

**SYNTHESIS AND CHARACTERIZATION OF  
M-AMINOPHENOXIDE FUNCTIONALIZED  
POLY(TETRAMETHYLENE OXIDE)**


by

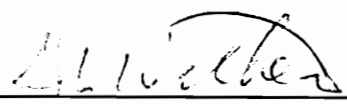
W. Lenore Carman

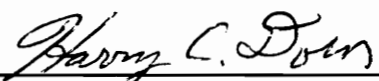
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**MASTER OF SCIENCE  
in  
CHEMISTRY**

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## ABSTRACT

The primary research objective of this thesis was to functionalize bifunctional cationic living poly(tetramethylene oxide) (PTMO) with m-aminophenoxide to produce aromatic amine telechelic PTMO of controlled molecular weight and narrow molecular weight distribution. Triflic anhydride was used to initiate a bifunctional cationic living polymerization of tetrahydrofuran (THF). An anhydrous solution of m-aminophenoxide was used to terminate the polymerization, which resulted in aromatic amine telechelic PTMO of controlled molecular weight. The order of addition of the m-aminophenoxide to the living PTMO was found to be crucial. In order to produce linear aromatic amine telechelic PTMO, the living PTMO must be charged to the m-aminophenoxide solution.

The aromatic amine telechelic PTMO was characterized using IR spectroscopy,  $^1\text{H}$  NMR spectroscopy, HBr titration and  $^{19}\text{F}$  NMR spectroscopy. Trifluoroacetic anhydride was reacted with the m-aminophenoxide terminated PTMO to serve as a fluorine tag, then analyzed using  $^{19}\text{F}$  NMR spectroscopy to quantify the amount of hydroxy end groups present (if any) relative to primary amine end groups. In order to compare  $^{19}\text{F}$  NMR spectra, the model compounds m-phenetidine (Model  $\text{NH}_2$ ) and 3-dimethylaminophenol (Model OH) were also reacted with trifluoroacetic anhydride and analyzed using  $^{19}\text{F}$  NMR spectroscopy.

The aromatic amine telechelic PTMO may be further reacted in a step growth polymerization to form segmented block copolymers. PTMO segments show promise serving as flexible low  $T_g$  blocks between reinforcing high  $T_g$  blocks such as polyamides, polyurea copolymers and epoxies, and may act to toughen these types of materials.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Poly(tetramethylene oxide)

Poly(tetramethylene oxide) (PTMO) is a soft, flexible polymer with a glass transition temperature of  $-86^{\circ}\text{C}$  and a melting temperature of approximately  $43^{\circ}\text{C}$ . It is an inert, nontoxic material, that can be incorporated into a variety of consumer products.<sup>1,2</sup> While high molecular weight PTMO has no commercial applications as a homopolymer due to its low melting temperature, low molecular weight PTMO has many applications. Homo-PTMO of low molecular weight is used as a plasticizer for cellulose, chlorinated rubber and artificial leather.<sup>1,2,3</sup> Low molecular weight PTMO has numerous commercial applications when incorporated as a copolymer into polyesters and, more predominantly, polyurethanes.<sup>4</sup> PTMO-based polyurethanes are used as adhesives, coatings, finishes, thermosets, thermoplastics and in fibers such as elastomeric "spandex" fibers.<sup>1,2,4</sup> PTMO-based elastomers have shown excellent fungal resistance, good tensile strength, high vapor transmission and low hysteresis loss.<sup>1,2,5</sup>

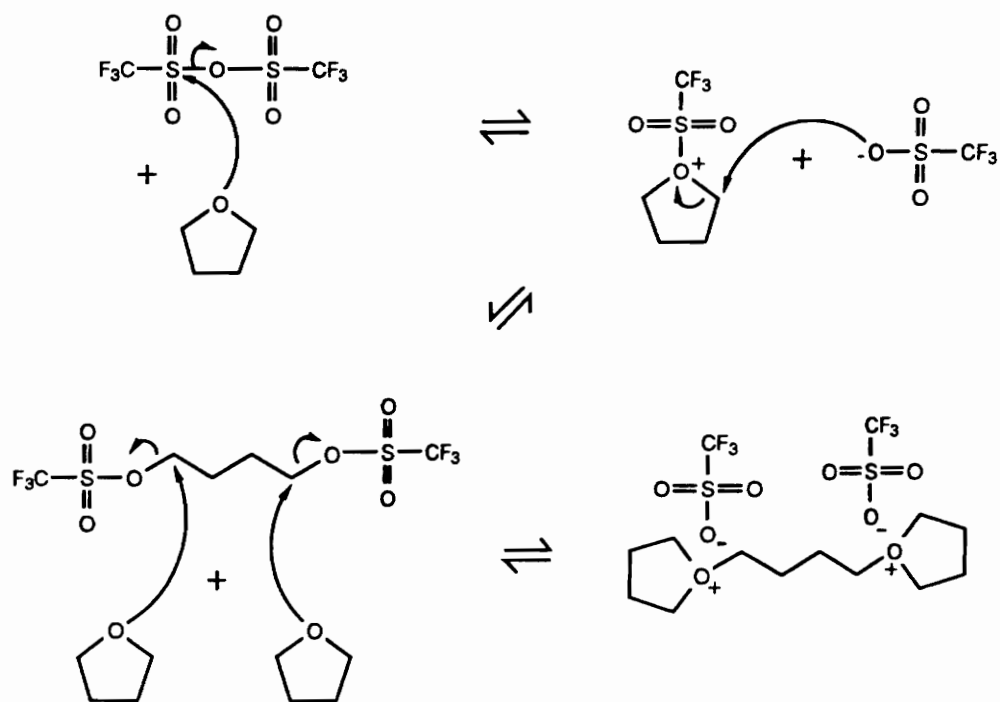
By selectively functionalizing PTMO and then incorporating PTMO into a block copolymer, the PTMO segments serve as flexible "soft" segments between reinforcing "hard" segments. A material with a slight amount of resilience could be less prone to crack or split, and may therefore form an overall tougher material.<sup>6</sup>

PTMO is produced by polymerizing the monomer (and common solvent) tetrahydrofuran (THF). By using triflic anhydride (trifluoromethanesulfonic anhydride,  $\text{CF}_3\text{SO}_2\text{OSO}_2\text{CF}_3$ ) as the initiator to ring open THF, a living bifunctional cationic polymerization of THF can be induced (scheme 1).<sup>7,8</sup> Any suitable nucleophile acts as a terminating agent, producing PTMO where the end groups are determined by the nucleophile (scheme 1). Since water is a good nucleophile, it acts as a terminating agent. Thus, the polymerization of THF must be performed under scrupulously dry conditions. By using this synthetic technique, PTMO of controlled molecular weight, narrow molecular weight distribution and selected functionality of end groups can be obtained.<sup>6,7,8,9</sup>

