

**DESIGN, SYNTHESIS, AND OPTIMIZATION OF NON-FLUOROUS,  
CO<sub>2</sub>-PHILIC POLYMERS: A SYSTEMATIC APPROACH**

by

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## ABSTRACT

### DESIGN, SYNTHESIS, AND OPTIMIZATION OF NON-FLUOROUS, CO<sub>2</sub>-PHILIC POLYMERS: A SYSTEMATIC APPROACH

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Research done during the last 15 years has proven that one can use CO<sub>2</sub> as a solvent in many processes. There have been compounds from surfactants to chelating agents that were shown to be soluble in CO<sub>2</sub> to low pressures. By attaching CO<sub>2</sub>-philic groups to polymer chains, previously insoluble polymers have exhibited miscibility with CO<sub>2</sub>, allowing for applications such as emulsion polymerization, dispersion polymerization, dissolution of proteins, extraction of heavy metals, and other processes. Unfortunately, the most successful CO<sub>2</sub>-philes, the fluorinated polymers, have a very unfavorable economic drawback that makes their commercial use impractical. As a result, this work seeks to determine the characteristics that could be built into a carbon based polymer to allow for the polymer to be miscible with CO<sub>2</sub> down to low pressures.

Several design elements were considered in this work: the cohesive energy density, the free volume, and the Lewis acid/base interactions with CO<sub>2</sub> acting as a Lewis acid. Lowering the cohesive energy density and increasing the free volume limited undesirable polymer-polymer interactions, while the addition of Lewis base groups to the polymer in the backbone and as grafted side chains increased the favorable polymer-CO<sub>2</sub> interactions. Several side chains

containing Lewis base groups were first grafted onto silicon-backbone polymers. The effects of the grafting and degree of substitution were determined, and the best performing side chains were then grafted onto a polyether backbone to investigate their interactions with the carbon/oxygen backbone.

This work made clear the importance of adding optimal amounts of a Lewis base group to the polymer, whether in the backbone or as a grafted side chain. While attaining a low cohesive energy density and maintaining a low glass transition temperature are important, polymers with these features alone performed very poorly in CO<sub>2</sub>. The addition of Lewis base groups in the backbone or as a side chain dramatically improved the solubility of the polymers and showed the importance of favorable polymer-CO<sub>2</sub> interactions. A key observation was that an ether functional group may provide the same Lewis acid/base interaction with CO<sub>2</sub> that is seen with the acetate group.

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## NOMENCLATURE

CO <sub>2</sub>	Carbon Dioxide
scCO <sub>2</sub>	Supercritical Carbon Dioxide
CED	Cohesive Energy Density
T <sub>g</sub>	Glass Transition Temperature
T <sub>c</sub>	Critical Temperature
P <sub>c</sub>	Critical Pressure
CFC	Chlorofluorocarbon
PDMS	Poly(dimethyl siloxane)
PPO	Poly(propylene oxide)
PEO	Poly(ethylene oxide)
PECH	Poly(epichlorohydrin)
PP	Poly(propylene)
PEVE	Poly(ethyl vinyl ether)
PVAc	Poly(vinyl acetate)
PVME	Poly(vinyl methyl ether)
FEP <sub>19</sub>	Poly(tetrafluoroethylene-co-19 mol % hexafluoropropylene)

## 1.0 INTRODUCTION

The possibility for the use of carbon dioxide as a process solvent has been investigated in industry and academia due to CO<sub>2</sub> being considered an environmentally benign, low-cost, and abundant material. Solubility parameter studies using equation of state data showed that CO<sub>2</sub> had the solvent power of short n-alkanes<sup>(1)</sup>, and it was hoped that CO<sub>2</sub> could be used to replace an array of environmentally and financially unfriendly non-polar organic solvents. Although, CO<sub>2</sub> initially looked to be useful only for non-polar materials, it was thought that polar materials could be brought into solution by adding conventional alkyl-functional surfactants into the mixture. However, early attempts to put these surfactants to use were hindered due to the poor solubility of these amphiphiles in CO<sub>2</sub>. The fact that these amphiphiles showed adequate solubility in short alkanes such as ethane and propane and were quite insoluble in CO<sub>2</sub><sup>(2)</sup> revealed a gap between the theoretical models and experimental data for CO<sub>2</sub> solubility. Bridging that gap, Johnston and colleagues suggested polarizability/free volume as a better method of evaluated solvent power<sup>(3,4)</sup>, and by this method CO<sub>2</sub> is correctly seen as a very poor solvent when compared to short n-alkanes. A number of groups began a search for CO<sub>2</sub>-philic materials that would be soluble in CO<sub>2</sub> at significantly lower pressures than similarly sized alkyl-functional equivalents, and it was soon found that by fluorinating materials they could be made to dissolve in CO<sub>2</sub>. Harrison et al. synthesized a hybrid alkyl/fluoroalkyl surfactant that dissolved in CO<sub>2</sub> and solubilized a significant amount of water<sup>(5)</sup>. Polymers were dissolved in CO<sub>2</sub> at moderate pressures when DeSimone and coworkers produced homo- and copolymers of fluorinated acrylates<sup>(6)</sup>. Dispersion

polymerization in CO<sub>2</sub> was supported by block polymers composed of fluorinated acrylate monomers<sup>(7)</sup>, leading to the generation of monodisperse, micron-sized spheres. Other developments with fluoro-functional amphiphiles were to support emulsion polymerization<sup>(8)</sup>, solubilize proteins<sup>(9,10)</sup>, and extract heavy metals from soil and water<sup>(11)</sup>.

While very successful as CO<sub>2</sub>-philic polymers, fluorinated amphiphiles have two substantial barriers limiting practical application. First, they are very expensive approaching \$1/gram, making them economically impractical unless the material can be recycled at almost 100% efficiency. Secondly, fluorine has a debated and suspect environmental record. Consequently, a more economical and environmentally friendly method of dissolving polymers in supercritical carbon dioxide would be beneficial on many levels. The development of a CO<sub>2</sub>-philic polymer composed of carbon, hydrogen, and oxygen would greatly increase the practical use of CO<sub>2</sub> as a solvent.

## 2.0 BACKGROUND AND LITERATURE REVIEW

### 2.1 Overview of Supercritical/Liquid CO<sub>2</sub>

A significant amount of time and effort has been put into the use of supercritical carbon dioxide (scCO<sub>2</sub>) as a solvent due to the many advantages that it presents. Supercritical CO<sub>2</sub> is considered an environmentally benign solvent and is also low-cost, abundant, non-toxic, non-flammable, and easy to discard after use. Reaching the critical point of CO<sub>2</sub> is also relatively easily accomplished as its critical temperature (31.0 °C) is low, and only modest effort is required to achieve its critical pressure (73.8 atm)<sup>(12)</sup>. A glaring disadvantage of using scCO<sub>2</sub> as a solvent lies in the fact that CO<sub>2</sub> is a very feeble solvent<sup>(2)</sup>. This barrier to CO<sub>2</sub> application was overcome as an effort was made to create and optimize CO<sub>2</sub>-philic substances, materials which will dissolve in or be miscible with CO<sub>2</sub> at relatively mild conditions (T < 100 °C, P < 200 atm).

Beyond environmental and cost benefits, scCO<sub>2</sub> exhibits other desirable properties that lend to its usefulness in application. Supercritical fluids exhibit properties of both liquids and gases. For example, gases can be quite miscible with a supercritical fluid while having only limited solubility in a liquid solvent<sup>(13)</sup>, and the density of a supercritical fluid may be changed by simply altering temperature or pressure. The ability to easily change the density of CO<sub>2</sub> can be used in separations. Though not without complications in the repressurization process, the removal of scCO<sub>2</sub> from the products of a reaction can be accomplished by opening a valve and discharging the gas.

Again, the disadvantages to using CO<sub>2</sub> as a process solvent are its poor solvent power and the pressure requirements to achieve the supercritical state. It is worth noting that liquid CO<sub>2</sub> can sometimes be used in the place of scCO<sub>2</sub> in certain procedures. Near the critical point, liquid CO<sub>2</sub> has many of the same properties of the supercritical fluid and can be achieved at milder conditions. Overall, CO<sub>2</sub> has great potential to be a valuable process solvent as industry continues to realize its environmental and economic advantages.

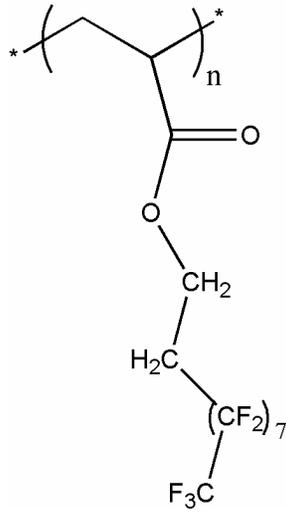
## 2.2 Uses for CO<sub>2</sub>-philic Polymers

The search for CO<sub>2</sub>-philic polymers has a great deal of importance due to the many applications that these materials can serve. CO<sub>2</sub>-philic monomers can be polymerized using liquid or supercritical CO<sub>2</sub> as a solvent, eliminating the need for organic solvents and allowing for easy removal of the solvent<sup>(14-20)</sup>. The synthesis of CO<sub>2</sub>-phobic polymers in CO<sub>2</sub> can be supported by the use of CO<sub>2</sub>-philic materials via a dispersion or emulsion polymerization<sup>(7,8,21-24)</sup>. CO<sub>2</sub>-philic chelating agents can be used to extract heavy metals<sup>(11,25,26)</sup>. For example, metal contamination in water can be cleaned effectively since the CO<sub>2</sub> does not leave residual solvent-contamination like that of conventional organic solvents. CO<sub>2</sub>-philic fluorinated and siloxane-functional oligomers have been applied in biotechnology as a means of bringing proteins into solution in CO<sub>2</sub><sup>(9,27)</sup>. The process of producing hydrogen peroxide was aided by using fluoroether oligomers to bring the necessary material into solution in CO<sub>2</sub><sup>(28,29)</sup>. Poly(vinylidene fluoride) and poly(4-vinylbiphenyl) were dissolved in scCO<sub>2</sub> and used to provide a protective film for fused silica plates and metal (Al, Mg) powders<sup>(30)</sup>.

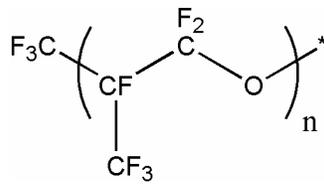
Poly(dimethylsiloxane) has been especially useful in sensing applications, in one case showing a quick, reversible response to hexane vapor<sup>(31)</sup>. This overview of the many uses of CO<sub>2</sub>-philic polymers, illustrates the diversity and large scope of their potential application.

### 2.3 Literature Review

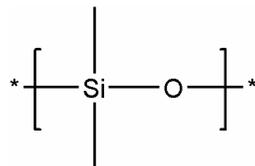
Many common polymers such as the poly(propylene) seen in this work are CO<sub>2</sub>-phobic; like many hydrocarbon polymers<sup>(32)</sup> they are not miscible in CO<sub>2</sub> even at high pressures. Another example of this is poly(isobutylene)<sup>(33)</sup>, which also requires extremely high pressures to exhibit miscibility with CO<sub>2</sub>. Due to the usefulness of CO<sub>2</sub> as a solvent and the perceived benefit of using polymers that would be miscible with CO<sub>2</sub> at moderate to low pressures, a great deal of work was done in the early 1990's to discover methods of dissolving common polymers in CO<sub>2</sub>. It was soon found that by adding fluorine groups to polymers, they could be made to be miscible with CO<sub>2</sub> down to low pressures. DeSimone et al. began to produce fluoropolymers (see **Figure 1**) using CO<sub>2</sub> as a solvent, replacing the expensive and environmentally suspect chlorofluorocarbons (CFCs) that were previously the most used of the few solvents for these materials<sup>(6)</sup>. Hoefling et al showed that adding a fluorinated ether (see **Figure 2**) functional group to polymers or surfactants greatly reduced the pressures required to dissolve the materials in CO<sub>2</sub><sup>(34)</sup>. Other studies also demonstrated the benefits of adding fluorinated groups to create CO<sub>2</sub>-philic surfactants<sup>(5,10)</sup>. Further studies were done using fluorinated compounds to decrease the miscibility pressures of polymers in scCO<sub>2</sub><sup>(32,35-39)</sup>.



**Figure 1:** Sample Poly(Fluoroacrylate)



**Figure 2:** Sample Poly(Fluoroether)



**Figure 3:** Poly(Dimethylsiloxane)

Given the success found in the solubility of fluorinated materials, can one assume that adding fluorinated groups in any fashion will always lower the miscibility pressures of a polymer? Poly(fluoroacrylates) have some of the lowest surface tensions and thus cohesive energy density values of all polymers<sup>(32)</sup>, and this along with their low glass transition temperature ( $T_g$ ) values are indications of low polymer self-interactions causing these materials to be among the most CO<sub>2</sub>-philic of all polymers. There are three main interactions that govern the solubility of a polymer in CO<sub>2</sub>: solvent-solvent interactions, solvent-solute interactions, and solute-solute interactions<sup>(40)</sup>. Ideally, the solvent-solute interactions should be high, while the other interactions are kept to a minimum, meaning that the polymer should have strong interactions with CO<sub>2</sub>, while not interacting with itself. However, simply adding fluorinated groups to a polymer will not guarantee lower miscibility pressures in CO<sub>2</sub>. Beckman and co-workers showed that there is an optimal amount of fluorinated groups necessary to achieve the lowest cloud point pressures<sup>(37)</sup>. Beckman also indicated that incorporating many short chains with the same fluoroether content given by fewer long chains resulted in lower miscibility pressures for the polymers. This was attributed to a more favorable entropy of mixing and increased free volume, giving the polymer a lower  $T_g$ <sup>(37)</sup>.

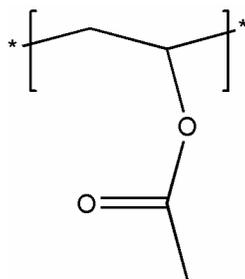
McHugh et al. conducted work showing that a small amount of polarity plays a role in dissolving fluorinated polymers in CO<sub>2</sub>. The works compared poly(vinylidene fluoride-co-22 mol % hexafluoropropylene) (Fluorel) and poly(tetrafluoroethylene-co-19 mol % hexafluoropropylene) (FEP<sub>19</sub>). Fluorel stays in solution to temperatures down to approximately 100 °C and pressures of 750 bar while FEP<sub>19</sub> falls out of solution below

185 °C regardless of the pressure. Despite the incorporation of fluorinated groups, FEP<sub>19</sub> lacks the polar vinylidene group of Fluorel. McHugh observed that the dipole moment of vinylidene fluoride interacted favorably with the quadrupole moment of CO<sub>2</sub>, resulting in the solubility of Fluorel at lower temperatures where polar interactions are suspected to be magnified<sup>(36,41,42)</sup>. The effect of polarity and the dipole-quadrupole interactions was observed by McHugh et al in a study of the fluorination of poly(isoprenes)<sup>(43)</sup>. The McHugh group also studied the benefits of polar character in a variety of fluorinated hydrocarbon polymers<sup>(44)</sup>. This dipole-quadrupole interaction allows for favorable polymer-CO<sub>2</sub> interactions, which in combination with low polymer-polymer interactions will allow the polymer to dissolve in CO<sub>2</sub> at lower pressures. In addition to fluorinated compounds, Hoefling and colleagues found silicone-based amphiphiles to exhibit CO<sub>2</sub> miscibility at temperatures up to 313 K and at pressures of less than 40 MPa<sup>(45)</sup>. Silicone-based polymers (see **Figure 3**), poly(dimethylsiloxanes), have also been found to dissolve in CO<sub>2</sub> at low pressures<sup>(46,47)</sup>.

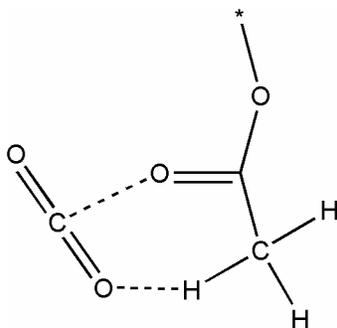
While very successful at lowering cloud point pressures of polymers, fluorinated amphiphiles carry with them economic drawbacks. Seeing this shortcoming, researchers began to search for non-fluorous functional groups that could have the effect of lowering miscibility pressures similar to the extent of the fluorous compounds. In order to design a polymer that was likely to exhibit low miscibility pressures in CO<sub>2</sub>, several factors had to be taken into account. As noted previously and seen numerous times in the literature, most polymers must have a low T<sub>g</sub> and CED to exhibit CO<sub>2</sub> miscibility down to low pressures<sup>(32,48)</sup>. In addition to having limited self-interactions, the polymer must interact

favorably with CO<sub>2</sub>. In the case of McHugh's work with fluoropolymers, polarity provided the dipole-quadrupole interactions necessary for dissolution in CO<sub>2</sub><sup>(36,42-44)</sup>. For non-fluorous polymers, the focus of interaction between CO<sub>2</sub> and the polymer became the Lewis acid/base interactions, since carbon dioxide has been shown to act as a Lewis acid<sup>(3)</sup>. Kazarian et al used FT-IR to determine that electron rich functional groups such as the carbonyl group exhibited specific interactions (Lewis acid-base) with CO<sub>2</sub>. This study presented the evidence for the Lewis acid-base interactions between the electron donor (Lewis base on polymer) and the electron acceptor (Lewis acid carbon in CO<sub>2</sub>)<sup>(49)</sup>. Given this information about the carbonyl group, many researchers began to see the potential of a Lewis base in creating a non-fluorous CO<sub>2</sub>-phile. Using this information, many polymers consisting of only carbon, hydrogen, and oxygen were dissolved in CO<sub>2</sub><sup>(36,50,51)</sup>. Fink and colleagues produced a work that investigated the effect that various side chains had on the miscibility pressure of poly(dimethylsiloxanes) in CO<sub>2</sub><sup>(52)</sup>. By placing different side chains and varying amounts of those side chains onto a constant chain-length silicon backbone, the effects of each chain and the extent of substitution could be independently observed. Using a carbonyl group, a Lewis base to promote polymer-CO<sub>2</sub> interactions, as an electron donor group and copolymers of ethers and CO<sub>2</sub>, Sarbu and colleagues produced non-fluorous polymers with low miscibility pressures<sup>(50,51)</sup>. Polyethers were also successfully studied for their CO<sub>2</sub> solubility by Drohmann and Beckman<sup>(53)</sup>. McHugh et al investigated the effects of placing the carbonyl group in the backbone rather than as part of a side chain<sup>(54)</sup>. Though many functional groups containing a Lewis base have been effective in lowering the cloud point pressure of non-fluorous polymers, incorporating the acetate group as a side chain

of a hydrocarbon chain [poly(vinyl acetate)] (see **Figure 4**) currently yields the most versatile non-fluorous CO<sub>2</sub>-philic polymer as it is miscible with CO<sub>2</sub> at relatively low pressures at high molecular weights and weight percentages<sup>(55)</sup>. Wallen et al has investigated the interactions between CO<sub>2</sub> and the methyl acetate group on sugars. The work speculates that not only is there a Lewis acid/base interaction between the carbonyl and the carbon in CO<sub>2</sub>, but there is also a weaker, complementary hydrogen bonding interaction (see **Figure 5**) from the methyl protons and the oxygen in CO<sub>2</sub>. The results give a possible explanation as to why the acetate group has proven to be the most effective Lewis base in lowering miscibility pressures of polymers<sup>(56,57)</sup>. It is upon these works that the current work is based.



