
3b	In SC CO <sub>2</sub>	1:1	306
3 c	In Toluene	1:3	323
3 c	In SC CO <sub>2</sub>	1:3	286

Table 19. Thermal Stability of Poly(HFMPPPA-co-FOA)

Similar results were also obtained by DeSimone and the intrinsic viscosities of random copolymers of FOA with methyl methacrylate (MMA), styrene, butyl acrylate (BA) and ethylene were measured in Freon-113.<sup>[1]</sup>

## 4.3.4 Elemental Analysis

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Elemental analysis is a useful tool to investigate the composition of copolymers. As we know, for copolymers prepared *via* chain polymerization, their composition not only depends on the initial feed ratio of the used monomers, but also on their relative reactivity ratios.

Elemental analyses on the copolymers of HFMPPPA with MA were performed and the results are listed in Table 20.

Polymer Number	[HFMPPPA]/[MA] in the feed (mol)	Reaction Conditions	Elemental Analyses Obs. (Calc.)
2b*	1:1	In Toluene	44.04 (42.56) %C 3.50 (2.86) %H
2 b	1:1	In SC CO <sub>2</sub>	42.93 (42.56) %C 2.73 (2.86) %H
2c**	1:3	In Toluene	46.75 (45.66) %C 4.39 (3.84) %H
2 c	1:3	In SC CO <sub>2</sub>	45.44 (45.66) %C 3.51 (3.84) %H

Table 20. Elemental Analyses on Poly(HFMPPPA-co-MA)

From Table 20 above, it can be seen that the composition of those copolymers prepared in SC  $CO_2$  are closer to the initial feed ratio compared with their analogues prepared in toluene. Table 21 is the elemental analysis of fluorine on these copolymers.

Polymer Number	[HFMPPPA]/[MA] in the Feed (mol)	Reaction Conditions	Elemental Analysis Obs. (Calc.)
<b>2</b> b	1:1	In Toluene	35.81 (40.40) %F
2 b	1:1	In SC CO <sub>2</sub>	38.50 (40.40) %F
2 c	1:3	In Toluene	27.93 (30.96) %F
2 c	1:3	In SC CO <sub>2</sub>	31.73 (30.96) %F

Table 21. Fluorine Analysis of Poly(HFMPPPA-co-MA)

Again, as can be seen, the compositions of those copolymers obtained in SC  $CO_2$  are closer to the initial feed ratios compared with their analogues prepared in toluene.

Meanwhile, based on the fluorine analysis, the composition of these copolymers has been back-calculated and the results are listed in Table 22.

Polymer Number	[HFMPPPA]/[MA] in the Feed (mol)	Reaction Conditions	(HFMPPPA) <sub>n</sub> (MA-) <sub>m</sub>
2 b	1:1	In Toluene	n=0.35, m=0.65 (Obs.) n=0.50, m=0.50 (Calc.)
2b	1:1	In SC CO <sub>2</sub>	n=0.43, m=0.57 (Obs.) n=0.50, m=0.50 (Calc.)
2 c	1:3	In Toluene	n=0.20, m=0.80 (Obs.) n=0.25, m=0.75 (Calc.)
2 c	1:3	In SC CO <sub>2</sub>	n=0.26, m=0.74 (Obs.) n=0.25, m=0.75 (Calc.)

Table 22. Compositions of Poly(HFMPPPA-co-MA)

Table 22 clearly demonstrated that the compositions of the copolymers made in SC  $CO_2$  are very close to their initial feed ratios. Meanwhile, the composition determined by carbon and hydrogen analyses in Table 20 is consistent with the one calculated by fluorine analysis. So, it can be concluded that the compositions of copolymers prepared in SC  $CO_2$  are more consistent with their individual initial feed ratios than their counterparts made in toluene and the HFMPPPA monomer is more reactive in SC  $CO_2$  than in toluene. Also, in SC  $CO_2$ , the composition of these copolymers are almost determined only by the initial feed ratios, *i.e.*, in SC  $CO_2$ , both HFMPPPA and MA have the same reactivity.

Another piece of evidence comes from the <sup>1</sup>H-NMR spectra of those copolymers which is shown in Figure 41 below.