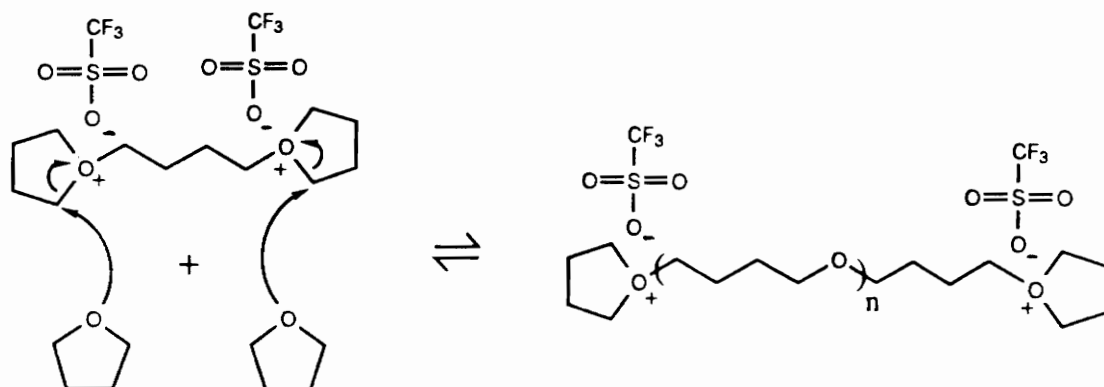
### Scheme 1

## Reaction Mechanism for Living Cationic Polymerization of Tetrahydrofuran Initiated with Triflic Anhydride

### INITIATION



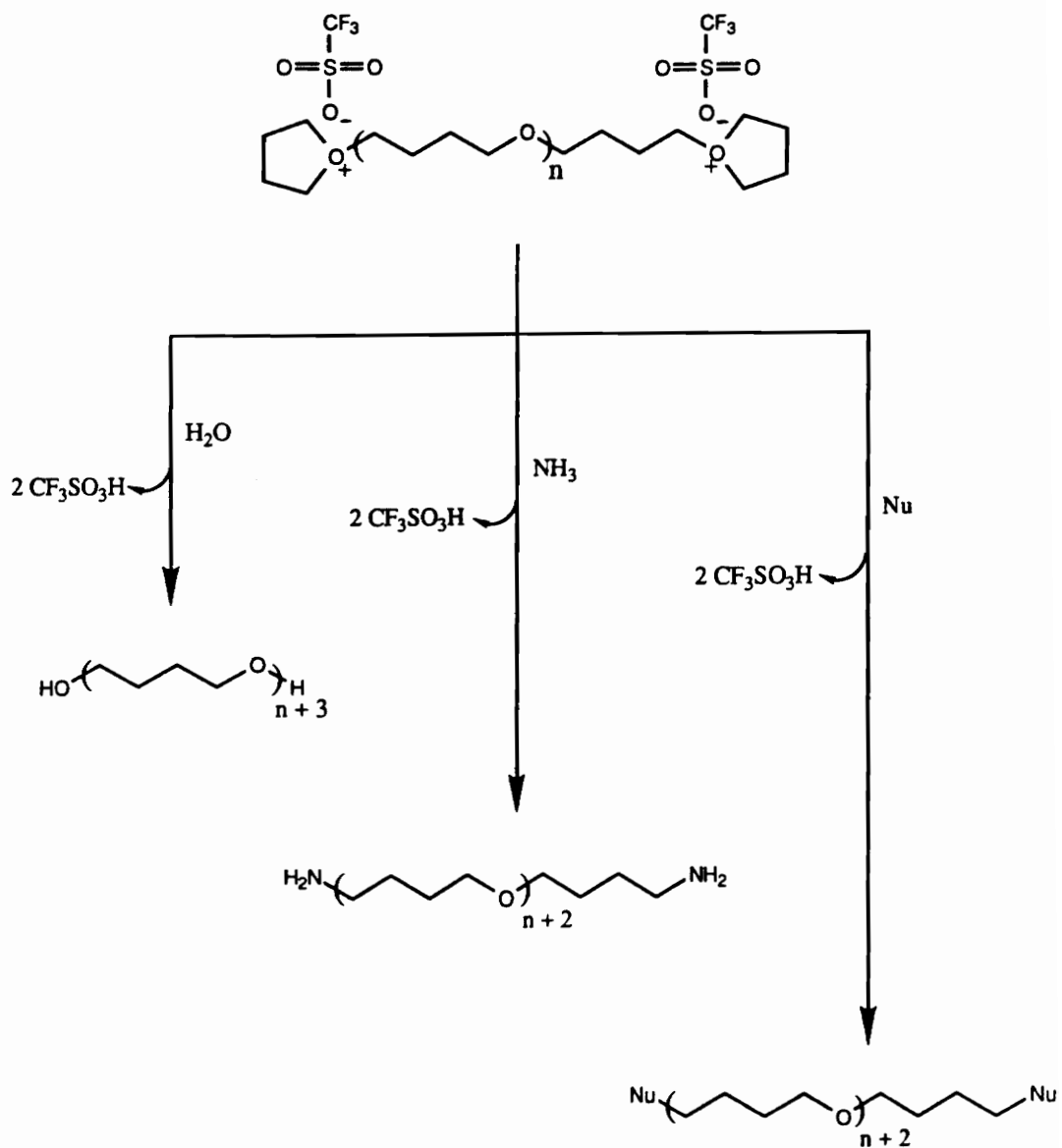
### PROPAGATION



Scheme 1 (cont.)

Reaction Mechanism (cont.)

TERMINATION



where Nu = any suitable nucleophile

## 1.2 Thesis Statement

By initiating the polymerization of THF with triflic anhydride, followed by selective termination of the bifunctional cationic living PTMO with m-aminophenoxide, aromatic amine telechelic PTMO was obtained (scheme 2), which may be further incorporated in a step growth polymerization to form segmented block copolymers. Theoretically, both the negatively charged oxygen group and the amine group of the m-aminophenoxide could act as terminating agents for cationic living PTMO. This thesis discusses the reaction conditions necessary to synthesize linear aromatic amine telechelic PTMO and characterization of these products.

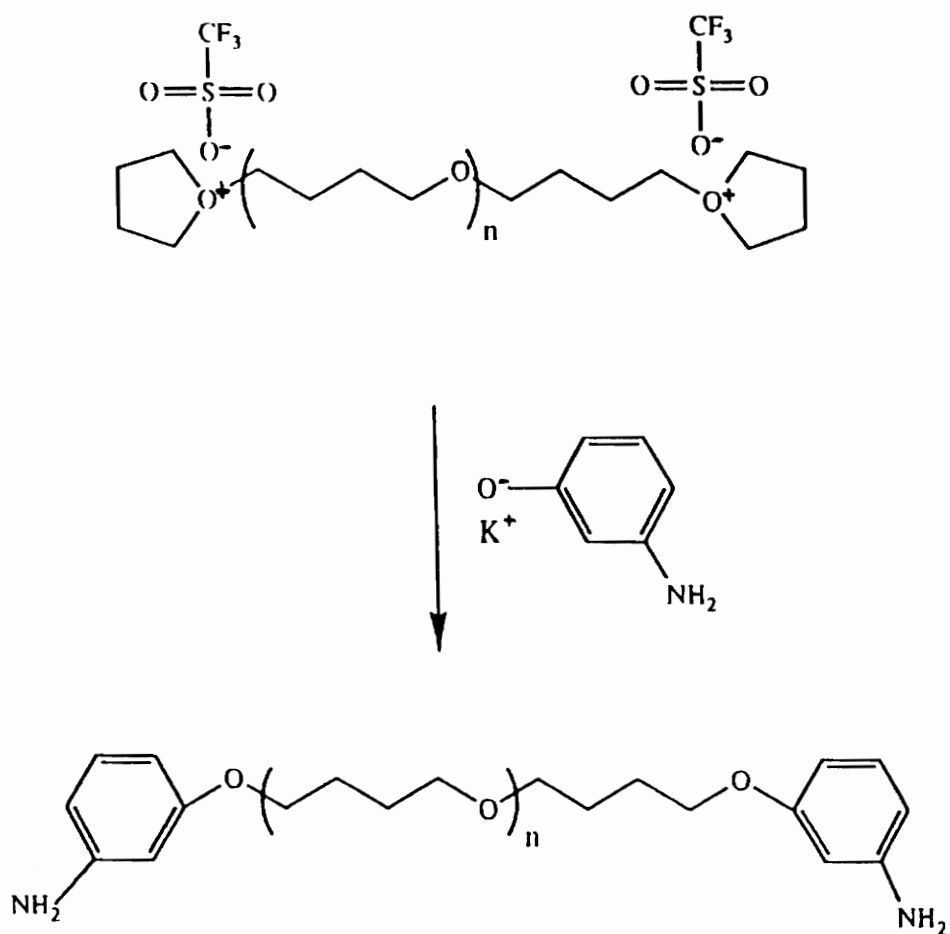
## 1.3 Characterization

The m-aminophenoxide functionalized PTMO was characterized using HBr titration, IR spectroscopy,  $^1\text{H}$  NMR spectroscopy and  $^{19}\text{F}$  NMR spectroscopy.