**Figure 4:** Poly(Vinyl Acetate)



**Figure 5:** Proposed CO<sub>2</sub>-Acetate Interaction<sup>(56,57)</sup>

### 3.0 RESEARCH OBJECTIVES

The purpose of this work was to systematically examine the effects of Lewis base groups on the miscibility pressures of polymers in CO<sub>2</sub> by noting the effects of small changes in side chain or backbone composition. The ultimate goal of the project is to develop a polymer made from only carbon, hydrogen and oxygen that exhibits solubility in CO<sub>2</sub> at pressures similar to that of the known fluorinated CO<sub>2</sub>-philes. Lewis base groups were placed on various pre-made oligomers, and they were compared to each other as well as to various degrees of substitution of the same group. Also, several purchased polymers were tested to observe their behavior in CO<sub>2</sub>. This research had the following goals:

- 1) To investigate the effects on miscibility pressures in CO<sub>2</sub> resulting from the placement of ketones, ethers, hydrocarbon branching, silicon branching, and alkane side chains on a poly(dimethylsiloxane) (PDMS) backbone with 25 repeat units.
- 2) To investigate the effect of molecular weight on miscibility pressures in CO<sub>2</sub> of PDMS and poly(propylene oxide) (PPO).
- 3) To investigate the effect of miscibility pressures in CO<sub>2</sub> resulting from the placement of acetate and ethyl ether Lewis base side chains on a polyether backbone.
- 4) To investigate the effect of miscibility pressures in CO<sub>2</sub> resulting from replacing the hydroxyl end groups of the substituted and unaltered poly(propylene oxide) with acetate-functional groups.

- 5) To determine the importance of the polymer-CO<sub>2</sub> interactions versus the polymer self-interactions by comparing PPO to a polymer lacking Lewis base groups but having a low T<sub>g</sub> and CED, poly(propylene) (PP).
- 6) To find a correlation between the work done on the PDMS and the PPO backbones and gain fundamental knowledge concerning the use of Lewis base side chains to lower the miscibility pressures in CO<sub>2</sub> of non-fluorous polymers.
- 7) To determine whether the acetate group is the most effective Lewis base that can be employed on a non-fluorous polymer for the purpose of lowering miscibility pressures in CO<sub>2</sub>.

## 4.0 EXPERIMENTAL METHODOLOGY

### 4.1 Materials

Argon was purchased from Praxair of Danbury, CT at 99.99% purity. The copolymers of methylhydrosiloxane [a) 3.5 mole%, b) 6.5 mole %, c) 16.5 mole%, and d) 27.5 mole%] and dimethylsiloxane, polydimethylsiloxanes (MW = 1250, 2000, and 3780), and platinum-(vinyl tetramethyldisiloxane) catalyst in xylene (low color) were purchased from Gelest of Morrisville, PA. The poly(epichlorohydrin) mixture (85% poly(epichlorohydrin), 15% 1,3-Dioxolane) was obtained from 3M with the poly(epichlorohydrin) having an approximate molecular weight of 2400. Low molecular weight atactic poly(propylene) (MW 425 and 1000) was obtained from Sunoco Chemicals. Anhydrous solvents, all materials to be grafted to the polymers, and all other chemicals were purchased from Aldrich and used without purification unless otherwise noted.

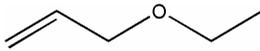
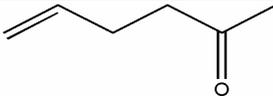
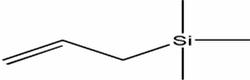
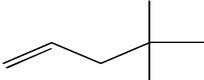
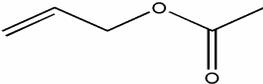
### 4.2 Analyses

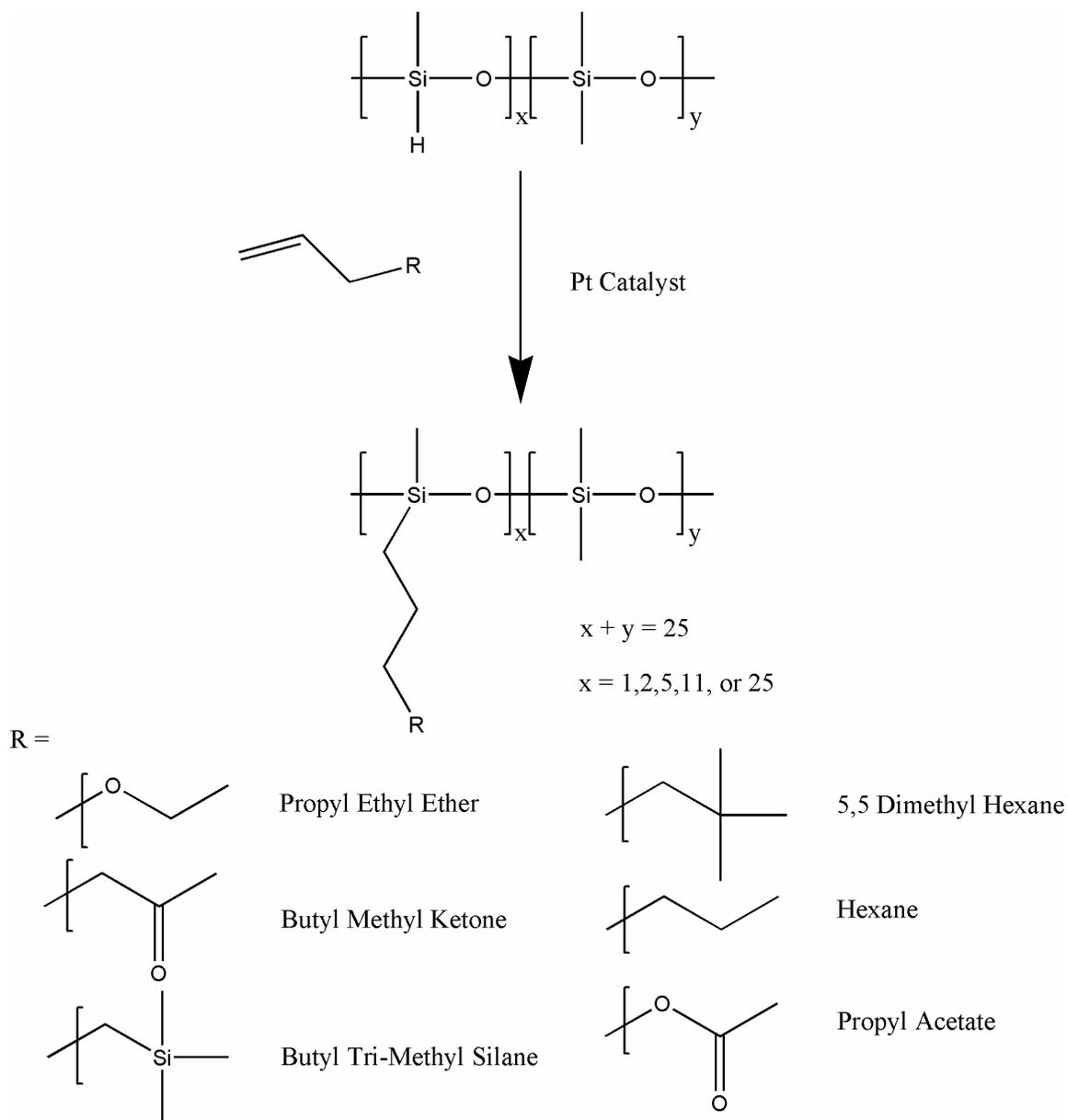
All  $^1\text{H-NMR}$  spectra were obtained using a Bruker DMX 300 instrument with a deuterated chloroform solvent containing tetramethylsilane as an internal reference. FT-IR spectra were taken on a Matson Instruments Research Series FT-IR.

### 4.3 Synthesis of Grafted MethylHydrosiloxane-Dimethylsiloxane Copolymers

Grafted copolymers were synthesized according to the procedure used by Fink et al.<sup>(52)</sup> (see **Figure 6**). The glassware was oven-dried overnight and purged with ultra-high purity argon before use. In a typical experiment 10 g (27.6 mmol) of copolymer(16.5% MethylHydrosiloxane – 83.5% Dimethylsiloxane) and 2.39 g (27.8 mmol) allyl ethyl ether were charged into a 500 ml three-neck, round-bottomed flask. The system was then equipped with a magnetic stir-bar, a condenser, and an argon feed. 60 mL of anhydrous toluene and 100 mg of platinum-vinyl tetramethyldisiloxane complex in xylene (low color) were added to the reaction mixture. The solution was stirred for 3 – 4 hours at room temperature under an argon atmosphere. Then, it was heated to 45 °C and stirred overnight. During heating the color of the solution turned a slight brownish-yellow. The completion of the reaction was verified by the disappearance of the Si-H band at 2157<sup>-1</sup> using FT-IR (see **Figure A1** in **Appendix A**). 0.3 g of decolorizing carbon was added to the hot solution, and the mixture was stirred at 65 °C for 1 – 2 hours. The solution was then filtered while hot. Upon evaporation of the solvent under reduced pressure, a slightly yellow copolymer was isolated.

**Table 1** shows a summary of the syntheses conducted using the siloxane backbone. Each siloxane oligomer had 25 repeat units. The table displays the number of substituted side chains, the structure of the side chain, the amount of polymer used, and the amount of side chain base material used. The volume of solvent, the duration of reaction, the temperature, and amount of catalyst remained constant through all reactions.

Table 1: Synthesis of Grafted MethylHydrosiloxane-Dimethylsiloxane Copolymers			
Reactive Sites	Side Chain	mmol Si-H	mmol allyl compound*
1		2.68	6.40
2		5.42	12.7
5		27.7	27.8
11		32.2	39.0
1		2.70	3.37
2		5.42	5.82
5		27.6	27.6
11		63.5	71.3
25		82.0	82.9
1		2.70	3.25
1		2.67	3.57
5		14.1	16.1
5		27.6	27.6
* In some cases an excess was used to ensure complete conversion			



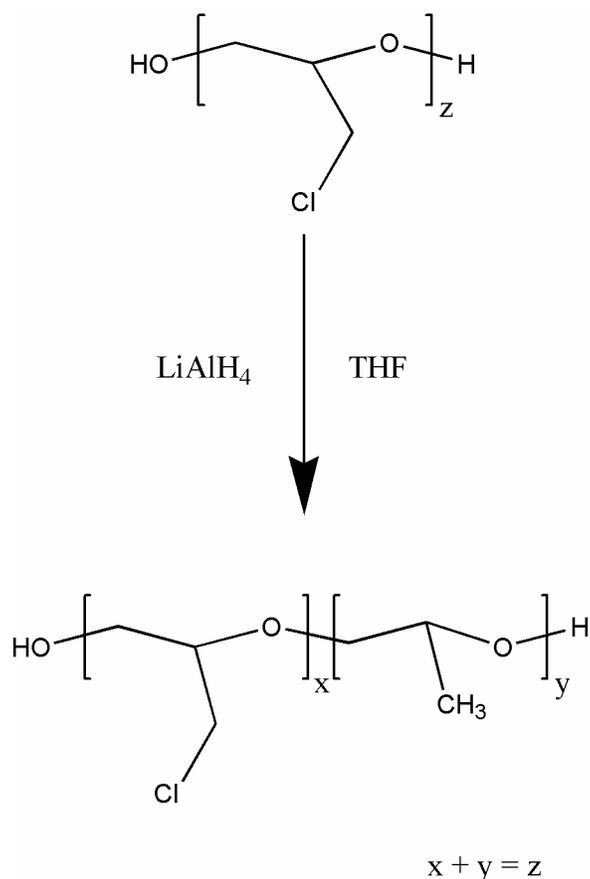
**Figure 6: Silicon Backbone Reaction Mechanism**

The various siloxane polymers were characterized using  $^1\text{H-NMR}$  (see **Figures B1 – B7** in **Appendix B**). The complete removal of starting material was verified by the disappearance of the allyl double bond peaks that are typically between 5 and 6 ppm. Following is the  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) peak data for each of the grafted side chains on the silicon-backbone polymers. **MethylHydrosiloxane:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 4.70 (s, Si- $\text{H}$ ). **Propyl ethyl ether:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 0.63 (Si- $\text{CH}_2\text{-CH}_2$ ), 1.31 (t, -O- $\text{CH}_2\text{-CH}_3$ ), 1.75 (-Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ ), 3.49 (-O- $\text{CH}_2\text{-CH}_3$ ), 3.59 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$ ). **Butyl methyl ketone:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 0.52 (t, Si- $\text{CH}_2\text{-CH}_2$ ), 1.36 (-Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ ), 1.61 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ ), 2.14 (s, - $\text{CH}_2\text{-CO-CH}_3$ ), 2.42 (t, - $\text{CH}_2\text{-CO-CH}_3$ ). **Butyl tri-methyl silane:**  $\delta$  0.14 (Si- $\text{CH}_3$ ), 0.55 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$ ), 1.41 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$ ). **5,5 dimethyl hexane:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 0.56 (Si- $\text{CH}_2\text{-CH}_2$ ), 0.94 (s, C- $\text{CH}_3$ ), 1.40 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}$ ). **Hexane:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 0.55 (Si- $\text{CH}_2\text{-CH}_2$ ), 0.94 (- $\text{CH}_2\text{-CH}_3$ ), 1.33 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ). **Propyl acetate:**  $\delta$  0.11 (Si- $\text{CH}_3$ ), 0.38 (Si- $\text{CH}_2\text{-CH}_2$ ), 1.50 (Si- $\text{CH}_2\text{-CH}_2$ ), 1.83 (s, -O- $\text{CO-CH}_3$ ), 3.82 (Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O}$ ).

#### 4.4 Partial Reduction of Poly(epichlorohydrin) to form Epichlorohydrin/Propylene Oxide Copolymers

In order to achieve varying degrees of substitution with a polyether backbone, poly(epichlorohydrin) was first reduced to a poly(epichlorohydrin)/poly(propylene oxide) copolymer using lithium aluminum hydride ( $\text{LiAlH}_4$ ). This allowed for the replacement with methyl groups of a known amount of chloride groups (see **Figure 7**). The remaining chloride groups were later allowed to react in a grafting mechanism to incorporate functional side chains onto the polymer chain (see **Figures 8 and 9**). The degree of the reduction can be directly controlled by the amount of lithium aluminum hydride ( $\text{LiAlH}_4$ ) added to the reaction. The degrees of reduction used in this work and the corresponding amounts of reducing agent are shown in **Table 2**. The glassware was oven-dried overnight and purged with ultra-high purity argon before use. As adapted from an existing procedure<sup>(58)</sup>, in a typical reaction (**Figure 7**) 6.30 g (57.9 mmol  $\text{CH}_2\text{-Cl}$ ) of polymer mixture (85% poly(epichlorohydrin) (PECH) – 15% dioxolane) was charged into a 500 ml three-neck, round-bottomed flask. The system was then equipped with a magnetic stir-bar, a condenser, and an argon feed. 50 ml of anhydrous THF was added to completely dissolve the polymer mixture. After dissolution, 58 mL (58.0 mmol)  $\text{LiAlH}_4$  (1.0 M in THF) was added to the flask dropwise. The solution was heated to 45 °C and stirred for 3 days. After cooling, the excess  $\text{LiAlH}_4$  was eliminated with approximately 55 mL of a (1:1) mixture of THF/DI  $\text{H}_2\text{O}$  mixture. This mixture was added dropwise with a syringe since the result was rapid hydrogen gas formation. To complex the aluminum salts, 16.26 g (57.6 mmol) of potassium sodium tartrate was added. The

mixture was stirred for 30 minutes, and the salts were then removed by filtration. To ensure the complete removal of the salts, the THF/H<sub>2</sub>O mixture was evaporated under reduced pressure, and the sample was dissolved in toluene. After a second filtration, the toluene and any residual 1,3-dioxolane from the original polymer mixture were removed under reduced pressure, and the product formed was a very pale-yellow, transparent, viscous liquid. The polymer was characterized by <sup>1</sup>H-NMR analysis, and the CH<sub>3</sub> peak was clearly visible in the NMR spectrum at about 1.1 ppm (see **Figure B8** in **Appendix B**). **Partially reduced PECH:** δ 1.16 (-CH<sub>3</sub>), 3.65 (-CH<sub>2</sub>-CH-O), 3.65 (-CH<sub>2</sub>-Cl).