Figure 41. <sup>1</sup>H-NMR Spectra of Poly(HFMPPPA-co-MA)

By doing the proton integration on the aromatics and methoxy groups in the copolymers in Figure 41, the compositions of these copolymer were determined and the results are listed in Table 23.

Polymer Number	[HFMPPPA]/[MA] in the Feed (mol)	Reaction Conditions	(-HFMPPPA-) <sub>n</sub> (-MA-) <sub>m</sub>
2b	1:1	In Toluene	n=0.45, m=0.55 (Obs.) n=0.50, m=0.50 (Calc.)
2b	1:1	In SC CO <sub>2</sub>	n=0.56, m=0.44 (Obs.) n=0.50, m=0.50 (Calc.)
2 c	1:3	In Toluene	n=0.22, m=0.78 (Obs.) n=0.25, m=0.75 (Calc.)
2 c	1:3	In SC CO <sub>2</sub>	n=0.32, m=0.68 (Obs.) n=0.25, m=0.75 (Calc.)

Table 23. Compositions of Poly(HFMPPPA-co-MA) by <sup>1</sup>H-NMR

Compared with the composition determined by elemental analyses, the individual composition by NMR is not very consistent with the result by elemental analysis. However, the tendency here is very clear, *i.e.*, the HFMPPPA monomer is more reactive in SC CO<sub>2</sub> than in toluene. Meanwhile, we believe that elemental analysis is more accurate than <sup>1</sup>H-NMR in composition determination.

Table 24 below shows the elemental analysis results of copolymers of HFMPPPA with FOA prepared in toluene and SC  $CO_2$  respectively.

Polymer Number	[HFMPPPA]/[FOA] in the feed (mol)	Reaction Conditions	Elemental Analyses Obs. (Calc.)
3b*	1:1	In Toluene	33.17 (34.78) %C 1.40 (1.62) %H
3 b	1:1	In SC CO <sub>2</sub>	35.33 (34.78) %C 2.06 (1.62) %H
3 c	1:3	In Toluene	31.21 (31.97) %C 1.20 (1.37) %H
3 c	1:3	In SC CO <sub>2</sub>	31.99 (31.97) %C 1.39 (1.37) %H

Table 24. Elemental Analysis of Poly(HFMPPPA-co-FOA)

\* Observed value indicates 36/64 mol% ratio of HFMPPPA to FOA in the obtained copolymer.

In this case, FOA seemed more reactive than the fluorinated monomer in solution polymerization when toluene was used as a reaction medium. However, again, in SC  $CO_2$ , both HFMPPPA and FOA almost have the same reactivity. As a result, the compositions of these copolymers prepared in SC  $CO_2$  only depend on the initial feed ratios of the used monomers.

## 4.3.5 DSC Analysis Result

DSC analyses have also been performed on the homo- and copolymers of the fluorinated monomer-HFMPPPA with MA. Their glass transition temperatures were determined and the results are listed in Table 25.

Polymer Number	[HFMPPPA] /[MA] (mol)	Reaction Conditions	Tg, °C
1	1:0	Bulk	70
2a	3:1	In Toluene	36
<b>2</b> b	1:1	In Toluene	43
2 b	1:1	In SC CO <sub>2</sub>	39
2 c	1:3	In Toluene	36
2 c	1:3	In SC CO <sub>2</sub>	35

Table 25. Glass Transition Temperatures of Poly(HFMPPPA-co-MA)

As can been seen, all these copolymers show very similar glass transition temperatures, *i.e.*, about 40 °C. Since the homopolymer of MA (PMA) has a glass transition around 10 °C, <sup>[42]</sup> these results are reasonable because PMA has a relatively lower glass transition temperature than PolyHFMPPPA.

Also, the glass transition temperatures of Poly(HFMPPPA-co-FOA) have also been measured and the DSC results are listed in Table 26.

Polymer Number	[HFMPPPA] /[FOA] (mol)	Reaction Conditions	Tg, °C
3b	1:1	In Toluene	3
3b	1:1	In SC CO <sub>2</sub>	3
3 c	1:3	In SC CO <sub>2</sub>	2

Table 26. Glass Transition Temperatures of Poly(HFMPPPA-co-FOA)

As shown in Table 26, the glass transition temperatures of these copolymers are below room temperature possibly due to the long pendant group in the FOA monomer.