HBr titration was used to determine the number average molecular weight ( $M_n$ ) of the aromatic amine telechelic PTMO. Additionally, the profile of the HBr titrations, i.e., the number of equivalence points in the titrations, was used to indicate

Scheme 2

**Functionalization of Bifunctional Cationic Living PTMO with *m*-Aminophenoxide**



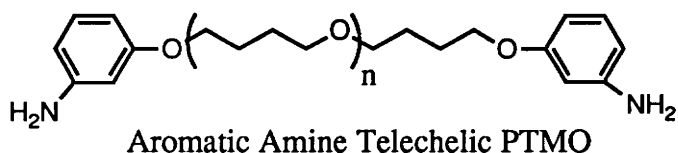
whether only PTMO with primary amine end groups was present, or if PTMO with both primary and secondary end groups were also present.

$^1\text{H}$  NMR spectroscopy and IR spectroscopy was used to confirm the identity of the functionalized PTMO.  $^1\text{H}$  NMR spectroscopy was also used to determine the  $M_n$  of the m-aminophenoxide functionalized PTMO.

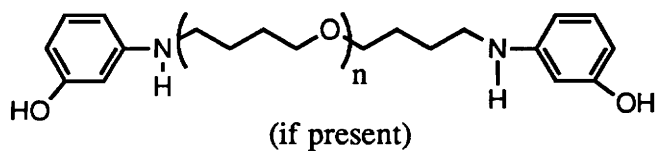
$^{19}\text{F}$  NMR spectroscopy has an inherent advantage in comparison with  $^1\text{H}$  NMR spectroscopy because of the greater range of  $^{19}\text{F}$  chemical shifts. Trifluoroacetic anhydride reacts quantitatively with primary amine, secondary amine and hydroxy end groups, serving as a fluorine tag for these functionalities.<sup>10,11</sup> The m-aminophenoxide functionalized PTMO was fluorine tagged with trifluoroacetic anhydride (scheme 3), and  $^{19}\text{F}$  NMR spectroscopy was performed to determine the relative amounts of hydroxy end groups present (if any) relative to primary amine end groups. Fluorine tagged m-phenetidine (Model  $\text{NH}_2$ ) and 3-dimethylaminophenol (Model OH) were used as model compounds for comparison to the tagged m-aminophenoxide functionalized PTMO  $^{19}\text{F}$  NMR spectra (scheme 4).

**Scheme 3**  
**Possible Reactions of Trifluoroacetic anhydride**  
**with m-Aminophenoxide Functionalized PTMO**

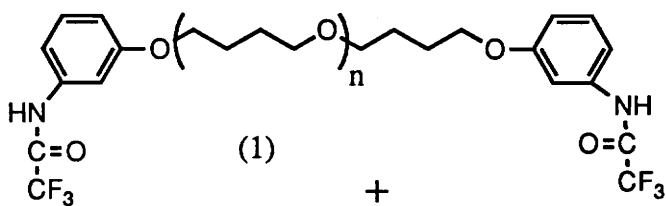
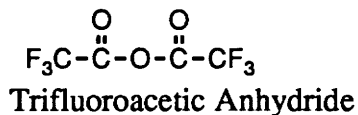
m-Aminophenoxide Functionalized PTMO



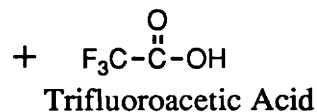
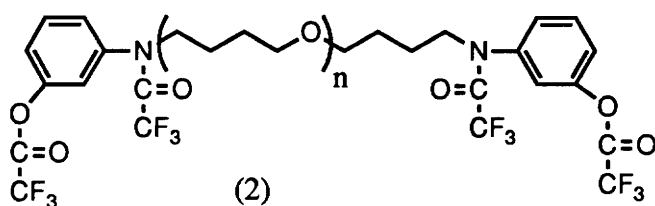
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1 hour  
 Room temp.  
 N<sub>2</sub> atm.



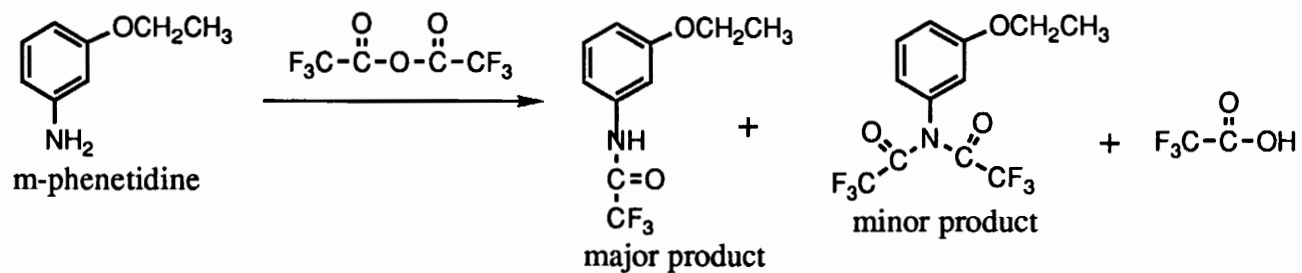
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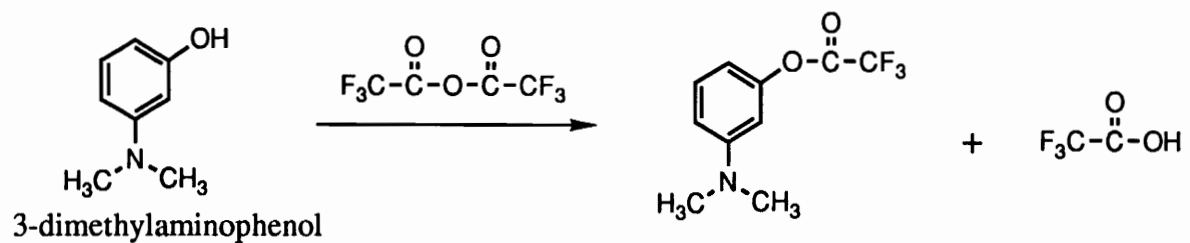
Note: The amine group in (1) may react further with trifluoroacetic anhydride. The amine group in (2) may not react completely with trifluoroacetic anhydride in given time.