**Figure 7:** Reduction of Poly(epichlorohydrin)

<b>Reaction Composition</b>		<b>Integration Results</b>		
<b>mmol Repeat Units</b>	<b>mmol LiAlH<sub>4</sub></b>	<b>Backbone Peak</b>	<b>Methyl Peak</b>	<b>% Reduction</b>
321	80	1	0.21	31
317	165	1	0.42	54
421	360	1	0.57	69
222	165	1	0.59	71
381	400	1	0.81	85
187	195	1	0.99	100

Complete conversion was verified by the integration of the CH<sub>3</sub> peak at about 1.1 ppm and the backbone carbon peaks between 3.4 and 3.8 ppm. The ratio of these peaks (see **Table 2**) was used to determine the approximate degree of reduction. The peak ratios and corresponding degrees of reduction were calculated by the following equation:

$$\frac{BackbonePeak}{MethylPeak} = \frac{5x + 3y}{3y} \quad (4-1)$$

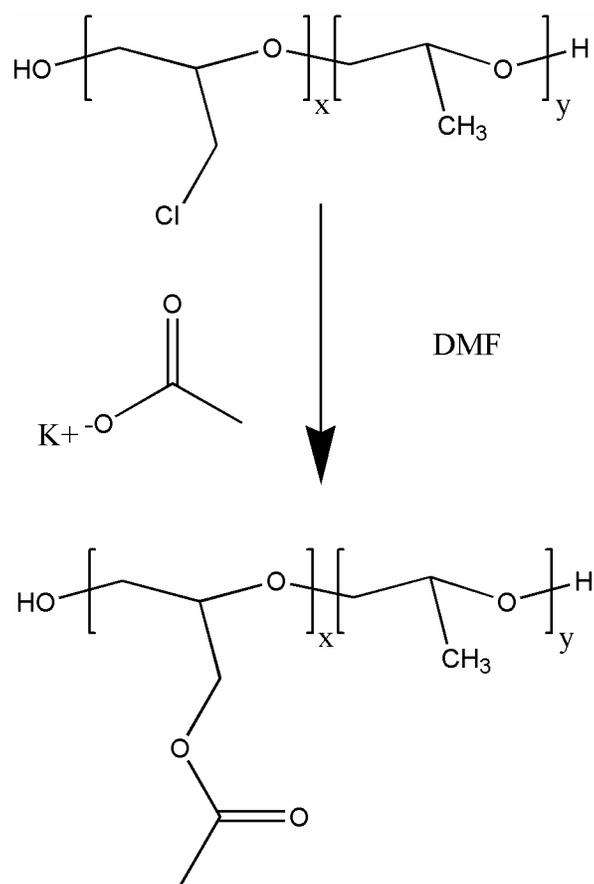
where x is the ratio of unreduced repeat units (containing five protons) and y is the ratio of reduced repeat units (containing three protons that contribute to the backbone peak and the three methyl protons). x and y must add up to 1. Solving these equations for y gives the approximation for the degree of reduction.

#### 4.5 Synthesis of Acetate-functionalized Poly(propylene oxide)

Acetate functional poly(propylene oxide) was synthesized according to the procedure used by Cohen<sup>(59)</sup>. The glassware was oven-dried overnight and purged with ultra-high purity argon before use. (Note: A large excess (see **Table 3**) of potassium acetate was used in all cases to ensure a complete reaction.) In a typical experiment 4.7 g (15.3 mmol CH<sub>2</sub>-Cl) of partially reduced PECH (30%) was charged into a 500 ml three-neck, round-bottomed flask and mixed with approximately 50 mL of DMF. The system was then equipped with a magnetic stir-bar, a condenser, and an argon feed and heated to 135 °C. After the dissolution of the polymer, 10.5 g (107 mmol) potassium acetate was added to the solution. The solution was stirred overnight under an argon atmosphere. During the reaction, the solution became cloudy from KCl salt precipitation. The reaction was then cooled, and the polymer was precipitated in DI water. The polymer was washed with DI water, and the water/DMF mixture was decanted several times. To remove the residual water, the polymer was dissolved in toluene and dried over magnesium sulfate (MgSO<sub>4</sub>). The solution was filtered through Whatman #1 filter paper, and the toluene was removed under reduced pressure, yielding a yellow, transparent, viscous liquid.

**Table 3** shows a summary of the syntheses conducted to graft the acetate onto the poly(propylene oxide). The table displays the percentage of acetate substitution, the base polymer used, the amount of polymer used, and the amount of acetate salt used. The

duration of reaction and the temperature remained constant through all reactions. **Figure 8** illustrates the reaction scheme.



**Figure 8:** Synthesis of Acetate-Functional PPO

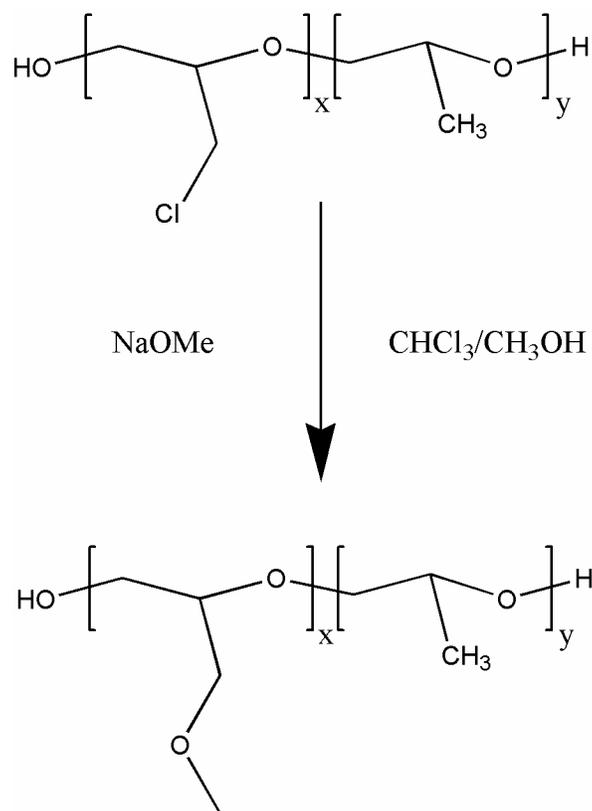
<b>Starting Polymer (Theoretical)</b>	<b>Reaction Composition</b>		<b>% Acetate (Actual)</b>
	<b>mmol CH<sub>2</sub>-Cl</b>	<b>mmol KAc</b>	
85% Reduced PECH	12.8	52.0	12
71% Reduced PECH	16.5	50.9	22
54% Reduced PECH	30.4	103	44
31% Reduced PECH	40.0	107	69
0% Reduced PECH	64.4	124	100

To verify the acetate-substituted product, the <sup>1</sup>H-NMR spectra were analyzed for the appearance of the Ac-CH<sub>3</sub> peak at 2.1 ppm. The CH<sub>2</sub> protons in the acetate chain were seen in a doublet at 4.1 - 4.2 ppm which should integrate at two-thirds of the peak at 2.1 ppm. To determine the degree of acetylation and to verify the original approximation for degree of reduction, the Ac-CH<sub>3</sub> peak at 2.1 ppm was compared to the methyl peak in the PPO repeat unit at 1.1 ppm (see **Figure B9** in **Appendix B**). The sum of the integrations should be one, with the integration of the peak at 2.1 indicating the percentage of repeat units with acetate substitution. Due to the isolation of the peaks and clear integration results, this method is more accurate than the method used to determine the degree of reduction and was the method used for the final results. **Acetate Grafted PPO:** δ 1.13 (-CH<sub>2</sub>-CH(-CH<sub>3</sub>)-O-), 2.07 (s, -O-CO-CH<sub>3</sub>), 3.64 (-CH<sub>2</sub>-CH-O-), 4.17 (d, -CH<sub>2</sub>-O-CO-CH<sub>3</sub>).

#### 4.6 Synthesis of Methyl Ether-Functionalized Poly(propylene oxide)

The glassware was oven-dried overnight and purged with ultra-high purity argon before use. (Note: A large excess of sodium methoxide was used (see **Table 4**) in all cases to ensure a complete reaction.) In a typical experiment 7.10 g (13.3 mmol CH<sub>2</sub>-Cl) of partially reduced PECH (88% reduced) was charged into a 500 ml three-neck, round-bottomed flask and mixed with approximately 50 mL of chloroform. The system was then equipped with a magnetic stir-bar, a condenser, and an argon feed. After the dissolution of the polymer, approximately 65 mL (32.5 mmol) of sodium methoxide (NaOMe) solution (0.5 M in methanol) was added to the solution. The solution was stirred overnight under an argon atmosphere at 35 °C. During the reaction, the solution became cloudy with NaCl salt precipitation. The reaction was then cooled, and the chloroform/methanol solvent mixture was removed under reduced pressure. The polymer was dissolved in toluene, and the salt was filtered through Whatman #1 filter paper out of the mixture. The toluene was removed under reduced pressure, yielding a yellow, transparent, viscous liquid.

**Table 4** shows a summary of the syntheses conducted to graft the methyl ether onto the poly(propylene oxide). The table displays the percentage of ether substitution, the base polymer used, the amount of polymer used, the amount of ether salt used, and the volume of chloroform added. The duration of reaction and the temperature remained constant through all reactions. **Figure 9** illustrates the reaction scheme.



**Figure 9:** Synthesis of Methyl Ether-Functional PPO

Table 4: Synthesis of Methyl Ether-Functional Poly(propylene oxide)				
Starting Polymer (Theoretical)	Reaction Composition			% Ether (Actual)
	mmol CH <sub>2</sub> -Cl	mmol NaOMe	mL Chloroform	
85% Reduced PECH	13.3	32.5	50	12
71% Reduced PECH	22.7	45.0	100	22
50% Reduced PECH	18.1	25.0	75	44
0% Reduced PECH	78.1	80.0	100	100

To characterize the ether-substituted product, the <sup>1</sup>H-NMR spectra were analyzed in a similar manner to the analysis of the partially reduced PECH. The CH<sub>2</sub> and CH<sub>3</sub> protons in the methyl ether chain show up in the same location as the backbone protons of the PECH. To verify the addition of the ether chains, the ratio of the methyl group

peak from the reduced repeat units at 1.1 ppm and the broad PECH/ether peaks from 3.4 to 3.8 ppm was taken (see **Figure B10** in **Appendix B**). The new ratio was compared to the original degree of reduction ratio and showed that the appropriate amount of protons was attached to the polymer backbone. The peak ratios and corresponding degrees of reduction calculated by the following equation:

$$\frac{(\text{Backbone} + \text{Ether})\text{Peak}}{\text{MethylPeak}} = \frac{8x + 3y}{3y} \quad (4-2)$$

where x is the ratio of ether-substituted repeat units (containing eight protons) and y is the ratio of reduced repeat units (containing three protons that contribute to the backbone peak and the three methyl protons). The sum of x and y must be one. Solving these equations for x verified the degree of substitution. There was one case in which this method could not be applied. For the 100% ether substituted PECH, there was no methyl peak at 1.1 ppm since none of the repeat units had been reduced. In this case the weight of the sodium chloride salt byproduct was taken, and its molar equivalence to the polymer reactant was used to verify the completed reaction. **Methyl Ether Grafted PPO:**  $\delta$  1.14 (-CH<sub>2</sub>-CH(-CH<sub>3</sub>)-O-), 3.71 (-CH<sub>2</sub>-CH(-CH<sub>2</sub>-O-CH<sub>3</sub>)-O-).

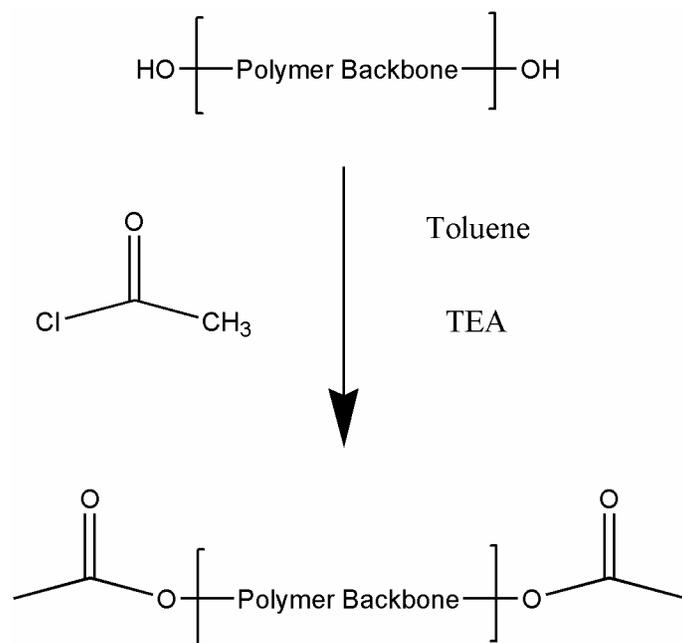
#### 4.7 Capping of the Hydroxyl End Groups of Select PECH/PPO Polymers

The glassware was oven-dried overnight and purged with ultra-high purity argon before use. (Note: A large excess of acetyl chloride was used in all cases to ensure a complete reaction.) In a typical experiment 10.51 g (10.5 mmol -OH) of PPO (MW 2000) was charged into a 500 ml three-neck, round-bottomed flask and mixed with approximately 100 mL of toluene. The system was then equipped with a magnetic stir-

bar, a condenser, and an argon feed. After the dissolution of the polymer, approximately 3 mL (42.2 mmol) of acetyl chloride (AcCl) and approximately 3 mL (21.5 mmol) of triethylamine were added to the solution. The solution was stirred overnight under an argon atmosphere at room temperature. During the reaction, the solution became cloudy with salt precipitation. The reaction was then filtered twice through Whatman #1 filter paper to remove the salt; the toluene, excess acetyl chloride, and excess triethylamine (TEA) were removed under reduced pressure. The capped polymers showed no physical differences from their uncapped counterparts, appearing as yellow, viscous oils.

**Table 5** lists the polymers that were capped at 100% conversion. The duration of reaction and the temperature remained constant through all reactions. **Figure 10** illustrates the reaction scheme.

<b>Table 5: Polymers Capped with Acetate</b>
100% Acetate Substituted PECH PPO (MW 2000)
12% Acetate Substituted PECH
12% Methyl Ether Substituted PECH
PECH



**Figure 10:** Capping of PECH/PPO Polymers with the Acetate Group

To verify the completion of the reaction, a FT-IR spectrum was taken. The -OH peaks at  $1080^{-1}$ ,  $1060^{-1}$ , and a broad peak at approximately  $3500^{-1}$  disappeared as the hydroxyl groups were replaced by the acetate. There was still a residual peak near  $3500^{-1}$  as there was water present. On the polymers without acetate substitution in the backbone, the methyl protons on the acetate end groups were easily visible in the  $^1\text{H-NMR}$  spectrum at 2.1 ppm (see **Figure B11** in **Appendix B**).

#### **4.8 Purification of Low Molecular Weight Poly(propylene)**

The solvents were removed from a solution of poly(propylene) (MW 425) oligomer in hexane and water. A  $^1\text{H-NMR}$  spectrum of the sample verified the removal of the solvents. The PP (MW 1000) was received as an amorphous, white solid mixed with crystalline beads of high molecular weight PP. An included GPC spectrum provided by Sunoco Chemicals indicated that a majority of the sample had a molecular weight of 1000. The mixture was placed in hexane which dissolved the PP 1000, while the high molecular weight material remained as an insoluble solid. The high molecular weight material was filtered through Whatman #1 filter paper out of the solution, and the hexane was removed under reduced pressure. The product was pure poly(propylene) at the desired molecular weight of approximately 1000.

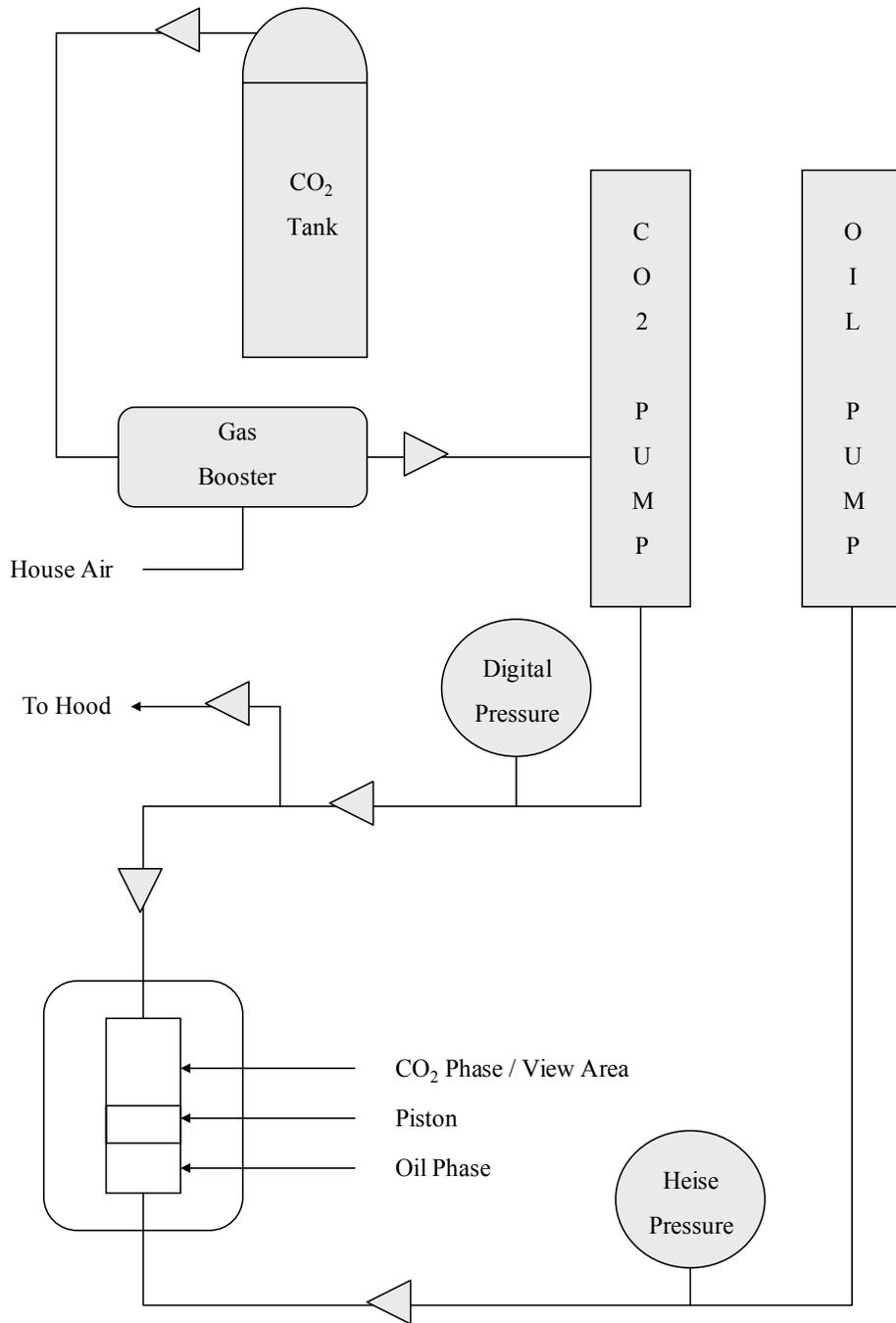
#### 4.9 Synthesis of Low Molecular Weight Poly(acetaldehyde)

Acetaldehyde was polymerized according to a procedure used by Vogl<sup>(60)</sup>. The glassware was oven-dried overnight and purged with ultra-high purity argon before use. 20 mL (356.8 mmol) of acetaldehyde was charged into a 200 ml volumetric flask and mixed with approximately 10 mL of ethyl ether. The system was then equipped with a magnetic stir-bar and purged with argon. The flask was lowered into a mixture of dry ice and acetone and brought to a temperature of approximately -78°C. After the cooling of the mixture, approximately 0.15 mL (0.95% wt. %) of concentrated hydrochloric acid (HCl) solution (aqueous) was added to the flask. The solution was stirred and the cold bath maintained for four hours. To cap and stabilize the polymer, 80 mL (843.8 mmol) of acetic anhydride and 10 mL (123.6 mmol) of pyridine were added to the reaction, and the system was allowed to slowly warm to room temperature overnight. The polymer was precipitated in ice water and extracted in a separatory funnel with chloroform. The chloroform/polymer solution was dried over magnesium sulfate (MgSO<sub>4</sub>) and filtered through Whatman #1 filter paper. The chloroform was removed under reduced pressure, yielding a yellow, transparent, viscous liquid. Poly(acetaldehyde) is not stable and can begin to depolymerize in a solvent or when heated. Therefore the <sup>1</sup>H-NMR spectrum will show trace amounts of monomer due to dissolution in chloroform. The product was verified by <sup>1</sup>H-NMR (see **Figure B13** in **Appendix B**). **Poly(acetaldehyde):** δ 1.35 (-CH(-CH<sub>3</sub>)-O-), 5.04 (-CH(-CH<sub>3</sub>)-O-). **Trace Acetaldehyde:** δ 2.22 (CHO-CH<sub>3</sub>-), 9.80 (CHO-CH<sub>3</sub>-). **Acetate End Groups:** δ 2.10 (-O-CO-CH<sub>3</sub>).