## **V. SUGGESTIONS FOR FUTURE RESEARCH**

# 5.1 ROMP in Supercritical CO<sub>2</sub>

The ROMP of norbornene and the ROMP of COD with chain transfer agent have been successfully effected in SC  $CO_2$  with Grubbs catalyst. The polymers made in SC  $CO_2$ were comparable to their counterparts prepared in organic solvents. Thus, the use of organic solvents has been minimized. The next step would be to examine some functionalized norbornene systems. One candidate would be the 5-methylene-2-norbornene (I) or 5-norbornenyl trimethoxy silane (II) as shown in Structure 9.



Structure 9. Structures of Functionalized Norbornenes

Through homopolymerization, or possible copolymerization with norbornene, the functional groups such as C=C and  $-Si(OCH_3)_3$  can be incorporated into the polynorbornene systems. These functional groups can be used for further reactions to obtain crosslinked polynorbornenes by hydrosilation, free radical reaction or hydrolysis. By adding an appropriate amount of these functional norbornenes, the crosslink density of the system can be adjusted for desired mechanical and/or thermal properties.

# 5.2 PolyHFMPPPA in Supercritical CO<sub>2</sub>

As can be seen, at the monomer-to-initiator ratio of 100:1 or 200:1, there was some polyHFMPPPA formed in SC CO<sub>2</sub> evidenced by their <sup>1</sup>H-NMR spectra. But the polymer

yield was still very low. Thus, the next step in this area would be to increase the conversion of HFMPPPA into its polymer in SC CO<sub>2</sub>. The following factors should be examined: 1) the pressure effect; 2) surfactants' effect; and 3) the amount of SC CO<sub>2</sub> used as a reaction medium. In addition, other polyfluoroacrylates, developed by the Polymer Research Group at Southwest Texas State University and similar to the fluorinated system used in this research, could also be investigated. One candidate would be the 2-(4-fluorophenyl)-2hexafluoropropyl acrylate (FPHFPA) or methacrylate (FPHFPM) as shown below in Structure 10.



Structure 10. Structures of FPHFPA and FPHFPM R=H for FPHFPA and R=CH<sub>3</sub> for FPHFPM

*Via* homopolymerization or copolymerization with methyl acrylate (MA) or methyl methacrylate (MMA) in SC CO<sub>2</sub>, various factors that may affect the formation of its homoor copolymers can be investigated, such as the monomer-to-initiator ratio, the amount of CO<sub>2</sub>, pressure, surfactants, temperature, *etc*.

# APPENDIX

<sup>1</sup>H- and <sup>13</sup>C-NMR, TGA, DSC, DMTA and IR Data



Figure 42. <sup>1</sup>H-NMR Spectrum of Cis-2-butene-1,4-diol





Figure 45. <sup>1</sup>H-NMR Spectrum of Chain Transfer Agent









Figure 52. <sup>1</sup>H-NMR Spectrum of Polynorbornene Prepared in SC CO<sub>2</sub> @ 5000 psi, 70  $^{\circ}$ C



@ 2500 psi, 70 °C























@ 5000 psi, 50 °C



Figure 75. <sup>1</sup>H-NMR Spectrum of the Fluorinated Acrylate Monomer-HFMPPPA




Figure 78. <sup>1</sup>H-NMR Spectrum of PolyHFMPPPA Prepared in SC CO<sub>2</sub> @ [M]/[I]=100:1



Figure 79. <sup>1</sup>H-NMR Spectrum of PolyHFMPPPA Prepared in SC CO<sub>2</sub> @ [M]/[I]=200:1





@ [HFMPPPA]/[MA]=50/50





4.0

5.0

1.17

8.0

9.0

7.0

6.0

ر ب 1.00 <u>2.82</u>

3.0

2.0

1.0

0 ppm



in SC CO $_2$  @ 3000 psi, 50  $^{\circ}\mathrm{C}$ 



@ HFMPPPA]/[MA]=75/25



@ [HFMPPPA]/[MA]=75/25





Figure 89. TGA Data of Polynorbornene Initiated by the Schrock Catalyst in SC CO<sub>2</sub>

@ 3000 psi, 50 °C



Polynorbornene: P17 (II), 6-28-00





Figure 91. TGA Data of Polynorbornene Made in SC CO<sub>2</sub> @ 5000 psi, 70 °C with Grubbs Catalyst