Scheme 4  
Possible Reactions of Trifluoroacetic Anhydride with  
m-Phenetidine and 3-Dimethylaminophenol

Model NH<sub>2</sub>



Model OH



## Chapter 2

### LITERATURE REVIEW

#### 2.1 Living Polymerization of THF

A living polymerization proceeds via a non-terminated active center; virtually no termination reactions nor chain transfer reactions occur. In order for a polymerization to be living, the active propagating center must be relatively stable. In a typical living polymerization, the molecular weight can be controlled by either controlling the ratio of monomer to initiator or by controlling the percent monomer conversion, which is directly proportional to the number average molecular weight. The latter is achieved by selective termination at specified percent conversions. If the rate of initiation is much greater than the rate of propagation ( $R_i \gg R_p$ ), then the initiation can be considered instantaneous. At higher molecular weights under these conditions, the molecular weight distribution approaches a monodisperse or poisson distribution (equation 1).

$$\text{MWD} = \frac{\langle \text{Mw} \rangle}{\langle \text{Mn} \rangle} = 1 + \frac{\langle \text{Mn} \rangle}{\langle \text{Mn} \rangle^2} \approx 1 + \frac{1}{\langle \text{Mn} \rangle} \quad \text{Equation 1}$$

As  $\langle \text{Mn} \rangle \rightarrow \text{infinity}$  (large macromolecule),  
 $\text{MWD} \rightarrow 1.0$

where  $\langle \text{Mn} \rangle$  = number average molecular weight  
 $\langle \text{Mw} \rangle$  = weight average molecular weight  
 $\text{MWD}$  = molecular weight distribution

Living polymerizations are useful because the molecular weight and molecular weight distribution can be controlled; block copolymers can be readily synthesized, where a living macromolecule initiates another set of monomers; and functionalization of end groups can be controlled by selective initiation and termination.

Trifluoroboron/epichlorohydrin, triethyloxonium tetrafluoroborate ( $\text{Et}_3\text{OBF}_4$ ), super acids such as  $\text{CF}_3\text{SO}_3\text{H}$  (triflic acid) and  $\text{CH}_3\text{OSO}_2\text{CF}_3$ , and super acid anhydrides can be used to initiate living polymerizations of THF.<sup>12</sup> Smith and Hubin discovered that using triflic anhydride as an initiator in the presence of tetrahydrofuran (THF) induced a bifunctional cationic living polymerization of THF (scheme 1).<sup>7,8</sup> Using triflic anhydride as an initiator in the polymerization of THF, the rate of initiation is much faster than the rate of propagation;<sup>13</sup> thus, under ideal conditions a narrow molecular weight distribution can be achieved. Any suitable nucleophile

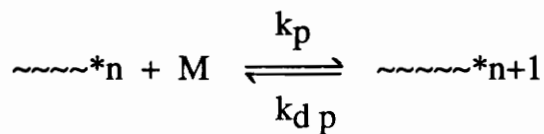
acts as a terminating agent, producing telechelic PTMO where the functionality is determined by the nucleophile (scheme 1). The polymerization of THF is an equilibrated process, so special considerations must be taken into account in order to synthesize PTMO of controlled molecular weight and narrow molecular weight distribution. These considerations are discussed in section 2.2 and section 2.3.

## 2.2 Equilibrium Considerations

The polymerization of THF is a highly equilibrated polymerization, as are most ring opening polymerizations. The change in enthalpy ( $\Delta H$ ) is approximately -5.6 kcal/mole and the change in entropy ( $\Delta S$ ) is approximately -19.7 cal/mole for the polymerization of THF,<sup>14</sup> which at low temperatures allow for a favorable change in Gibb's Free Energy ( $\Delta G$ ) in the direction of polymerization.<sup>14,15</sup> THF can only be polymerized cationically because 1) THF acts as a Lewis base and 2) the  $\Delta G$  for ring opening THF is small and negative, i.e., THF does not possess sufficient "ring strain" to be opened anionically.<sup>12,15</sup> Both temperature and monomer concentration play important roles in dictating polymerization. In order for the polymerization to occur and proceed, the temperature must be maintained below the ceiling temperature (equation 2), and the

monomer concentration must be maintained above the critical monomer concentration at a given temperature (equation 3). Both of these conditions must be met in order to drive the equilibrium towards polymerization.

Derivation for  $T_c$  and  $M_c$ :<sup>16</sup>



$$K = \frac{k_p}{k_{dp}} = \frac{[\sim\sim\sim^*n+1]}{[\sim\sim\sim^*n] [M]}$$

where  $\sim\sim\sim$  = growing polymer chain  
 $*$  = living end of growing polymer  
 $k_p$  = rate constant of propagation  
 $k_{dp}$  = rate constant of depropagation  
 $K$  = equilibrium constant  
 $[M]$  = monomer concentration

Generally,  $[\sim\sim\sim^*n+1] \approx [\sim\sim\sim^*n]$

so  $K \approx 1/[M]$

$$\Delta G = \Delta H - T\Delta S = -RT \ln K \approx RT \ln [M]$$

where  $\Delta G$  = change in Gibb's Free Energy  
 $\Delta H$  = change in enthalpy  
 $\Delta S$  = change in entropy  
 $T$  = temperature  
 $R$  = gas constant

At equilibrium,  $\Delta G = 0$

Rearranging in terms of T gives

$$T_c = \frac{\Delta H}{\Delta S + R \ln[M]} \quad \text{Equation 2}$$

where  $T_c$  = ceiling temperature

Rearranging in terms of [M] gives

$$\ln [M_c] = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad \text{Equation 3}$$

where  $[M_c]$  = critical monomer concentration

Ceiling temperature values recorded in the literature generally refer to the upper temperature limit above which polymer cannot be obtained, even from pure monomer.