#### 4.10 Phase Behavior Determination

All phase behavior measurements were made in a D. B. Robinson high pressure view cell (see **Figure 11**). In a typical experiment the clear view cell was charged with 0.5 to 1.0 g of polymer sample, mixing balls were added, and the lid of the vessel was sealed. All experiments in this work were conducted at room temperature (~295 K). Oil was introduced into the vessel to lift the piston and remove all atmospheric air, and the cell was filled with a predetermined amount of CO<sub>2</sub> to obtain the desired weight percentage of polymer. The CO<sub>2</sub> input was monitored at the pump by observing the volume that entered the cell at a constant pressure. The density of the CO<sub>2</sub> at the given conditions was calculated using an equation of state obtained from the International Thermodynamic Tables of the Fluid State<sup>(61)</sup> and integrated by Newton's method. After closing the CO<sub>2</sub> feed, the pressure in the vessel was raised by adding oil with a high pressure syringe pump until the polymer dissolves in the carbon dioxide [up to a maximum of 7000 psi (48.26 MPa)]. After dissolution, the oil was removed from the cell to slowly drop the pressure until a cloud point could be visually obtained. Cloud point measurements were taken as the pressure of the clear one-phase solution dropped and a cloud of polymer came out of solution, yielding an opaque two-phase mixture. The data point used was the pressure at which the mixture had 10% of its original transparency. After the cloud point was verified by several readings, the pressure was lowered, and more CO<sub>2</sub> was added until the next desired weight fraction of polymer was reached. The pressure in the cell was raised again, and the process was repeated until a sufficient amount of cloud point data was obtained. The resulting data was graphed to form a cloud

point curve showing the pressure at various weight percentages with an error of +/- 1 MPa.



**Figure 11: High Pressure Equipment for Phase Behavior Determination**

## 5.0 RESULTS AND DISCUSSION

### 5.1 The Effect of Grafted Side Chains on a PDMS Backbone

Model silicon oligomers made from dimethylsiloxane and hydromethylsiloxane were purchased at a total chain length of 25 repeat units. 5 unique oligomers were used with varying hydromethyl composition so that through hydrosilation samples with one, two, five, eleven, or twenty-five side chains were produced. Monitoring the reaction with FT-IR (see **Figure A1** in **Appendix A**) ensured complete conversion of the hydromethyl groups. All grafted side chains included a propyl spacer between the functional group and the PDMS backbone and totaled six atoms in length, with the exception of the branched samples which had a length of five atoms

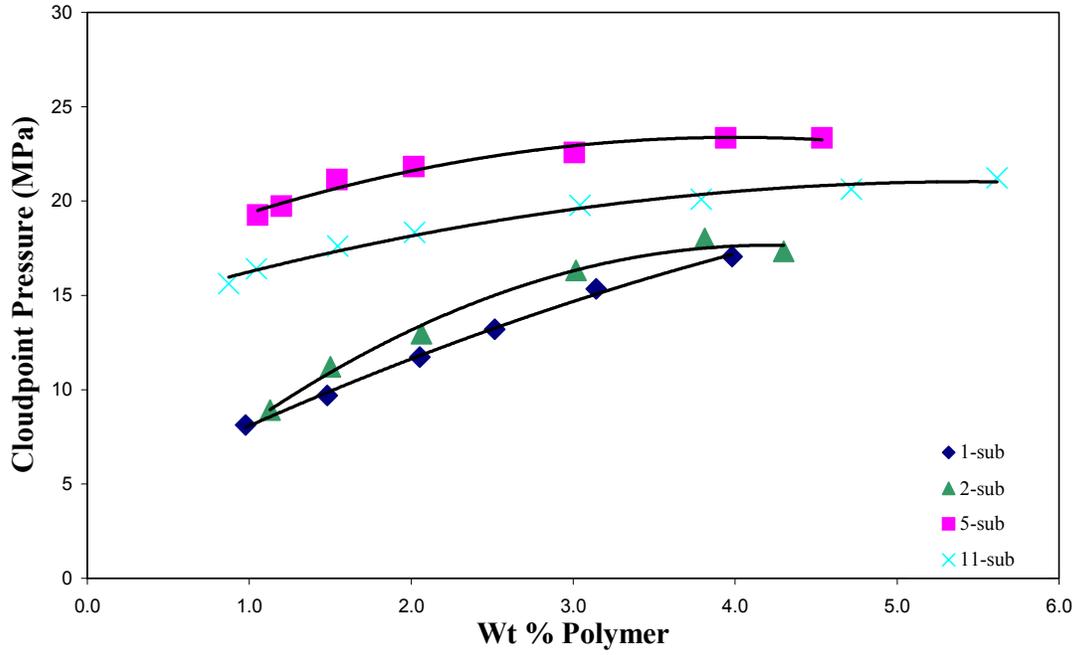
#### 5.1.1 Phase Behavior of PDMS with Grafted Ketone

Ketone groups were grafted onto all five oligomers, giving a full range of degrees of substitution. The one and two substituted ketone-siloxanes gave the best CO<sub>2</sub> solubility while increasing the degree of substitution to five and eleven increased the miscibility pressure of the polymer (see **Figure 12**). Substituting all 25 repeat units with a ketone group resulted in a polymer that was completely insoluble within the limits of the available equipment (48.26 MPa). This set of results was the first to show that there is an optimal amount of substitution for a given side chain. In the case of the ketone, the optimum was one or two substitutions or 4% - 8%. Addition of more ketone groups

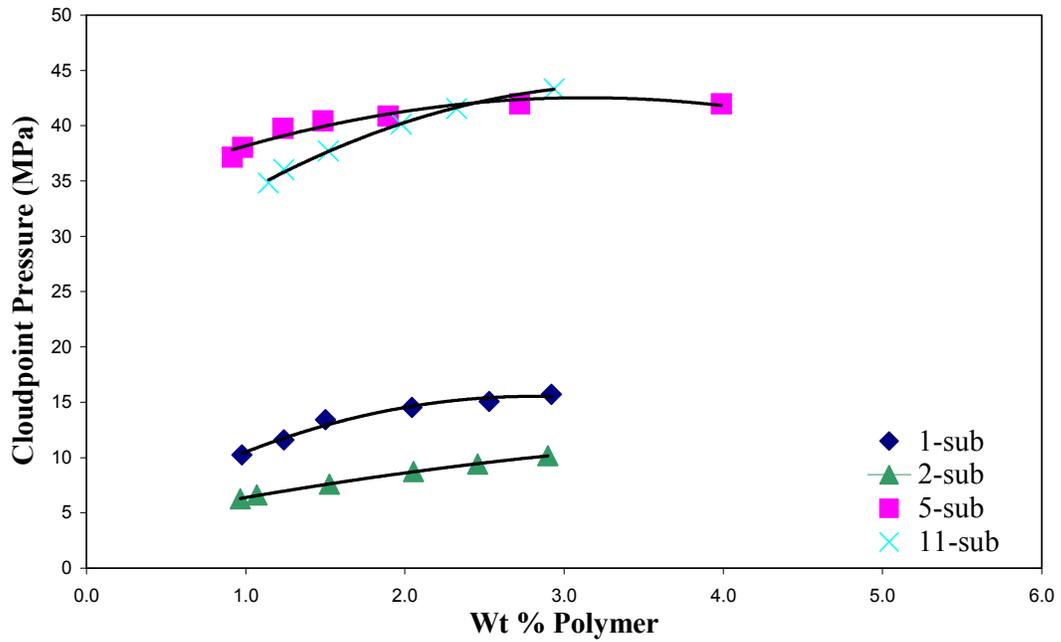
raised the cloud point pressure of the polymer. There are several reasons for this. First the addition of a six carbon chain with an oxygen atom added to the overall molecular weight of the oligomer, decreasing the entropy of mixing. According to the group contribution model developed by van Krevelen<sup>(62)</sup>, the addition of a side chain tended to stiffen the polymer structure allowing less freedom of movement and increasing the cohesive energy density (CED). The cohesive energy density of the base PDMS is very low (Surface Tension: 19.9 mN/m @ 20 °C)<sup>(32)</sup>, approaching the low cohesive energy density of the most CO<sub>2</sub>-philic fluoroacrylates (Surface Tension of poly(1,1-dihydrodecafluorooctyl acrylate): 10 mN/m @ 20 °C)<sup>(32)</sup>, and the addition of the Lewis base containing or branching groups lifted the overall cohesive energy density of the polymer. The ketone groups did have a Lewis base in the carbonyl oxygen, but the interactions between the base and CO<sub>2</sub>, while important, were not enough to overcome the other negative effects. A certain amount of the CED increase could be balanced by the Lewis base interaction with CO<sub>2</sub>, but after a certain point (5-substituted ketone) the effect from the higher cohesive energy density began to be dominant, finally leading to insolubility when all 25 repeat units were substituted.

### 5.1.2 Phase Behavior of PDMS with Grafted Ethyl Ether

Ethyl ether functional groups were grafted onto four of the five available oligomers, excluding the full 25 repeat unit substitution. As with the ketone substitution, the ether-substituted oligomer had an optimal degree of substitution (see **Figure 13**). The two-ether substitution (8%) was the optimal amount of ether content, and when the number of substituted units was increased to five and eleven, the cloud point pressure of the ethyl ether PDMS polymer became dramatically worse, narrowly remaining within the boundaries of the equipment (48.26 MPa). While the one substituted ethyl ether siloxane did not differ as drastically, it was clearly inferior to the 8% ethyl ether substitution. As with the grafted ketones, the cohesive energy density effects appeared to be the dominant characteristic over the Lewis acid/base interactions between the ether oxygen and the CO<sub>2</sub>.



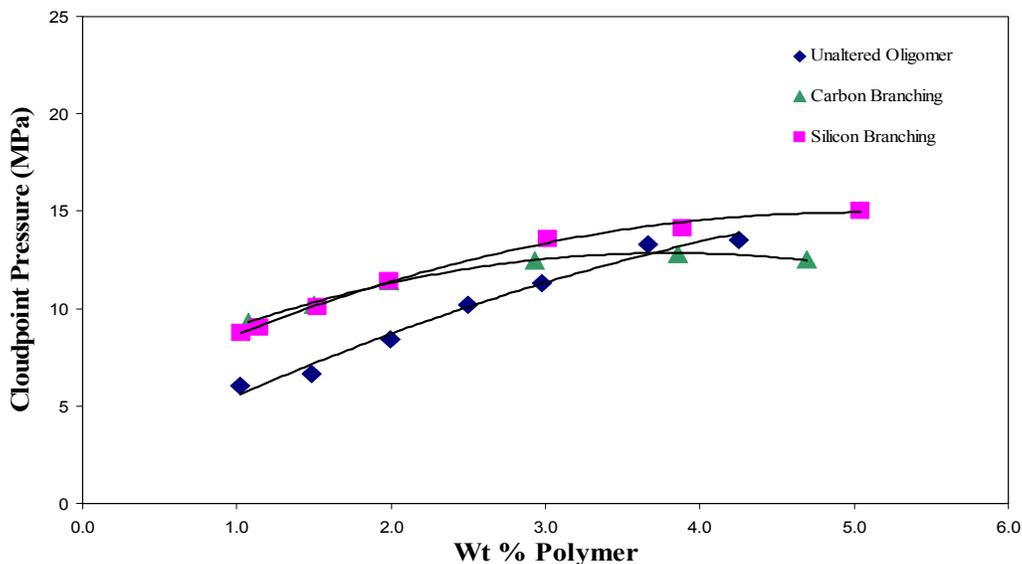
**Figure 12:** Phase Behavior of Ketone Substituted PDMS



**Figure 13:** Phase Behavior of Ethyl Ether Substituted PDMS

### 5.1.3 Phase Behavior of PDMS with Grafted Hydrocarbon Branching

Two forms of a tri-methyl branched group, one with carbon at the center and one with silicon at the center, were grafted onto a silicon oligomer with one hydromethyl reactive site. The results on cloud point pressure of placing these groups were compared to the miscibility pressures of the unaltered oligomer containing one Si-H group. At all observed concentrations, there was very little difference between the polymers with branching groups and the unmodified polymer (see **Figure 14**). Despite elevating the cohesive energy density<sup>(62)</sup>, the addition of the branched groups also contributed to the overall free volume by incorporating more end groups. This drop in  $T_g$  was able to compensate for the decrease in flexibility. Also, there was only one group added per oligomer so the effect of the increased CED was not overwhelming. There was no difference between the branching groups themselves; whether silicon or carbon was the central atom for the branching area, the miscibility pressure of the polymer was not affected. The Si-H group did not interact favorably with CO<sub>2</sub>, and this became more obvious as the Si-H concentration within the polymer was increased. As more hydromethyl groups were left unaltered, the miscibility pressure of the oligomer became steadily higher. In other work done on this project by co-worker, Sevgi Kilic, it was clear that having two Si-H groups in the oligomer greatly increased the cloud point pressure of the oligomer<sup>(47)</sup>.



**Figure 14:** Phase Behavior of Branching Group Substituted PDMS

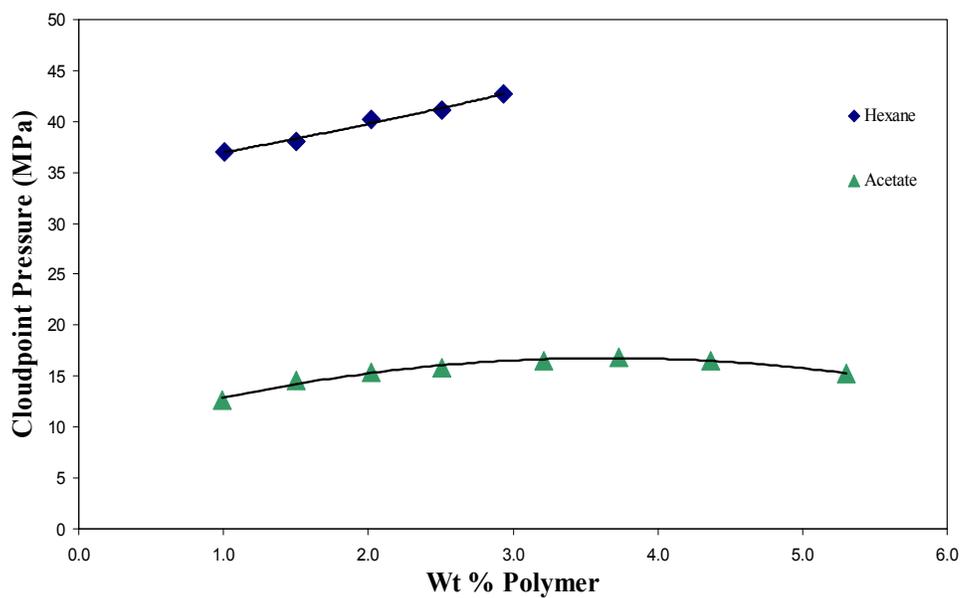
#### 5.1.4 Phase Behavior of PDMS with Grafted Acetate and Hexane

In a previous work<sup>(52)</sup> on this subject, the effects of grafting a hydrocarbon chain, hexane, and an acetate group onto PDMS were observed. In this work, that data was verified for the five-substituted PDMS sample. The hexane chain was a very poor addition as it added cohesive energy density to the polymer<sup>(62)</sup> without the benefit of extra branching groups or a Lewis base site. The acetate group<sup>(47)</sup> performed well as the Lewis base interactions with CO<sub>2</sub> allowed for increased solubility (see **Figure 15**). In this work, only the five-substituted acetate was observed. In efforts made by group member, Sevgi Kilic, five-substituted (20%) acetate was found to be the amount of substitution that allowed for optimal solubility<sup>(47)</sup>. At this degree, the adverse effect of the hydrocarbon on the cohesive energy density achieved the most favorable balance with the positive

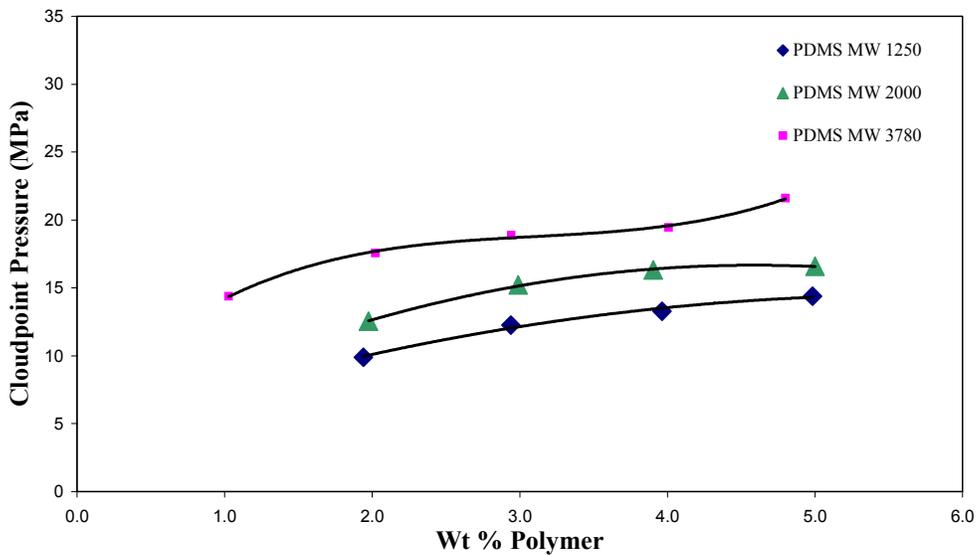
effects of the acetate Lewis base interactions with the solvent, carbon dioxide. With fewer acetate groups, there was less Lewis acid/base interaction resulting in higher cloud point pressures, and with more acetate substitution, the interaction with CO<sub>2</sub> was not strong enough to counterbalance the negative effects from the increased cohesive energy density<sup>(62)</sup>. This comparison clearly showed the vast decrease in cloud point pressure resulting from the incorporation of a Lewis base group in the side chain.