Figure 92. TGA Data of PolyHFMPPPA via Solution Polymerization @ [M]/[I]=50:1



P55(II), 9-11-00

Figure 93. TGA Data of PolyHFMPPPA via Bulk Polymerization @ [M]/[I]=50:1



Figure 94. TGA Data of Poly(HFMPPPA-co-MA) *via* Bulk Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:1



Figure 95. TGA Data of Poly(HFMPPPA-co-MA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:1

P57(II), 9-7-00



Figure 96. TGA Data of Poly(HFMPPPA-co-MA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:1



Figure 97. TGA Data of Poly(HFMPPPA-co-FOA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:1



Figure 98. TGA Data of Poly(HFMPPPA-co-FOA) *via* Solution Polymerization @ [M]/[I]=100:1, [HFMPPPA]/[FOA]=1:1



Figure 99. TGA Data of Poly(HFMPPPA-co-FOA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:1



Figure 100. TGA Data of Poly(HFMPPPA-co-FOA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:3



Figure 101. TGA Data of Poly(HFMPPPA-co-MA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=3:1



Figure 102. TGA Data of Poly(HFMPPPA-co-MA) via Solution Polymerization @





Figure 103. TGA Data of Poly(HFMPPPA-co-FOA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:3



Figure 104. TGA Data of Poly(HFMPPPA-co-FOA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=3:1



Figure 105. TGA Data of PolyHFMPPPA Prepared in SC CO<sub>2</sub> @ [M]/[I]=200:1

# 110



Figure 106. TGA Data of Poly(HFMPPPA-co-MA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:3



P12II-020901-2nd Run

Figure 107. DSC Scan of Polynorbornene Made in THF





Figure 108. DSC Scan of Polynorbornene Made in SC CO<sub>2</sub> @ 3000 psi, 50 °C with Schrock Catalyst

P18II-020901-2nd Run



Figure 109. DSC Scan of Polynorbornene Made in SC  $CO_2$  + 15% THF

@ 5000 psi, 70 °C



Figure 110. DSC Scan of Polynorbornene Prepared in SC CO $_2$  @ 5000 psi, 50  $^\circ C$ 



P34II-02102001-2nd Run

Figure 111. DSC Scan of Polynorbornene Prepared in SC CO<sub>2</sub> @ 3000 psi, 50 °C

#### P55II-020801-2nd Runnew



Figure 112. DSC Scan of PolyHFMPPPA via Bulk Polymerization



P57II-02102001-2nd Run

Figure 113. DSC Scan of Poly(HFMPPPA-co-MA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:1

#### P66II-02112001-2nd Run



Figure 114. DSC Scan of Poly(HFMPPPA-co-FOA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:1



Figure 115. DSC Scan of Poly(HFMPPPA-co-FOA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[FOA]=1:3



Figure 116. DSC Scan of Poly(HFMPPPA-co-MA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=3:1



Figure 117. DSC Scan of Poly(HFMPPPA-co-MA) *via* Solution Polymerization @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:3

P69II-02102001-2nd Run





Figure 118. DSC Scan of Poly(HFMPPPA-co-MA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:3

P83II-02102001-2nd Run



Figure 119. DSC Scan of Poly(HFMPPPA-co-MA) Prepared in SC CO<sub>2</sub> @ [M]/[I]=50:1, [HFMPPPA]/[MA]=1:1



Figure 120. DMTA Scan of Polynorbornene Made in THF with Grubbs Catalyst



P17 (II), 8-1-00

Figure 121. DMTA Scan of Polynorbornene Made in SC CO<sub>2</sub> @ 2500 psi, 70 °C with Grubbs Catalyst



Figure 122. DMTA Scan of Polynorbornene Made in SC  $CO_2$ @ 5000 psi, 70 °C



Figure 123. DMTA Scan of Polynorbornene Made in SC CO<sub>2</sub> + 10% THF @ 5000 psi, 70 °C

# 119



Figure 124. DMTA Scan of Polynorbornene Made in SC  $CO_2$  + 10% THF @ 2500 psi, 70 °C



Figure 125. FT-IR Spectrum of the Functionalized Polybutadiene *via* the ROMP of COD with CTA in SC CO<sub>2</sub>



Figure 126. FT-IR Spectrum of the Functionalized Polybutadiene *via* the ROMP of COD with CTA in THF

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