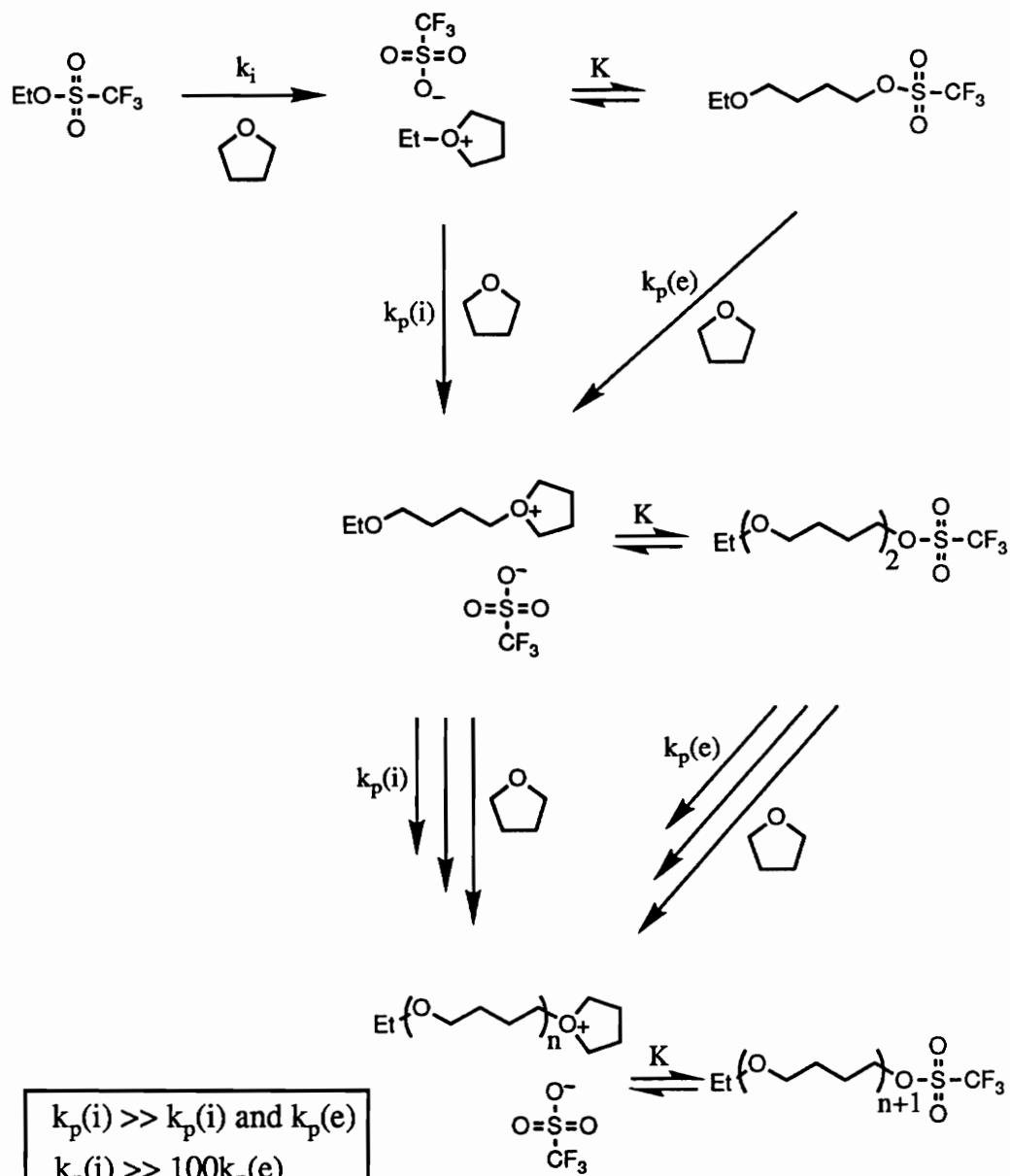
The predominant propagating species in the polymerization of THF is the tertiary oxonium ion, which is a relatively stable cation. Propagation occurs via a nucleophilic attack by the oxygen atom on the THF monomer at a carbon alpha to the oxonium ion. Depropagation occurs by a similar nucleophilic attack by the penultimate oxygen atom followed by expulsion of monomer (scheme 1).<sup>17</sup> In order for the polymerization to proceed, the polymerization temperature must be maintained below the ceiling temperature of 83°C. If

the polymerization temperature is lower than  $-20^{\circ}\text{C}$ , however, then the rate of propagation is so slow as to be considered stopped. Thus, the temperature "window" for the polymerization of THF must be maintained between  $-20^{\circ}\text{C}$  and  $83^{\circ}\text{C}$ .<sup>1,2</sup> To ensure that the polymerization is living, the polymerization temperature should be maintained at low temperatures, such as  $0^{\circ}\text{C}$ .<sup>2,12</sup>

An additional equilibrium exists between the tertiary oxonium ion species (macroion) and the macroester formed by nucleophilic attack of the triflate counter ion at a carbon alpha to the oxonium ion (see scheme 5).<sup>13,14,18-24</sup> In this scheme and discussion of kinetic experiments, ethyl trifluoromethanesulfonate ( $\text{CH}_3\text{CH}_2\text{OSO}_2\text{CF}_3$ ) was used as the initiator. Identical counter ions are produced as a polymerization using triflic anhydride as an initiator. The equilibrium interchange between the macroion and the macroester is much faster than the rate of propagation.<sup>19</sup> Penczek, et al, and Saegusa, et al, found that the rate of propagation through the macroions ( $k_p(i)$ ) is more than 100 times faster than the rate of propagation through the macroester ( $k_p(e)$ ).<sup>14,21,25</sup> Chain growth proceeds almost exclusively through the macroions.<sup>13,14,19-24</sup>

The equilibrium constant (K) is greatly influenced by the polarity of solvent used in the polymerization of THF. In a

**Scheme 5**  
**Polymerization of THF Through All Equilibrated Species**



where  $k_i$  = rate of initiation

$K$  = equilibrium constant

$k_p(i)$  = rate of propagation through macroions

$k_p(e)$  = rate of propagation through macroester

nonpolar solvent such as carbon tetrachloride,  $K = 14.3$ , and the macroester species dominates.<sup>14</sup> In an intermediate solvent such as methylene chloride,  $K = 1.7$ , and the macroion and macroester are both significantly present.<sup>14</sup> In a polar solvent such as nitromethane, the macroion species dominates.<sup>18,24</sup> Regardless of solvent, the chain growth proceeds almost exclusively through the macroions due to  $k_p(i)$  being much greater than  $k_p(e)$ . In addition, a faster overall rate of polymerization, i.e., a higher apparent rate constant, has been noted in more polar solvents.<sup>14,18-20,24</sup>

Another product that has been postulated is a macrocyclic oxonium ion as a result of the intramolecular reaction with polymeric oxygen and the tertiary oxonium ion.<sup>1,25</sup> In practical THF polymerizations, however, the number of macrocycles is so small (less than 3% of the total product) as to be considered negligible.<sup>1,26,27</sup>

### 2.3 Molecular Weight Control of PTMO

The molecular weight of PTMO is routinely controlled by controlling the percent conversion rather than the ratio of monomer to initiator (and allowing complete conversion). Too high of percent conversions can lead to broad molecular weight distributions.<sup>1</sup> In some respects, the living cationic

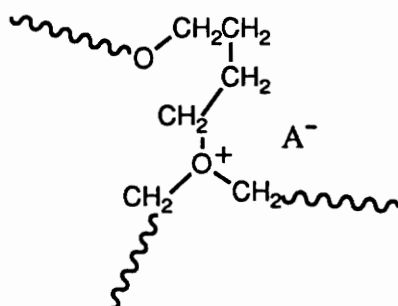
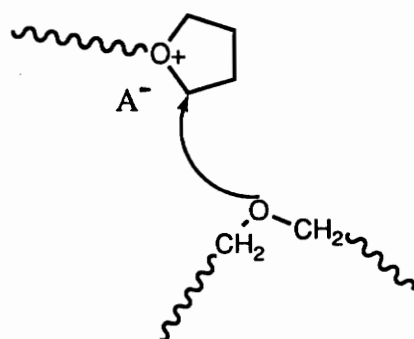
polymerization of THF resembles the living anionic polymerization of styrene. However, in the living anionic polymerization of styrene, polystyrene with a narrow molecular weight distribution can be readily obtained at high conversions, while in the living cationic polymerization of THF, PTMO with a narrow molecular distribution can only be obtained routinely at low percent conversions and short polymerization times. One reason for the differences in the two systems lies in the different rates of depropagation in the polymerizations of polystyrene and PTMO. The polymerization of THF is a highly equilibrated process; living PTMO depropagates at temperatures where propagation occurs at reasonable rates. Living polystyrene depropagates at an extremely slow rate. If "living" PTMO is heated to its ceiling temperature, pure THF monomer is obtained within a short time. Heating living polystyrene causes a very small change in monomer concentration. At lower conversions, high THF monomer concentrations effectively "push the equilibrium to the right" towards polymer product, and depropagation does not play as great a role. As the cationic living polymerization of THF progresses towards high conversions, the monomer concentration falls and approaches the critical monomer concentration; thus, depropagation plays a greater role

compared to the beginning of the polymerization. This leads to a broadening of the molecular weight distribution.<sup>1,28,29</sup>

Another reason for the differences between the two systems lies in the intramolecular transfer reactions that can occur with PTMO but not with polystyrene. The regularly spaced oxygen atoms along the backbone of PTMO can react in an intramolecular fashion with the tertiary oxonium ion to produce a branched ion. THF monomer can react at any of the three carbon atoms alpha to the acyclic polymeric oxonium ion (see scheme 6). This can result in a randomization of molecular weights of PTMO within as short a period of time as eight hours.<sup>1</sup>

Conversely, too low of percent conversions may also lead to broader molecular weights due to the finite time needed for initiation to be completed. As the percent conversion increases (but still well below the critical monomer concentration at a given temperature), the relative differences in the molecular weights of the polymer chains becomes smaller, producing overall a more narrow molecular weight distribution (equation 1).<sup>9</sup> An optimization of percent conversion is necessary to produce PTMO of low polydispersity.