### **5.1.5 The Effect of Molecular Weight on the Phase Behavior of PDMS**

As previously stated, increasing the molecular weight of a polymer results in a drop in the change in entropy of mixing and therefore increased cloud point pressures in CO<sub>2</sub>. This was confirmed with a molecular weight analysis of various PDMS samples. Oligomers of increasing molecular weights (1250, 2000, and 3780) were evaluated for cloud point pressure (see **Figure 16**), and they behaved as predicted. Though the increase in cloud point pressure was not staggering, there was a slight and steady increase as more repeat units were added to the oligomer. This study proved that while molecular weight made a difference in the CO<sub>2</sub> solubility of the polymer, it did not have the radical effect that were seen when a Lewis base was added or when the cohesive energy density was altered.



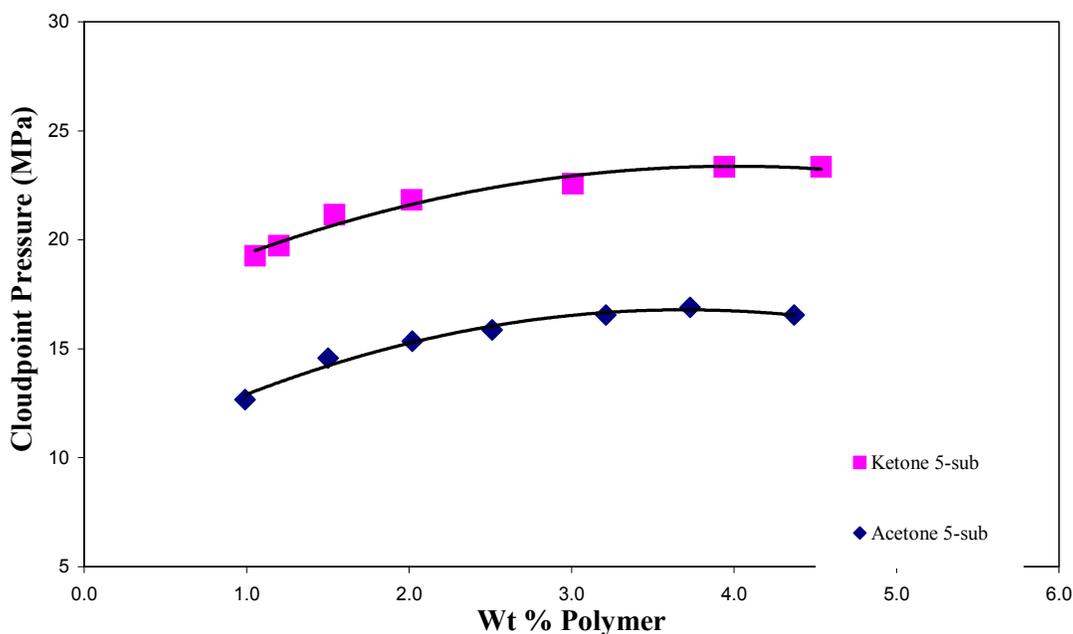
**Figure 15:** Phase Behavior of 5-Substituted Hexane and Acetate Substituted PDMS



**Figure 16:** Molecular Weight Effects on PDMS Solubility in Carbon Dioxide

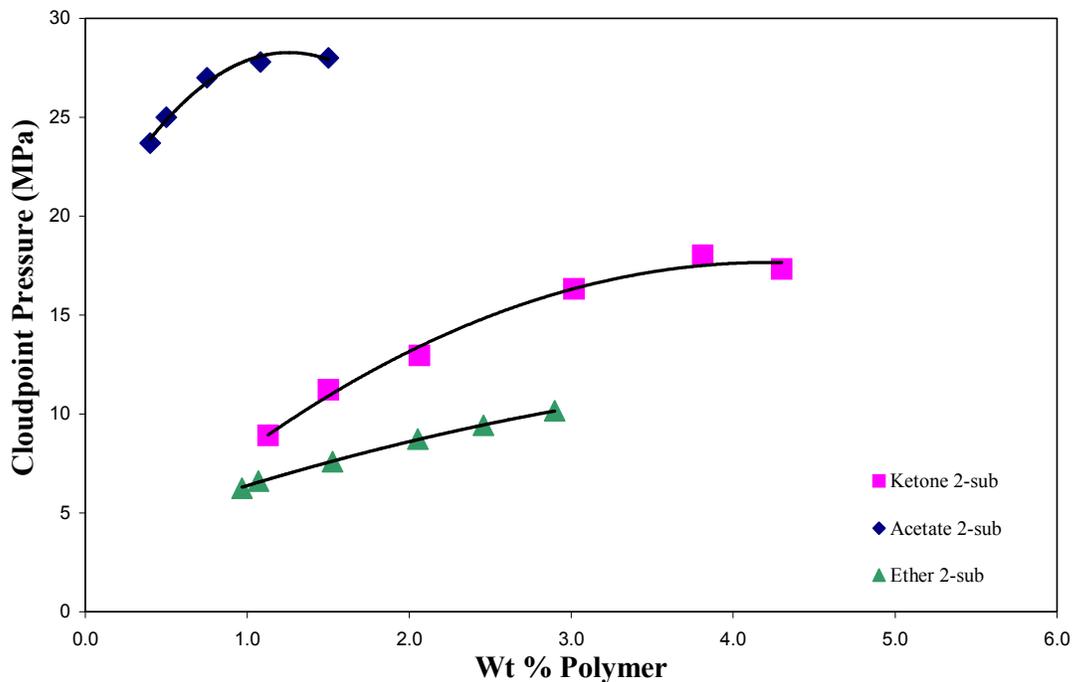
### 5.1.6 Comparison of Grafted Lewis Base Chains on PDMS

As stated previously, the carbonyl group interacts favorably with CO<sub>2</sub><sup>(55)</sup>. To evaluate whether the CO<sub>2</sub> interactions are caused by the acetate group as a whole or simply the carbonyl itself, the acetate grafted PDMS was compared to the ketone grafted PDMS (see **Figure 17**) with five repeat units substituted. While both groups contain a carbonyl group, the acetate group also has an oxygen in the grafted chain. It was hypothesized that the reason that acetate group interacted more with the CO<sub>2</sub> was because the oxygen atom allowed the carbonyl group to rotate more freely in the acetate than the CH<sub>2</sub> group allows the carbonyl in a ketone to rotate<sup>(47)</sup>. This allowed the carbonyl group to rotate to the most optimal position for interaction with CO<sub>2</sub>. The barriers to rotation for the C-O and C-C bonds were found to be 1.1 and 3.0 kcal/mole respectively<sup>(63)</sup>.

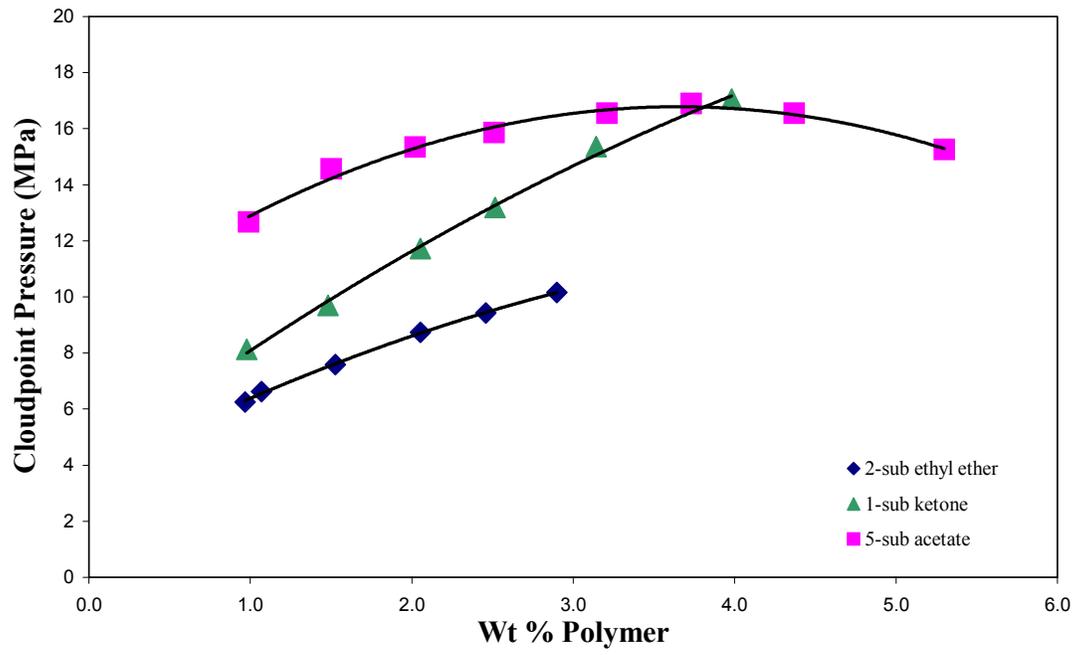


**Figure 17:** Acetate vs. Ketone (5-sub) Grafted PDMS

With two repeat units on the PDMS substituted, the ether group allows for lower miscibility pressures than ketone or acetate (see **Figure 18**). This is near the optimal amount of substitution for ketone and ether, while acetate requires more of a presence on the polymer chain to lower cloud point pressures to a minimum. When comparing the optimal degree of substitution of all tested functional groups (see **Figure 19**), the 2-substituted ether allows for the lowest miscibility pressures. This corresponds to calculations done by fellow group member, Yang Wang. His work for Dr. Karl Johnson indicates that the binding energy between CO<sub>2</sub> and a carbonyl oxygen is almost equal to the binding energy between CO<sub>2</sub> and the ether oxygen<sup>(47)</sup>. This new assertion was later tested on a polyether backbone (see **Section 5.6**).



**Figure 18:** Comparison of Acetate, Ketone, and Ether Groups Substituted on Two Repeat Units of PDMS



**Figure 19:** Comparison of the Optimal Substitution of Grafted Side Chains on PDMS

## 5.2 The Effect of Grafted Side Chains on a Polyether Backbone

The overall goal of this work is to develop a polymer that will be miscible with CO<sub>2</sub> down to low pressures and contain only carbon, hydrogen, and oxygen. Given the lessons from the study of grafted materials on a siloxane backbone, a similar study on a polyether backbone was undertaken. The model compound in the non-fluorous study was a polyether. The starting material was poly(epichlorohydrin) (PECH) which when reduced completely became poly(propylene oxide) (PPO) with hydroxyl end groups. The PECH was obtained at an approximate molecular weight of 2400, and this weight was verified by <sup>1</sup>H-NMR peak analysis (see **Figure B12** in **Appendix B**). In this procedure, the hydroxyl end groups of the PECH were capped with acetate groups. The CH<sub>3</sub> protons from the ends of these groups were visible in the <sup>1</sup>H-NMR at about 2.1 ppm, while the backbone protons gave a broad peak from 3.4 to 3.8 ppm. The integral ratio of these peaks was used to determine the number of the repeat units and then the approximate molecular weight. The following equation was used to verify the molecular weight of the PECH:

$$\frac{\text{BackbonePeak}}{\text{AcetatePeak}} = \frac{5x}{6} \quad (5-1)$$

where x is the total number of repeat units (containing five protons), and the six represents the two three-proton end groups on each polymer. Using this equation it was determined that the polymers had about 28 repeat units at a molecular weight of 92.5 each, giving an overall molecular weight of about 2600. The PECH was reduced to various degrees, and the effect of grafting acetate and methyl ether side chains to the polyether backbones was observed.

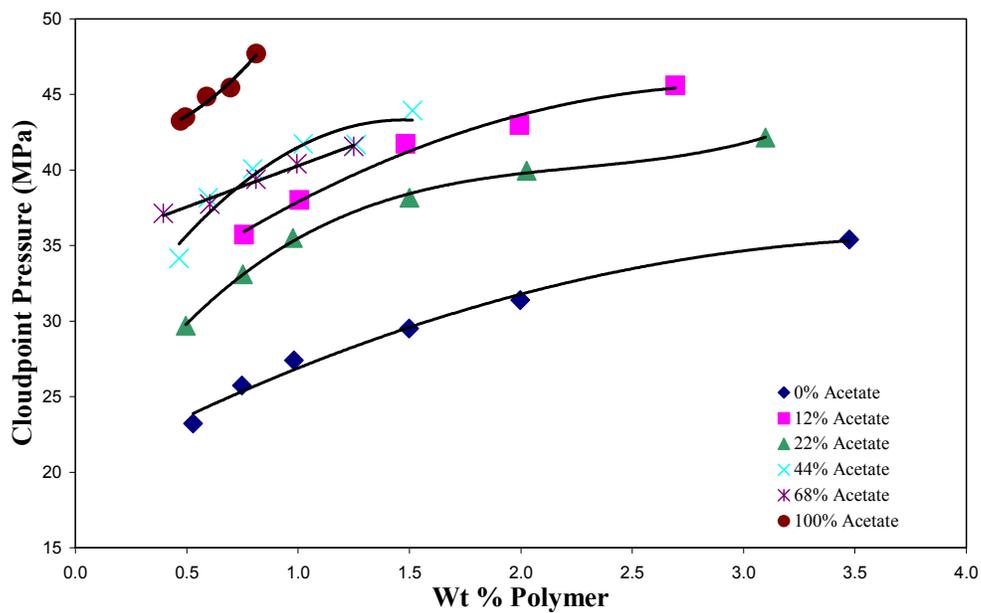
### 5.2.1 Phase Behavior of PPO with Grafted Acetate

Since acetate has proven to be an effective Lewis base side chain, it was chosen to be grafted onto a polyether backbone and evaluated to determine if it would have the same CO<sub>2</sub> solubility effects as observed on the siloxane backbone. The acetate groups were grafted onto the repeat units in the following degrees: 12%, 22%, 44%, 68%, and 100%. The oligomer with 22% of the repeat units containing grafted acetate was the most CO<sub>2</sub>-philic of the five samples (see **Figure 20**), though even the best acetate-substituted polymer had higher cloud point pressures than those of the base PPO polymers having no acetate substitution. This percentage of substitution is comparable to the optimal degree of acetate composition on the PDMS backbone, giving credibility to the results of the siloxane backbone study. As seen in the results of the acetate substituted PDMS, having too few acetate side chains resulted in a cohesive energy density increase<sup>(62)</sup> without the benefit of multiple Lewis base sites. On the other hand, if there were too many acetate groups, the polymer was stiffened, and the Lewis acid/base interactions were not strong enough to overcome the increase in CED. Grafting acetate groups onto approximately 20% of the repeat units, allows for the optimal balance between polymer-polymer and polymer-CO<sub>2</sub> interactions, yielding the lowest cloud point pressures.

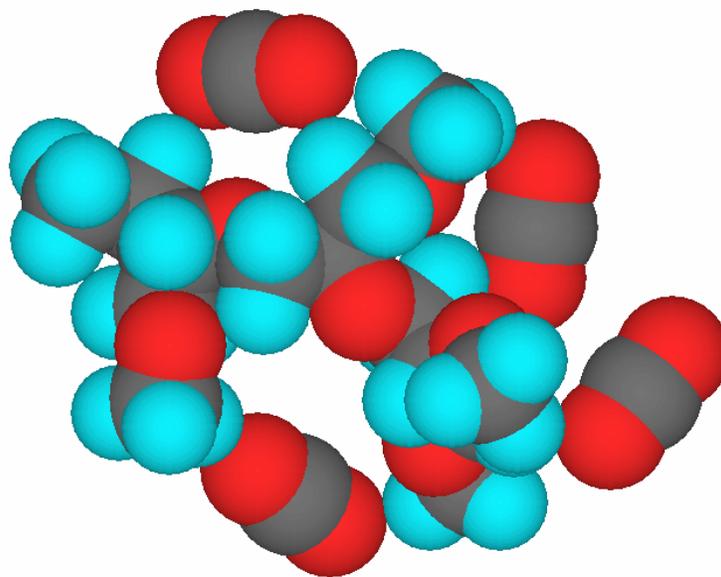
### 5.2.2 Phase Behavior of PPO with Grafted Methyl Ether

Given the work of Yang Wang stating that an ether group may interact with CO<sub>2</sub> as well as an acetate group, a methyl ether group was chosen as a second Lewis base to graft

onto a polyether backbone. Given the simplicity of the structure and the incorporation of an ether-oxygen as the electron-rich donor, the structure was assumed to interact favorably with CO<sub>2</sub>. The ether groups were grafted onto the repeat units in the following degrees: 12%, 22%, 44%, and 100%. None of the four samples were miscible with CO<sub>2</sub> to the limits of the equipment (48.26 MPa). Given their close proximity, it was hypothesized that the backbone oxygen would not allow the ether oxygen to interact with CO<sub>2</sub> and vice versa, as the oxygen atoms on the polymer repelled the oxygen atoms on the carbon dioxide when the carbon in CO<sub>2</sub> attempted to interact with either oxygen (see **Figure 21**). Since the CO<sub>2</sub> needed to interact with the oxygen atoms in order to draw the molecule into solution, the solubility of the polymer may have been greatly reduced because the oxygen atoms on all of the grafted repeat units were inaccessible. The 12% substituted PPO partially dissolved at the limits of the equipment, but as the degree of substitution rose, the polymers showed no tendency to dissolve at all. It should be noted that the structure of the methyl-ether-substituted PPO closely resembles a branched poly(ethylene oxide) (PEO), which is known to exhibit poor solubility in CO<sub>2</sub><sup>(53)</sup>. Also worth noting was the insolubility of low molecular weight poly(acetaldehyde). This sample also had oxygen atoms in close proximity and was not miscible with CO<sub>2</sub> to the pressure limits of the equipment and down to 0.7 weight percent.