Scheme 6  
Intermolecular Transfer Reactions of PTMO



where  $A^-$  = counter anion

## 2.4 Termination of PTMO Using p-Aminophenoxide

Kobayashi, et al, used triflic anhydride as the initiator for the living polymerization of THF, and experimented with various terminating agents to produce telechelic PTMO of controlled bifunctionality.<sup>30,31</sup> Telechelic PTMO with carboxyl end groups was produced in high yields.<sup>30</sup> p-Aminophenoxide was used as a terminating agent in the attempt to produce telechelic PTMO with aromatic amine end groups. When p-aminophenoxide was used as a terminating agent, the end groups of the PTMO consisted predominantly of aromatic amine end groups, however, approximately ten percent of the PTMO contained aromatic hydroxy end groups.<sup>31</sup>

## 2.5 Conclusions

PTMO and the polymerization of THF is an interesting area of polymer chemistry, from both a theoretical and practical viewpoint. The molecular weight, molecular weight distribution, functionality of end groups and block copolymer formation can all be highly controlled. The polymerization of THF has been, and should continue to be, beneficial in the understanding of living cationic polymerizations and of equilibrated polymerizations.

## Chapter 3

### EXPERIMENTAL

#### 3.1 Considerations of Purity

In order for the living polymerization of THF to occur, the monomer, solvents and glassware used must be scrupulously dry because water acts as a good terminating agent. Dry pre-purified nitrogen or argon gas (AIRCO, Murray Hill, NJ) was achieved by passing the gas through a column of dryrite (W. A. Hammond Corp., Xenia, Ohio) and molecular sieves (Fisher Scientific, Raritan, NJ), which was directly attached to the gas lines. Pre-purified nitrogen was used rather than house nitrogen because of the lowered water content.

Glassware was prepared by flaming under a dry nitrogen or argon atmosphere. All experiments were conducted under a partial positive pressure atmosphere of dry nitrogen or argon.

THF (Fisher Scientific, Raritan, NJ) was refluxed over sodium and benzophenone (Aldrich Chemical Co, Milwaukee, WI) under a dry nitrogen atmosphere. THF was distilled from this mixture after the solution had become a blue-purple color, indicating that the THF was completely dry. Benzophenone forms a complex with sodium under extremely dry conditions.

Toluene, DMSO, chloroform, and methylene chloride (Fisher Scientific, Raritan, NJ) were purified by distilling over calcium hydride under dry nitrogen.

Triflic anhydride (Aldrich Chemical Co., Milwaukee, WI) was used as purchased. Triflic anhydride is readily hydrolyzed by water and must be handled very carefully. Transfers of triflic anhydride were conducted by cannula or syringe.

### **3.2 Polymerization of THF**

THF was collected in a 1-neck round bottom flask equipped with a magnetic stir bar, by distillation as described previously, then sealed with a wired rubber septum and chilled to 0°C. The polymerization was performed in bulk, where THF served as both monomer and solvent. Triflic anhydride, in the ratio of 3 ml triflic anhydride to 100 ml THF, was added via syringe to the chilled THF. An exotherm was noted. The molecular weight was controlled by controlling the percent conversion, i.e., controlling the time that the polymerization was allowed to proceed. For low molecular weight PTMO in the range of 1000 to 3000 g/mole, polymerizations were allowed to proceed about two minutes or less. The polymerization time may be extended by reducing the amount of triflic anhydride relative to THF.

### 3.3 Preparation of Potassium m-Aminophenoxide

m-Aminophenol (Aldrich Chemical Co., Milwaukee, WI) was sublimed twice. The sublimed m-aminophenol was placed in a 2-neck round bottom flask, sealed with a wired rubber septa and flooded with dry nitrogen. Equal amounts of distilled, degassed toluene and DMSO were added to the m-aminophenol via syringe, while stirring with a magnetic stir bar, until the m-aminophenol was dissolved. KOH was dissolved in a small amount of distilled, degassed water and added to the m-aminophenol/toluene/DMSO solution in the ratio of 0.90 moles KOH to 1.00 moles m-aminophenol. The ratio of KOH to m-aminophenol could have been more equivalent, but a slight excess of m-aminophenol must be maintained since any unreacted KOH will terminate the living PTMO. The solution was refluxed at approximately 110°C under a dry nitrogen atmosphere. Water was removed via a Dean Stark trap. The color of the solution gradually changed from a yellow color to a deep reddish color as the potassium m-aminophenoxide salt formed. After all traces of water had been removed, the m-aminophenoxide salt was not completely soluble in the mixture of toluene and DMSO. Applying a vacuum and slight heat to the solution removed the toluene,

leaving the m-aminophenoxide completely dissolved in the remaining DMSO. By removing a small aliquot of the m-aminophenoxide/DMSO solution and performing a HCl titration, the normality of the m-aminophenoxide solution was determined. Additional DMSO could be removed using a vacuum and heating slightly to obtain a normality approaching 1N potassium m-aminophenoxide.

### **3.4 Functionalization of Living PTMO with m-Aminophenoxide**

The addition of m-aminophenoxide to terminate and functionalize living PTMO was performed using two different procedures. In the first procedure, the living PTMO was added via cannula to the m-aminophenoxide/DMSO solution in the molar ratio of approximately 0.9 moles living PTMO chain ends to 1.0 moles m-aminophenoxide. The ratio of living chain ends to excess m-aminophenoxide could have been more equivalent, but a slight excess of m-aminophenoxide to living chain ends must be maintained to insure that all the living ends of the PTMO are functionalized with m-aminophenoxide. Conversely, in the second procedure, the m-aminophenoxide/DMSO solution was added via fast syringing to the living PTMO using the same molar ratios.

### 3.5 Purification of m-Aminophenoxide Functionalized PTMO

Higher molecular weight PTMO (greater than approximately 4000 g/mole) was precipitated in an ice slurry using a blender. A small amount of sodium bicarbonate was added to the ice slurry to neutralize any residual triflate anion.

Lower molecular weight PTMO (less than approximately 4000 g/mole) was purified by first removing most of the excess THF by using a vacuum pump with a cold finger in line before the trap or a rotary evaporator. It is imperative that no heat be used since PTMO rapidly degrades in the presence of the triflate anion. Separatory funnel extraction was performed using an organic phase of diethyl ether and an aqueous phase of approximately 5% aqueous sodium bicarbonate. Low molecular weight PTMO was extracted three times with the ether/aqueous bicarbonate solution, then two times with ether and pure water. PTMO remained in the organic layer; triflate and excess m-aminophenoxide migrated to the aqueous layer.

A small amount of deoxidizing agent, such as Irgonox-1010 (Ciba-Geigy, Hawthorne, NY), was added to PTMO of all molecular weights to stabilize against oxidation over time. All PTMO samples were placed in a vacuum oven overnight. The

vacuum ovens were used with no heat to minimize degradation.

### **3.6 Analysis of m-Aminophenoxide Functionalized PTMO**

#### **3.6.1 Titration**

An MCI Model GT-05 automatic titrator was used for HCl and HBr titrations. HBr titrations were used to determine the molecular weight of the m-aminophenoxide functionalized PTMO by reacting with the tertiary amine groups. THF was used as the solvent for the HBr titrations. The normality of the m-aminophenoxide/DMSO solution was determined using HCl titration. The m-aminophenoxide/DMSO solution was further dissolved in water for the HCL titrations. Water was used as a solvent instead of THF for the HCl titrations because THF gave a second endpoint, which was not desirable.

#### **3.6.2 $^1\text{H}$ NMR Spectroscopy and Infrared Spectroscopy**

Proton NMR spectroscopy was performed using a Varian 400 MHz NMR.  $\text{CDCl}_3$  and d-acetone (NMR grade, Aldrich Chemical Co., Milwaukee, WI) were predominantly used as the

deuterated solvents. A Nicolet FTIR was used to obtain infrared spectra.

### 3.6.3 $^{19}\text{F}$ NMR Spectroscopy

The fluorine tagging reactions were conducted in wired rubber septa sealed test tubes which had been flooded with dry nitrogen or argon to eliminate the presence of atmospheric water. A five-fold molar excess (approximately 100  $\mu\text{l}$ ) of trifluoroacetic anhydride (Aldrich Chemical Co., Milwaukee, WI) was added by syringe to approximately 100 mg each of m-aminophenoxide terminated PTMO samples (0.94 g of WLC-0067,  $M_n = 2600$  g/mole; 0.110 g of WLC-0085,  $M_n = 1500$  g/mole). The reactions were allowed to proceed one hour at room temperature, with occasional swirling of the sealed test tubes. After 30 minutes, color changes from orange-brown solutions to dark yellow solutions were noted, indicating that the reactions had occurred.

Excess trifluoroacetic anhydride was removed via vacuum. Approximately 0.5 ml of dry  $\text{CDCl}_3$  (NMR grade, Aldrich Chemical Co., Milwaukee, WI) was added to each test tube via syringe, then removed by vacuum. 1.0 ml of dry  $\text{CDCl}_3$  was then added to each test tube, and the contents of

the test tubes transferred to 5 ml NMR tubes for analysis using  $^{19}\text{F}$  NMR spectroscopy.

$^{19}\text{F}$  NMR spectroscopy was performed using a Varian 400 MHz NMR instrument. Hexafluorobenzene (PCR Inc., Gainesville, FL) was used as the standard and referenced to Freon 11 ( $\text{CFCl}_3$ ) in the  $^{19}\text{F}$  NMR spectroscopy experiments.

$\text{CDCl}_3$  was dried by passing it through a small column of neutral alumina (Fisher Scientific, Raritan, NJ). The column was composed of a disposable pasteur pipette with a plug of glass wool (or piece of Kimwipe) and a small bed of vacuum dried neutral alumina. Nitrogen was blown through the glass wool plug (or Kimwipe) before the addition of alumina to remove dust particles.<sup>32</sup>

10.3 mg of m-phenetidine (Aldrich Chemical Co., Milwaukee, WI), 10.5 mg of 3-dimethylaminophenol (Aldrich) and 22 mg of m-aminophenol were reacted with trifluoroacetic anhydride under the same reaction conditions as described above and analyzed accordingly. Again, color changes were noted 20 to 30 minutes after the addition of trifluoroacetic anhydride, indicating that the reactions had occurred.

$^1\text{H}$  NMR spectra were obtained on the m-phenetidine and 3-dimethylaminophenol samples after the  $^{19}\text{F}$  NMR experiments were completed to insure that no cross contamination of the model compounds had occurred.

A  $^{19}\text{F}$  NMR spectrum of trifluoroacetic anhydride was obtained to facilitate peak identification and to determine how much, if any, had hydrolyzed to trifluoroacetic acid during storage. Additionally, several samples were spiked with trifluoroacetic anhydride after initial  $^{19}\text{F}$  NMR spectra were obtained to conclusively determine the residual trifluoroacetic anhydride peak.

## CHAPTER 4

### RESULTS AND DISCUSSION

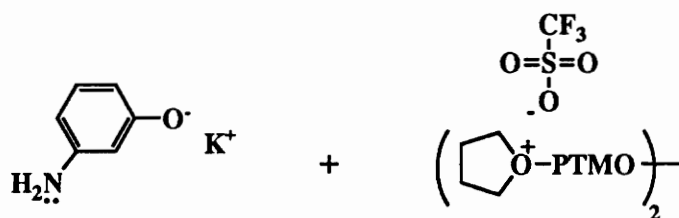
#### 4.1 Order of Addition of Living PTMO to m-Aminophenoxide

Aromatic amine telechelic PTMO of controlled molecular weight has been produced by terminating bifunctional cationic living PTMO with m-aminophenoxide. The order of addition of m-aminophenoxide to living PTMO was found to be crucial in order to obtain linear aromatic amine telechelic PTMO. Two different procedures were used to terminate living PTMO with m-aminophenoxide (scheme 7).

In the first procedure, living PTMO was added via cannula to a slight excess of the m-aminophenoxide/DMSO solution. The resulting product was a brown, tacky material that could be dissolved in many common solvents such as THF, DMSO, acetone, chloroform and ether. Molecular weight determination using HBr titration and  $^1\text{H}$  NMR spectroscopy gave consistent  $M_n$  values, which are discussed further in section 4.2 and section 4.3.

In the second procedure, a slight excess of

Scheme 7  
**Order of Addition of Living PTMO to m-Aminophenoxide**



**PROCEDURE 1**

Living PTMO added to slight excess  
 m-aminophenoxide/DMSO solution

**OBSERVATION:** brown "sticky" reaction product obtained that

- \* can be dissolved
- \* gives consistent molecular weight values when characterized

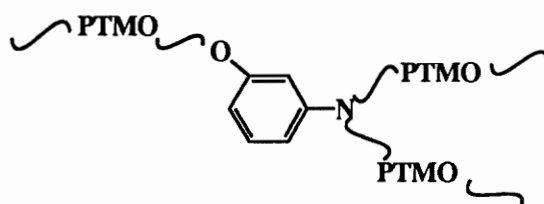
**PROCEDURE 2**

Slight excess m-aminophenoxide/DMSO solution  
 added to living PTMO

**OBSERVATION:** brown rubbery (suspected) gel obtained that

- \* does not dissolve in any common solvents (including acetone, CHCl<sub>3</sub>, THF)

**Suspected Crosslinking Reaction:**



m-aminophenoxide was added via fast syringing to the living PTMO. Before all of the m-aminophenoxide/DMSO solution was completely added, a brown and orange colored globular material had formed that could not be dissolved in any common solvents, including THF. The physical properties of the material were indicative of a cross-linked gel.

Both the negatively charged oxygen group and the amine group of the m-aminophenoxide could potentially act as terminating agents for cationic living PTMO (scheme 7). As the living PTMO was added to the m-aminophenoxide solution in the first procedure, the living PTMO chain ends may have "seen" an excess of m-aminophenoxide from a molecular "Maxwell demon" standpoint. The negatively charged oxygen probably preferentially terminated the living PTMO relative to the neutral amine group due to the greater nucleophilicity of the negatively charged oxygen, forming linear aromatic amine telechelic PTMO.