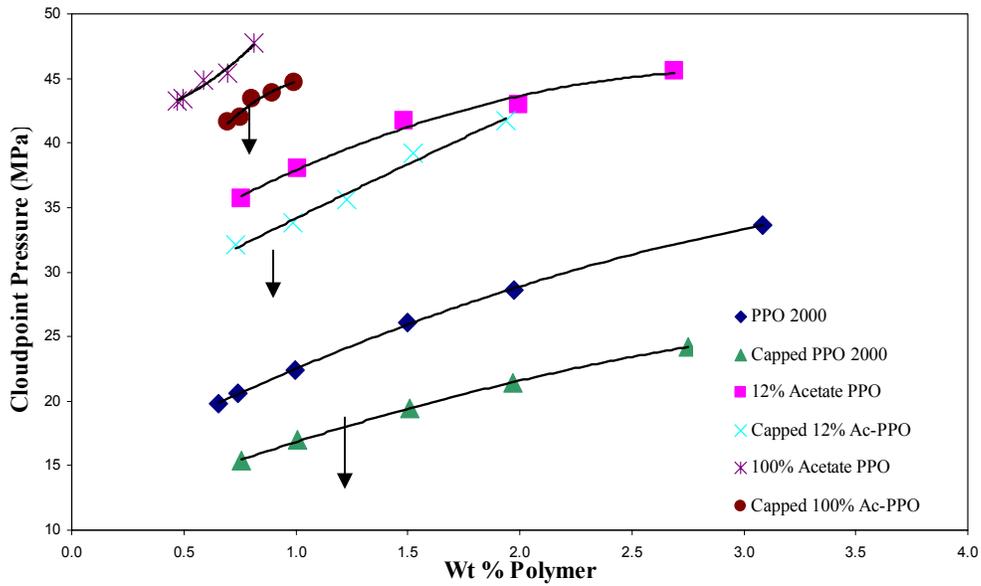
**Figure 20:** Phase Behavior of Acetate Substituted PPO



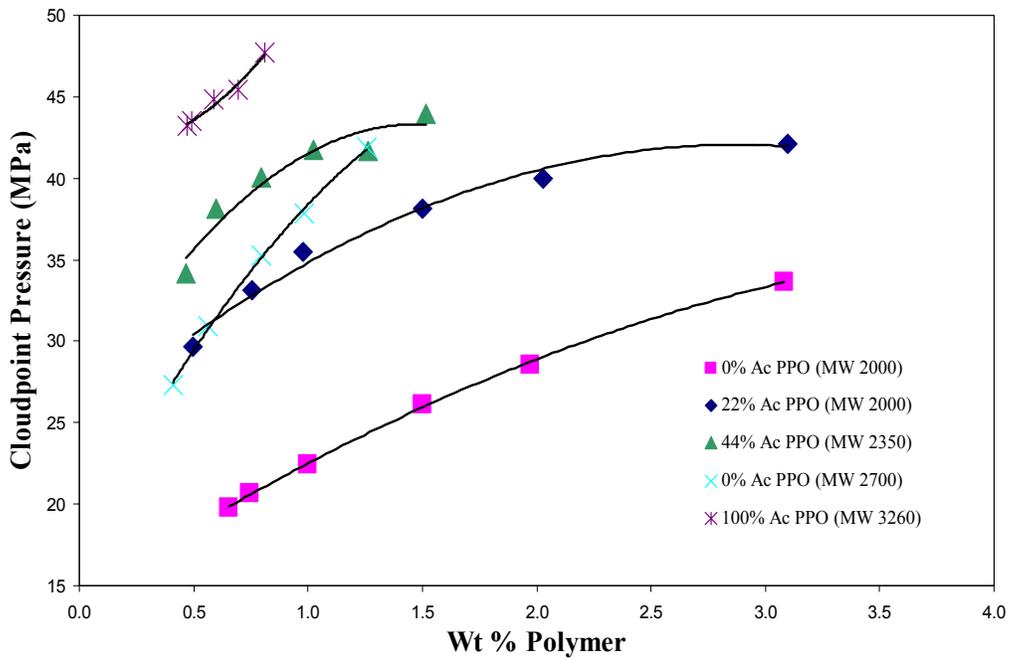
**Figure 21:** Hypothesized Steric Hindrance in 3 Repeat Units of Ether-Substituted PPO

### 5.3 The Effect of End Group Capping on PPO Polymers

The hydroxyl end groups had a detrimental effect on the solubility of the PPO polymers in CO<sub>2</sub> because they can hydrogen bond to each other, increasing their polymer-polymer interactions. This behavior was observed in similar work examining the effects of hydroxyl end groups observed on poly(isobutylene)<sup>(33)</sup> and on poly(ethylene oxide)<sup>(21)</sup>. To determine the effect that this phenomenon had on the polymers, the hydroxyl groups were reacted with acetyl chloride, leaving a CO<sub>2</sub>-philic acetate group on the ends of the polymer chain. PPO (MW 2000) with no side chains was tested as well as the 12% acetate, 100% acetate, and 12% ether samples (see **Figure 22**). While the ether sample was not miscible as capping did not improve the insoluble polymer enough to bring it into solution, the acetate polymers were more CO<sub>2</sub>-philic when capped with end groups. The degree of acetate substitution did not affect the cloud point pressure drop obtained by capping the end groups as all polymers exhibited a drop of 500 to 1000 psi (3.4 to 6.9 MPa) when capped.



**Figure 22:** The Effect of End Group Capping on Acetate-Substituted PPO



**Figure 23:** Molecular Weight Effects on PPO Solubility in Carbon Dioxide

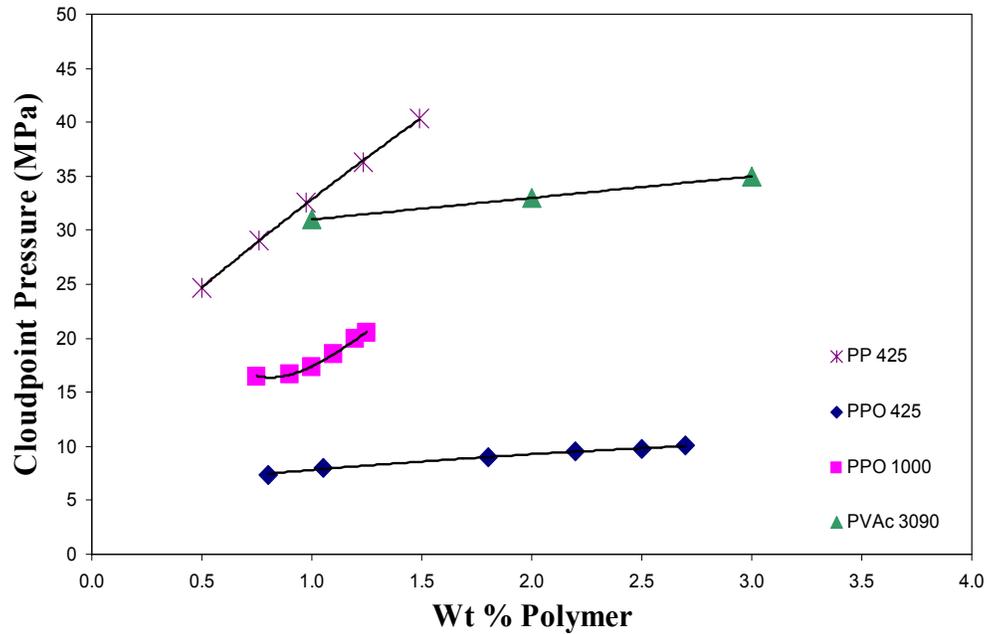
#### 5.4 The Effect of Molecular Weight on the Phase Behavior of PPO

Increasing the molecular weight of a polymer resulted in a drop in entropy of mixing and therefore decreased CO<sub>2</sub> solubility. This was confirmed with a molecular weight analysis of two PPO samples. Two polymers of differing molecular weights (2000 and 2700) were evaluated for cloud point pressure (see **Figure 23**), and they behaved as predicted. With the 35% increase in molecular weight from the PPO 2000 to the PPO 2700, the cloud point pressure increased substantially. The effect of molecular weight was much more pronounced for the non-fluorous polymers than it was in the siloxane samples. The PPO did not have the low cohesive energy density (Surface tension: 31.5 mN/m @20°C)<sup>(32)</sup> necessary to overcome the negative entropic effects caused by increased molecular weight. When comparing the acetate-grafted PPO on a molecular weight basis with unaltered PPO, it was seen that the polymers with acetate did not favorably compare to the base PPO polymer. At a molecular weight of 2000, the acetate-grafted polymer (22% Ac) had a cloud point pressure of about 10 MPa higher than that of the base PPO. The acetate-grafted polymer at a molecular weight of 2360 (44% Ac), showed a slightly higher cloud point pressure than an unaltered PPO with a molecular weight of 2700. The polymer with all of the repeat units grafted with acetate had the highest molecular weight (MW 3260) and had a higher cloud point pressure than the other polymers in the comparison.

## 5.5 Phase Behavior of Poly(propylene)

Poly(propylene) (PP) was chosen as an appropriate hydrocarbon counterpart to PPO as it had almost the same repeat unit with the lack of one oxygen atom. The PP was tested to determine the effects of oxygen in the backbone on the miscibility pressure in CO<sub>2</sub>. PP at a molecular weight of 425 (about 10 repeat units) had relatively high cloud point pressures in CO<sub>2</sub> (see **Figure 24**). At the next available molecular weight increment (MW 1000), the PP was insoluble at the limits of the equipment (48.26 MPa). Despite the low T<sub>g</sub> and CED (-10 °C and a surface tension of 29.4 mN/m<sup>(32)</sup>, respectively) of PP, it was evident that the lack of oxygen in the backbone harmed the solubility of the oligomer just as the suspected blocking of the backbone oxygen atoms in the methyl-ether substituted PPO severely debilitated the solubility of that polymer. In comparison the PPO, which has an ether group in the backbone, had a significantly lower cloud point curve than PP at the same molecular weight of 425<sup>(53)</sup>. At a molecular weight of 1000, the PP was not miscible with the CO<sub>2</sub> at the limits of our equipment (48.26 MPa), while the PPO dissolved in carbon dioxide at moderate pressures of 20 to 25 MPa from 0.6 to 1 weight percent<sup>(53)</sup>. The benefits of adding a Lewis base group were very obvious when comparing PP (MW = 425) and PVAc (MW = 3090)<sup>(55)</sup>. The miscibility pressures of these polymers were similar at one weight percent even with the PVAc having over seven times the molecular weight. At higher weight concentrations, the cloud point pressure of PP rose dramatically while the PVAc curve remained relatively flat. Placing the carbonyl group as a Lewis base in the backbone can lower the miscibility pressure of a non-fluorous polymer, though not to the extent seen when placing the group in a side chain

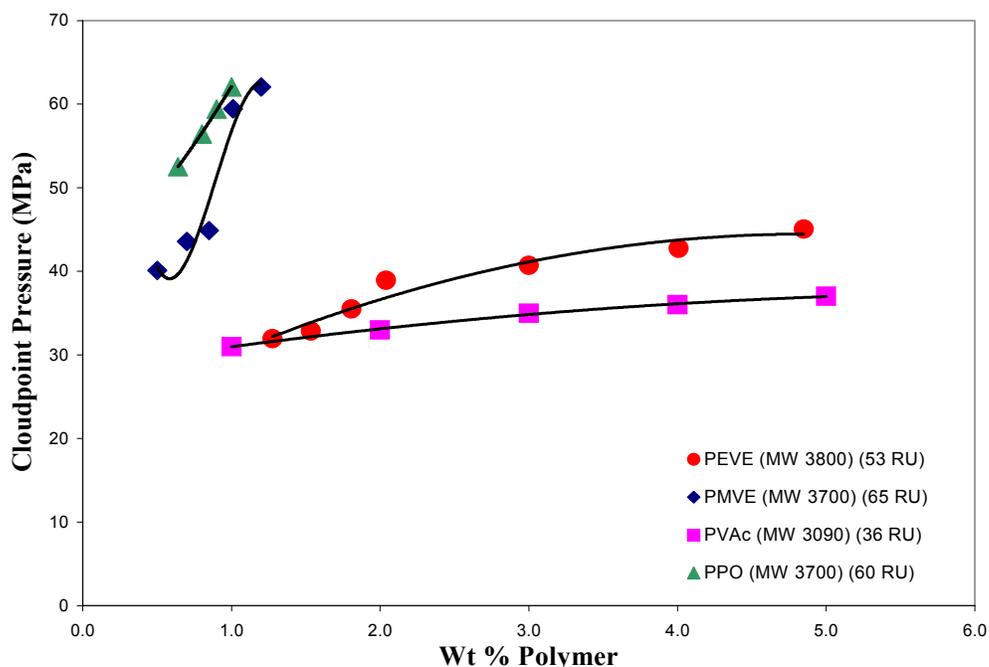
(PVAc). At 308 K, poly(lactide) (PLA) at a molecular weight of 128,500 at five weight percent will dissolve in CO<sub>2</sub> at about 140 MPa<sup>(54)</sup>. Under the same conditions and with the same molecular weight, PVAc exhibits a cloud point pressure of 70 MPa<sup>(55)</sup>. Poly(propylene) is not the only hydrocarbon to have high miscibility pressures in CO<sub>2</sub>. At 4.82 wt. percent and at ~383K, poly(isobutylene) (MW 1000) has a cloud point pressure of about 190 MPa<sup>(33)</sup>.



**Figure 24:** Cloud Point Effects of Lewis Base Groups on a Polymer

## 5.6 Phase Behavior of Poly(ethyl vinyl ether)

To further compare the effects of an ether-group and an acetate-group as functional Lewis base side chains, poly(ethyl vinyl ether) (PEVE) was purchased from Aldrich at a molecular weight of 3700. When tested, the polymer had higher cloud point pressures than PVAc<sup>(55)</sup> with a similar molecular weight of 3090 (see **Figure 25**). While the PEVE exhibited a comparable cloud point pressure to PVAc at lower concentrations, the PVAc had lower miscibility pressures as the weight concentration rose. However, the comparison was effectively equal as the molecular weight of the PVAc was lower than that of the PEVE, and the PVAc had about 17 fewer repeat units. This result was very important as it provided supporting evidence to the research by group member, Yang Wang, stating that the ether group was as effective as the acetate group for the purpose of



**Figure 25:** Phase Behavior Comparison of Ether and Acetate Containing Polymers

interacting with CO<sub>2</sub>. The PEVE had much lower miscibility pressures than that of poly(methyl vinyl ether) (PMVE), which was tested by group member, Sevgi Kilic. This large disparity was attributed to the increase in free volume and hence lower T<sub>g</sub> provided by the additional CH<sub>2</sub> spacer in PEVE. The T<sub>g</sub> of PEVE is -43°C, and the T<sub>g</sub> values for PEVE are generally lower than those of PMVE<sup>(64)</sup>. The PMVE had a similar cloud point curve to PPO with acetate capped end groups (also tested by Sevgi Kilic) at approximately the same molecular weight. Though not clearly superior, the PMVE had lower miscibility pressures than PPO, which has the same repeat unit composition. The only difference between the polymers is that the ether linkage is in the side chain of PMVE, while the PPO has ether in the backbone.

## 6.0 CONCLUSIONS

In the investigation of grafted side chains, it was found that each Lewis base group had an optimal degree of substitution on the PDMS polymers. In the case of the acetate group, the optimum (~20%) acetate substitution (excluding the base polymer) seen on the PDMS polymer was duplicated on the PPO backbone. The presence of an optimal amount of substitution is not a new discovery as it was observed on fluorinated polymers as reported by Beckman et al<sup>(37)</sup>. In each case there is a balance between the effect of the Lewis base interactions with CO<sub>2</sub> and the increase in cohesive energy density and T<sub>g</sub>.

While very important, the T<sub>g</sub> and CED of a polymer are not the dominant factors in governing the miscibility of the polymer in CO<sub>2</sub>. The need for a Lewis base bonding site on the polymer was obvious in this study. When comparing PP to PPO, this fact was quite apparent. The oxygen atom in PPO enabled that polymer to dissolve in CO<sub>2</sub> at much higher molecular weights than the pure hydrocarbon, even though PP has a low T<sub>g</sub> and a lower CED than PPO (see **Table 6**). Adding the acetate group yielded an even larger cloud point pressure difference despite the fact that PP has a far lower T<sub>g</sub> and CED than PVAc.

<b>Polymer</b> ---	<b>T<sub>g</sub></b> ° C	<b>Surface Tension</b> mN/m @ 20 °C
PP	-31	29.4
PPO	-83	31.5
PVME	-31	31.8
PEVE	-43	36.0
PVAc	32	36.5

While very important, Lewis base groups must be placed onto the polymer judiciously. As hypothesized in the case of methyl ether substituted PPO, having oxygen atoms in close proximity serves to repel CO<sub>2</sub> rather than facilitate interactions that would lower miscibility pressures. The base polymer, PPO, is miscible with CO<sub>2</sub> as is the methyl ether group which can be seen in the PMVE sample. However, when combined, the oxygen atoms are too closely aligned in space to interact with the carbon dioxide solvent. Also adding credibility to the spacing argument is the insolubility of poly(acetaldehyde), which arranges oxygen atoms in close spatial proximity.

Replacing the hydroxyl end groups with acetate groups resulted in lower cloud point pressures for the polymers. The grafted side chains did not appear to have any effect on the extent to which the miscibility pressure was lowered as each polymer was improved by approximately the same amount. When deriving the most CO<sub>2</sub>-philic polymer, the hydroxyl groups must be converted to a structure that interacts more favorably with carbon dioxide and less favorably with end groups on other polymer chains.

The addition of the acetate Lewis base group was proven effective in lowering miscibility pressures of a polymer in CO<sub>2</sub>, but there is now a challenge to the fact that acetate aids in lowering cloud point pressures more than any other Lewis base. Both simulation calculations and experimental results have shown that an ethyl ether may be just as effective at forming a Lewis acid/base bond with CO<sub>2</sub> as the acetate group.

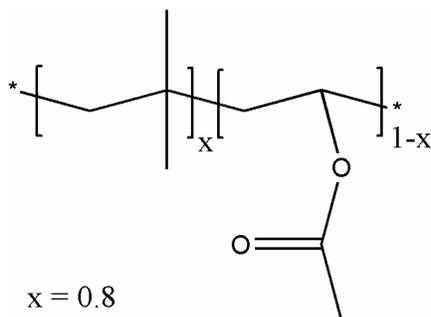
## 7.0 RECOMMENDED FUTURE WORK

To further validate the findings made in this work, there are several experiments to be undertaken. First, the acetate group displayed an optimal low cloud point pressure at about 20% acetate substitution on both the siloxane and polyether backbones. While PVAc is known to be an excellent non-fluorous CO<sub>2</sub>-phile, the effects of a 20% acetate-substituted hydrocarbon backbone should be investigated. This may be accomplished by co-polymerizing isobutylene<sup>(66)</sup> and (trimethylsiloxy)ethylene<sup>(67)</sup>, removing the protecting silyl group, and acetylating to yield poly(vinyl acetate-co-isobutylene) (see **Figure 26**).

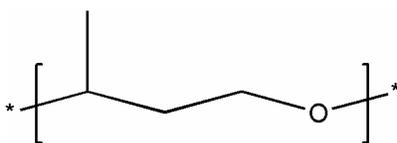
The spacing hypothesis posed to explain the lack of miscibility of the ether-substituted ether in CO<sub>2</sub> can be further supported by the synthesis of similar polymers with more space between the oxygen atoms. Polymers with one more carbon spacer than PPO (see **Figure 27**) can be synthesized by polymerizing 4 member oxetanes<sup>(68,69)</sup>. Additionally, it would be interesting to observe the effects of spacing in the grafted side chain, though the means to create such a polymer are not currently known (see **Figure 28**).

In addition to the materials that support the conclusions of this work, there are other materials that should be tested. Nitrogen as a Lewis base should be fully investigated on both the ether and hydrocarbon backbones. Both methyl amine and imidazole should be tested (see **Figure 29**) to determine whether or not nitrogen, a strong Lewis base, can aid in the lowering of the cloud point pressure of a polymer more than acetate or ether. Imidazole provides an exposed nitrogen atom that is not

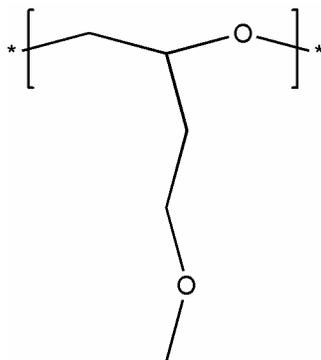
surrounded by methyl groups, eliminating steric interference in the CO<sub>2</sub> – Lewis base interactions. It has also been thought that CO<sub>2</sub> could position itself on the side of the ring to chelate between the two nitrogen atoms of imidazole.



**Figure 26:** Poly(vinyl acetate-co-isobutylene)



**Figure 27:** Poly(2-methyltrimethylene oxide)

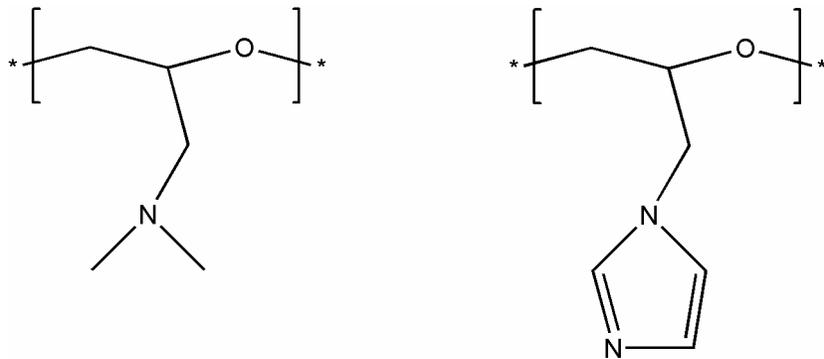


**Figure 28:** Ethyl Methyl Ether Substituted PPO

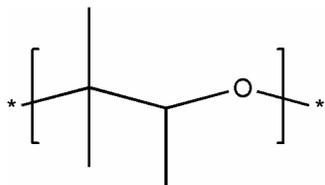
Methyl branching increases the free volume and has proven to aid in dissolving polymers in CO<sub>2</sub>, as seen in a poly(ethylene oxide)/poly(propylene oxide) comparison<sup>(53)</sup>. To increase the methyl branching 2-methyl-2-butene oxide can be polymerized<sup>(70)</sup> to form a PPO analog with additional methyl groups on the backbone carbon chain (see **Figure 30**).

In addition, simulation work done by Dr. Johnson's group at the University of Pittsburgh has shown that CO<sub>2</sub> should bond strongly with an acetate-like structure that contains a CH<sub>2</sub> spacer between the ether oxygen and carbonyl group (see **Figure 31**). According to the initial simulations, the group seems to chelate CO<sub>2</sub> between the oxygen atoms. If successful, this would be a very important development as it would be the first time that simulations have directed experimental work in this field.

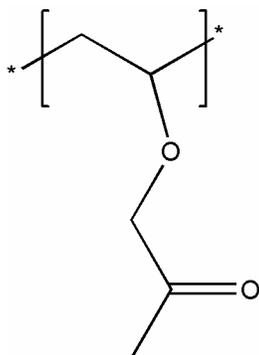
Finally, work by Dr. Johnson has also revealed that a sulfonyl group should interact with CO<sub>2</sub> more strongly than a carbonyl oxygen. Experimental investigation into this structure (see **Figure 32**) should be undertaken to evaluate the effects of replacing carbon with sulfur in an acetate group. Again, this would be an experimental study that was aided by simulation work.



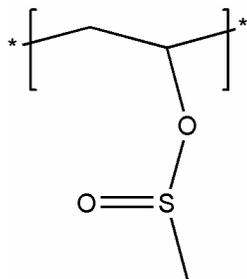
**Figure 29:** Grafted Nitrogen Lewis Base Groups



**Figure 30:** Poly(2-methyl-2-butene oxide)

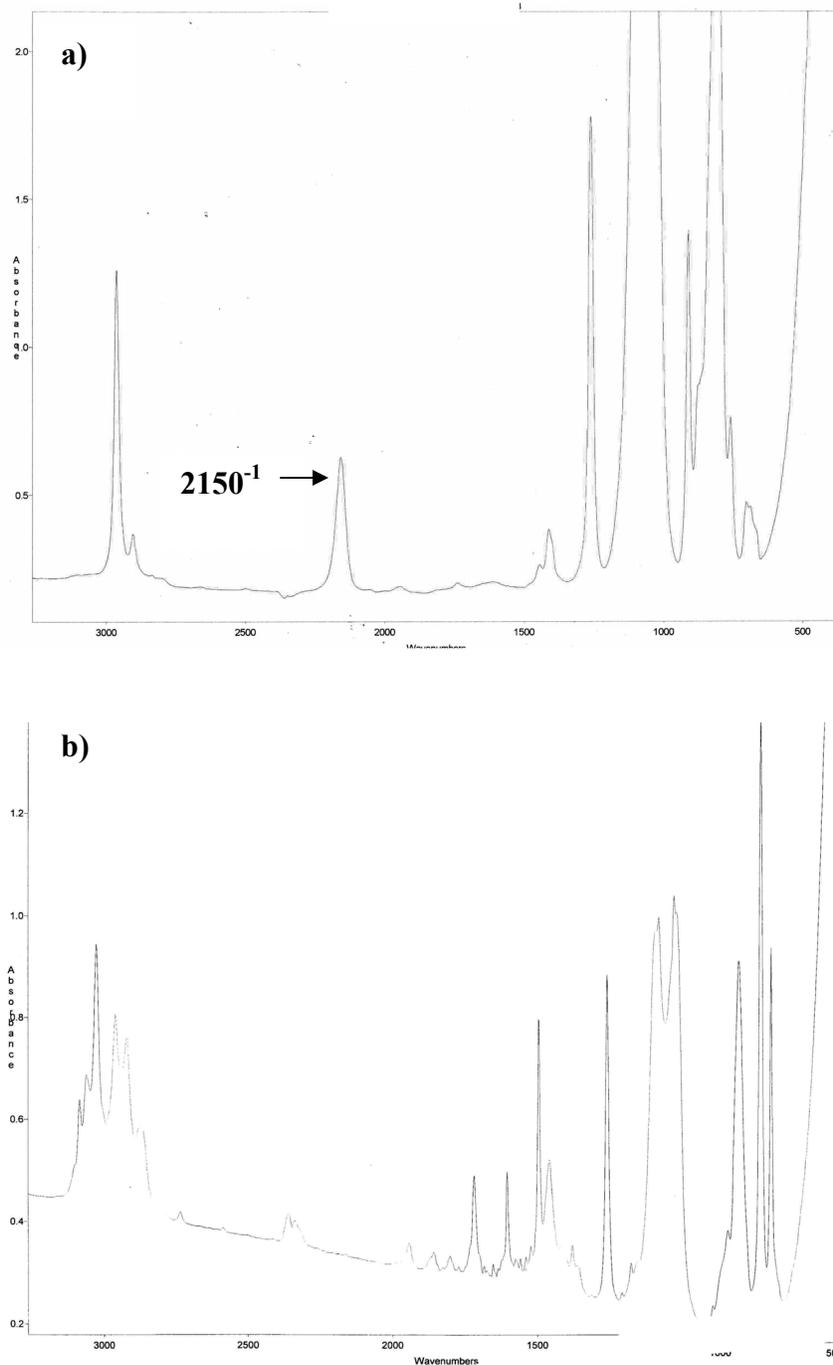


**Figure 31:** Poly(vinyl ether methyl ketone)



**Figure 32:** Poly(vinyl sulfonate)

## APPENDIX A: FT-IR SPECTRUM



**Figure A1:** The Monitoring of the Silicon Reaction by FT-IR through the disappearance of the Si-H peak at  $2150^{-1}$ . **a)** Before Reaction. **b)** After Reaction

## APPENDIX B: $^1\text{H-NMR}$ SPECTRA

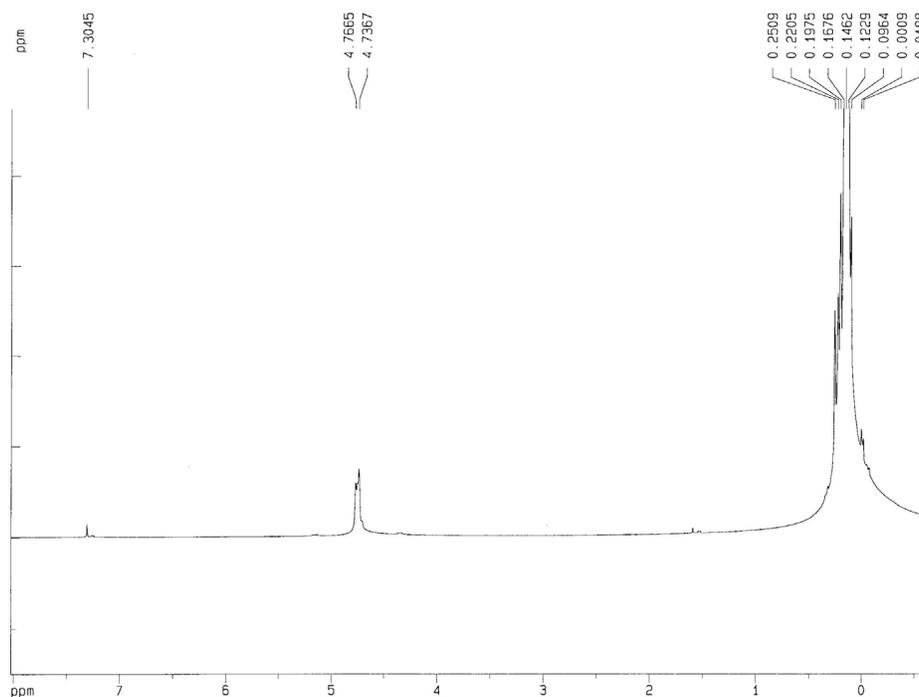


Figure B1:  $^1\text{H-NMR}$  Spectrum for Silicon Polymer

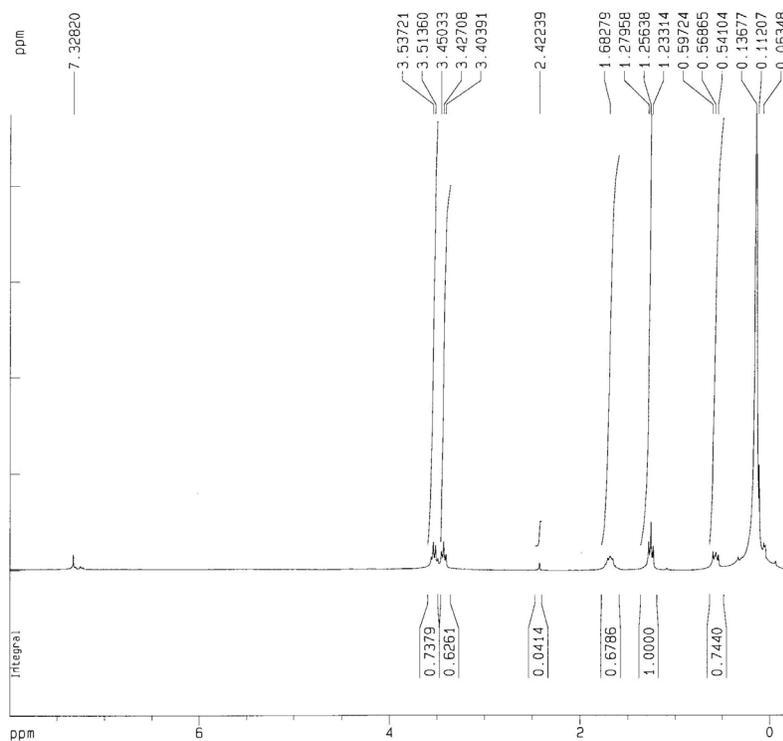
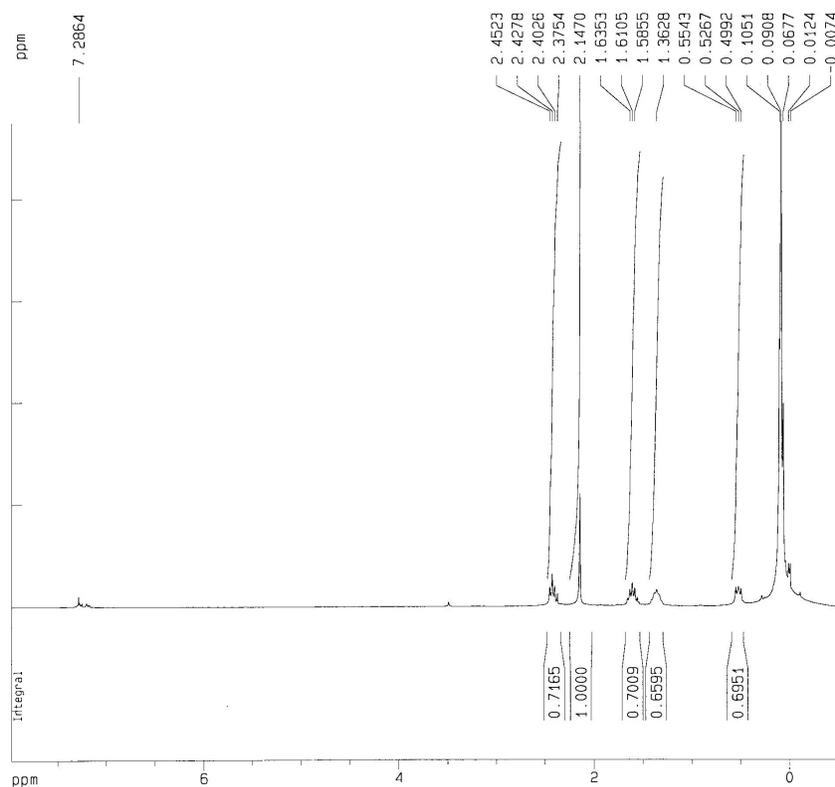
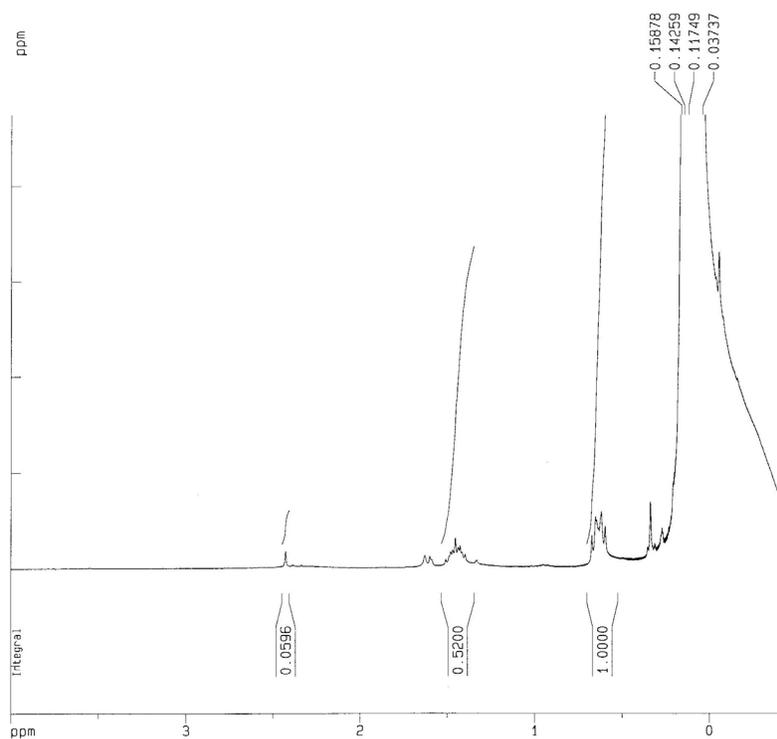


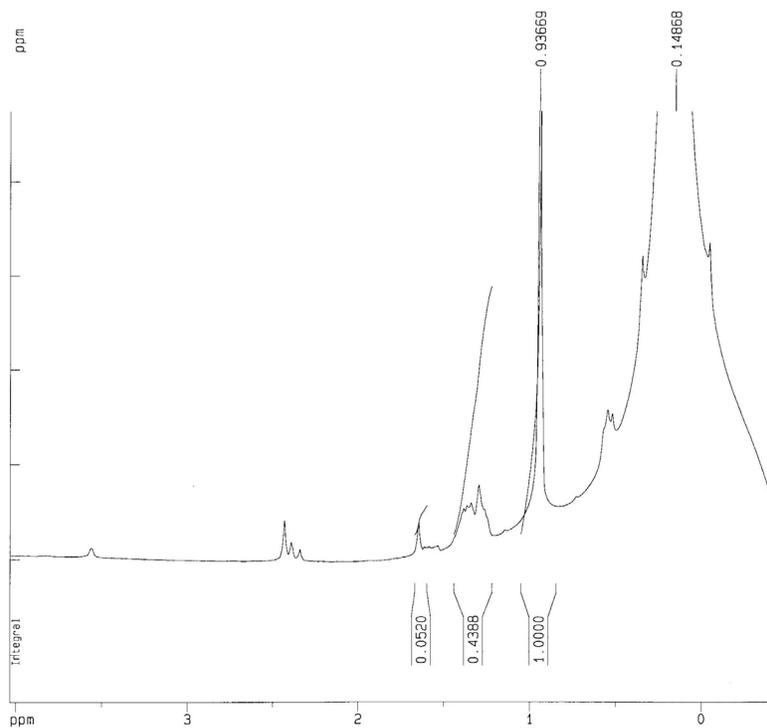
Figure B2:  $^1\text{H-NMR}$  Spectrum for Propyl Ethyl Ether Substituted PDMS



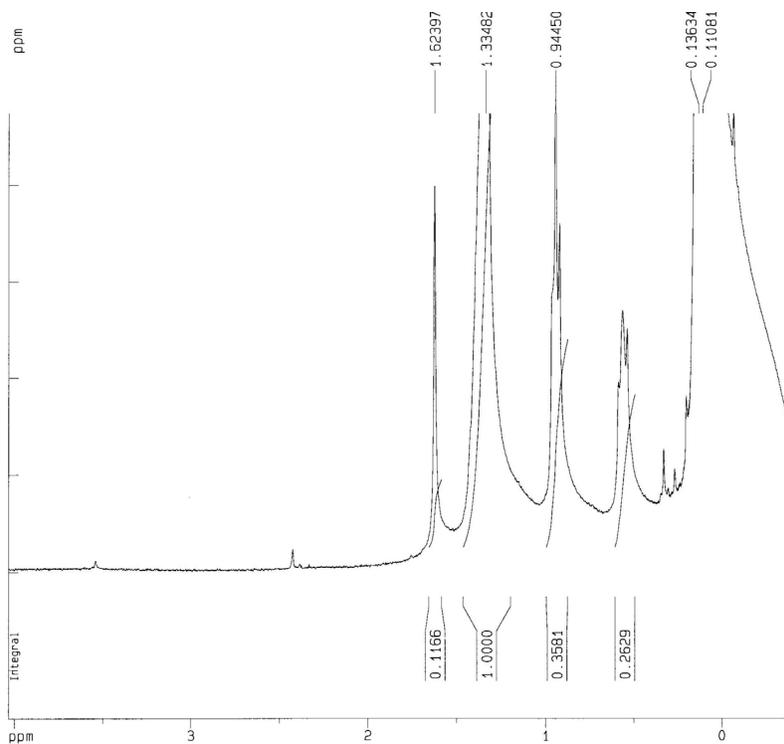
**Figure B3:**  $^1\text{H-NMR}$  Spectrum for Butyl Methyl Ketone Substituted PDMS



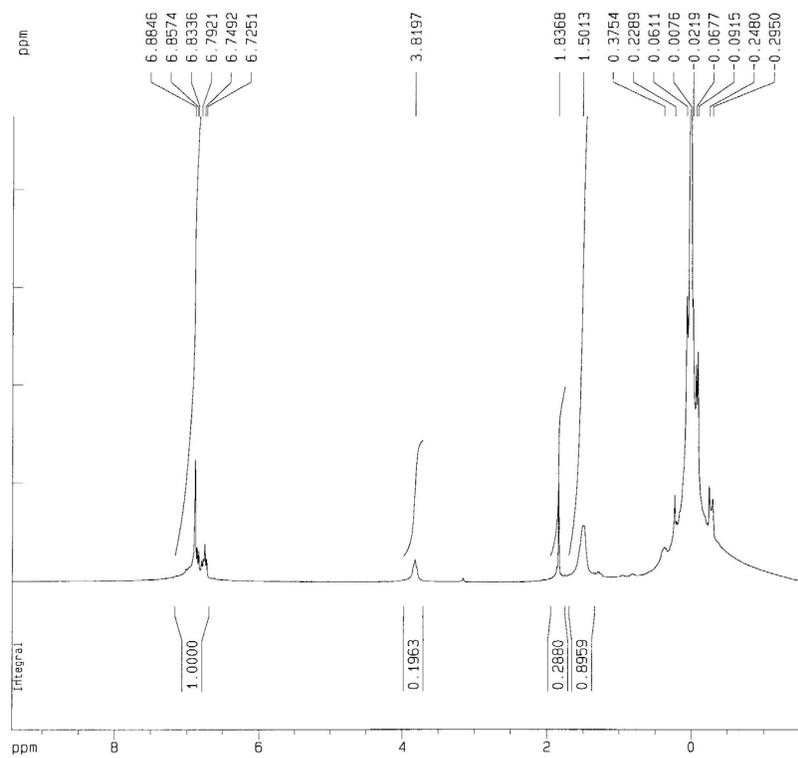
**Figure B4:**  $^1\text{H-NMR}$  Spectrum for Butyl Tri-Methyl Silane Substituted PDMS



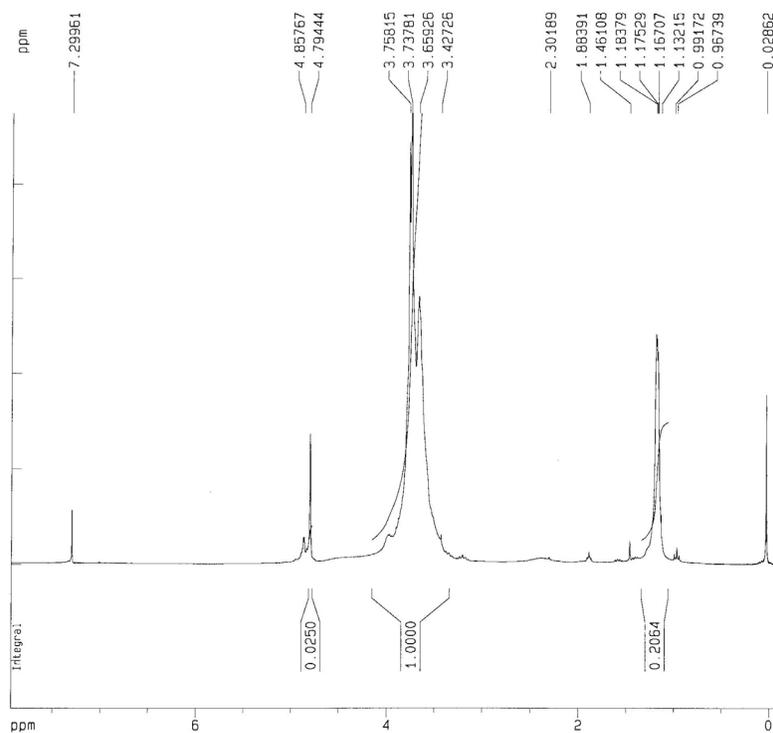
**Figure B5:** <sup>1</sup>H-NMR Spectrum for 5,5 Dimethyl Hexane Substituted PDMS



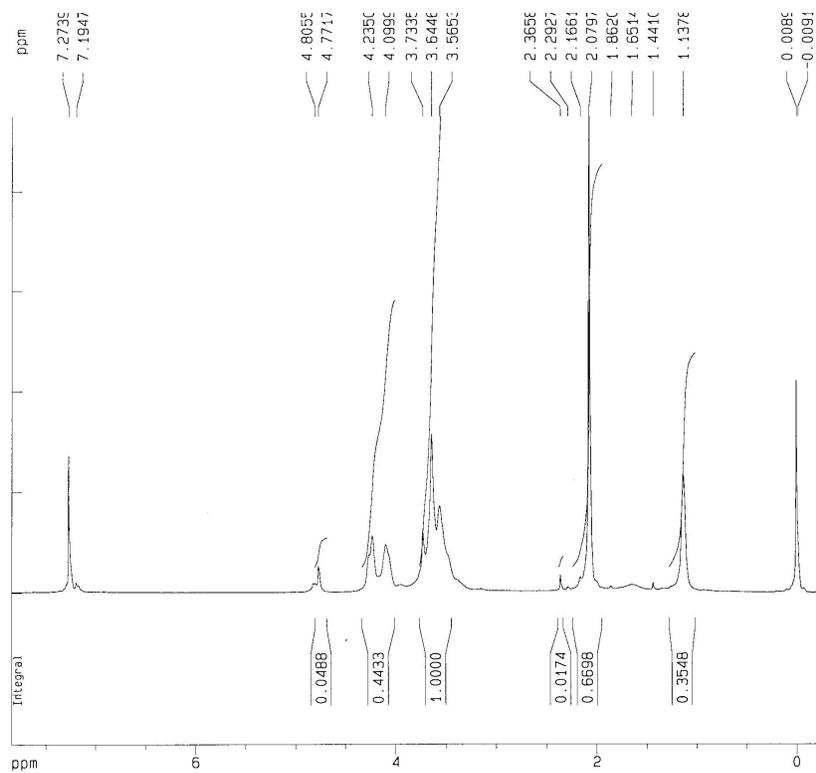
**Figure B6:** <sup>1</sup>H-NMR Spectrum for Hexane Substituted PDMS



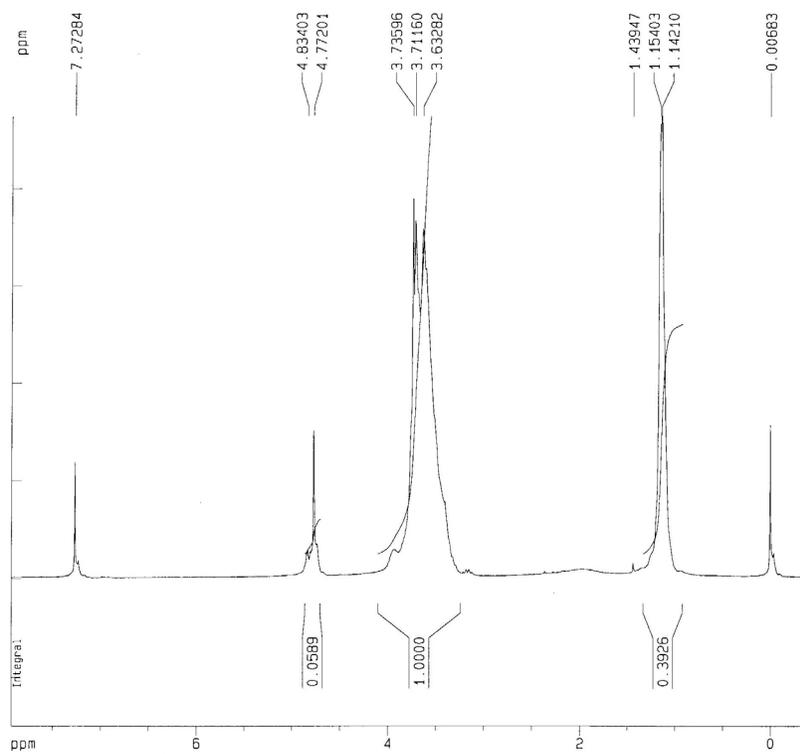
**Figure B7:**  $^1\text{H}$ -NMR Spectrum for Propyl Acetate Substituted PDMS



**Figure B8:**  $^1\text{H}$ -NMR Spectrum for Partially Reduced PECH



**Figure B9:** <sup>1</sup>H-NMR Spectrum for Acetate Substituted PPO



**Figure B10:** <sup>1</sup>H-NMR Spectrum for Methyl Ether Substituted PPO

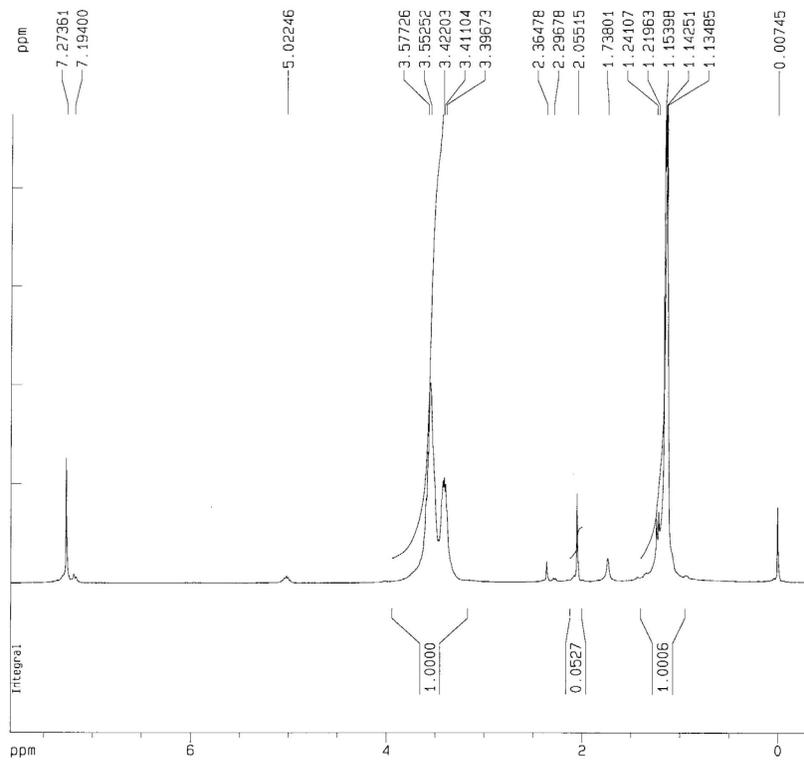


Figure B11: <sup>1</sup>H-NMR Spectrum for PPO with Acetate-Functional End Groups

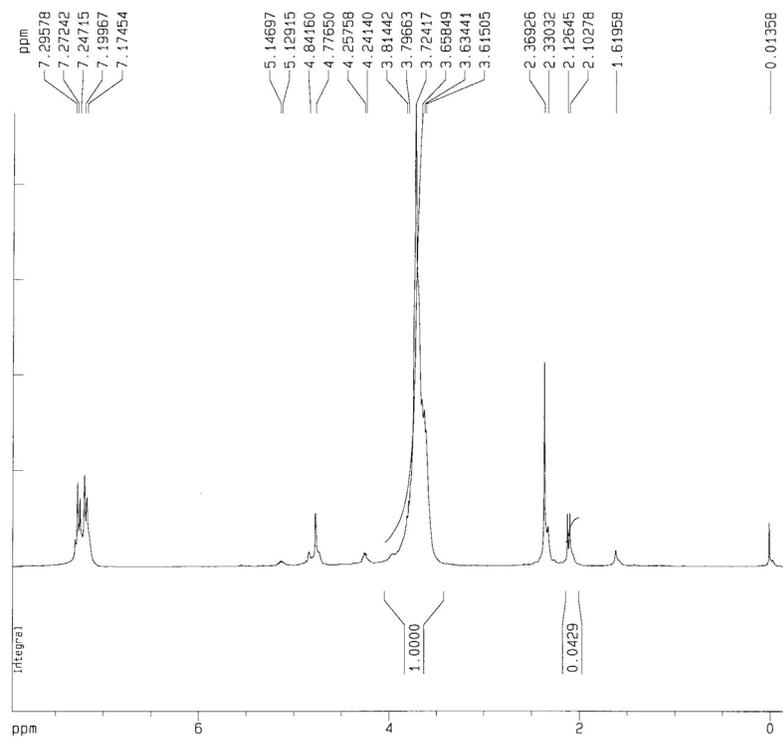
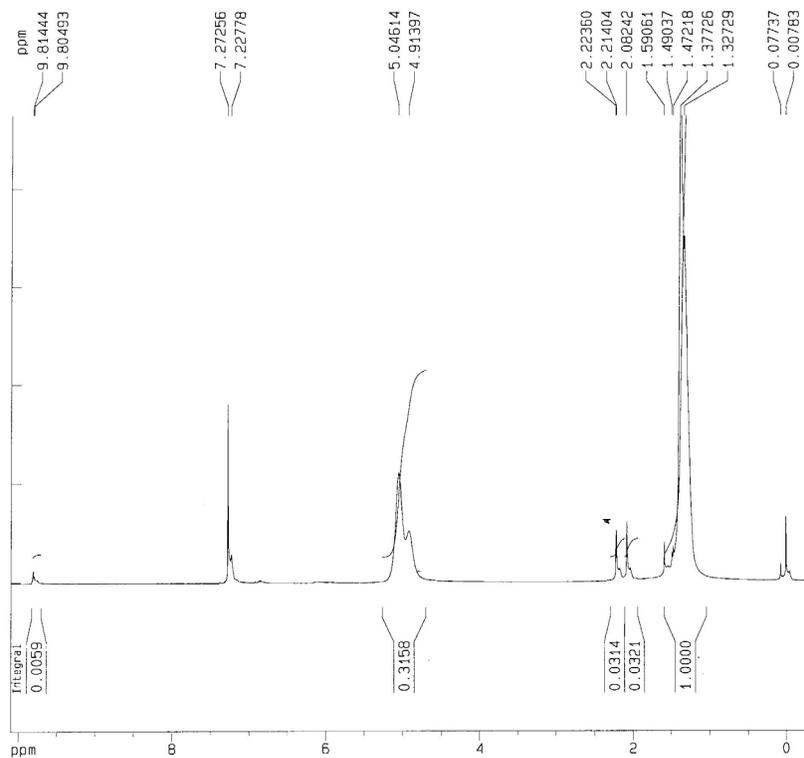


Figure B12: <sup>1</sup>H-NMR Spectrum for PECH with Acetate-Functional End Groups



**Figure B13:** <sup>1</sup>H-NMR Spectrum for Poly(acetaldehyde)

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