When p-aminophenoxide was used to terminate the living polymerization of THF, the end groups of the PTMO consisted predominantly of aromatic end groups, however, a significant amount of PTMO containing aromatic hydroxy end groups was also present.<sup>31</sup> The amine of the m-aminophenoxide is less nucleophilic than the amine of the p-aminophenoxide due to the lack of resonance between substituents in the meta

structure. By using m-aminophenoxide as a terminating agent for the living polymerization of THF, a higher ratio of aromatic amine end groups relative to aromatic hydroxy end groups was expected.

In the second procedure, as the m-aminophenoxide solution was added to the living PTMO, the m-aminophenoxide may have "seen" an excess of living PTMO chain ends from a molecular standpoint. Both the negatively charged oxygen and the amine group of the m-aminophenoxide probably terminated the living PTMO, forming a cross-linked material.

The linear aromatic amine telechelic PTMO obtained using the first procedure will be discussed throughout this thesis.

## **4.2 HBr Titration and Infrared Spectroscopy Results**

HBr titration is used to determine the  $M_n$  of polymers with amine end groups. A typical HBr titration of the aromatic amine telechelic PTMO is shown in figure 1. The presence of only one equivalence point indicated that a primary amine was the predominant end group of the functionalized PTMO. If an appreciable amount of secondary amine were present, then two equivalence points would have been expected. The  $M_n$  values using HBr titration for two successful polymerizations of aromatic amine telechelic PTMO were 2500 g/mole for sample

WLC-0067 and 1200 g/mole for sample WLC-0085 (table 1). The relative standard error was approximately one percent for HBr titrations using the automatic titrator.

The IR spectra of the m-aminophenol<sup>33</sup> is shown in figure 2 and aromatic amine telechelic PTMO (sample WLC-0085) is shown in figure 3. The peak between 3300 and 3600 cm<sup>-1</sup> indicated a strong primary amine stretch.

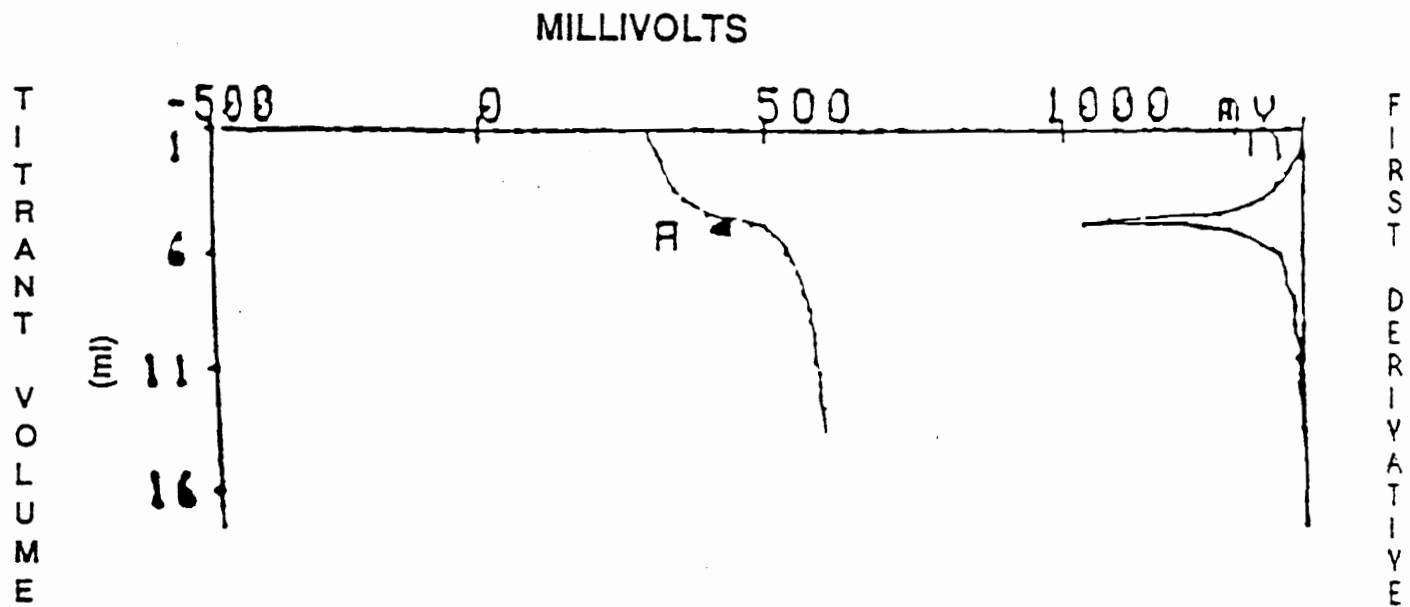


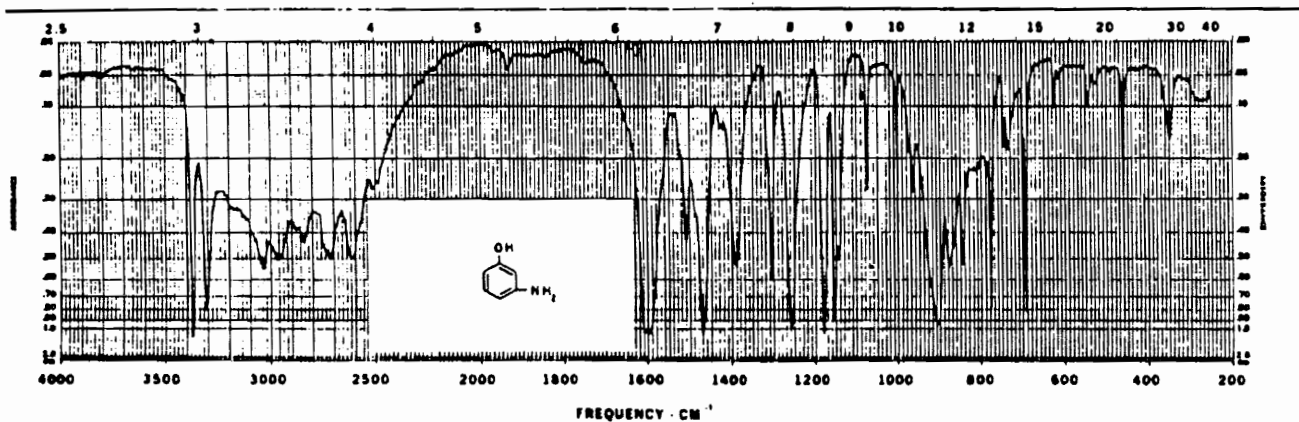
Figure 1  
HBr Titration of Aromatic Amine  
Telechelic PTMO

**Table 1**  
**Molecular Weight Determined from HBr Titration**

Sample	MW (g/mole)	$\langle MW \rangle_n$
WLC-0085	2328 2665 2362	2500
WLC-0067	1199 1156 1229 1285	1200

Note: The relative standard error is approximately one percent for HBr titrations using the MCI Model GT-05 automatic titrator. This produces an error of approximately 25 g/mole for WLC-0085, and an error of approximately 12 g/mole for WLC-0067.

m-AMINOPHENOL



$C_6H_7NO$

M.W. 109.13

M.P. 121-123°C

KBr Wafer



Source: The Matheson Co., Inc., E. Rutherford, N. J.

8088 K

Figure 2  
IR Spectrum of m-Aminophenol<sup>33</sup>

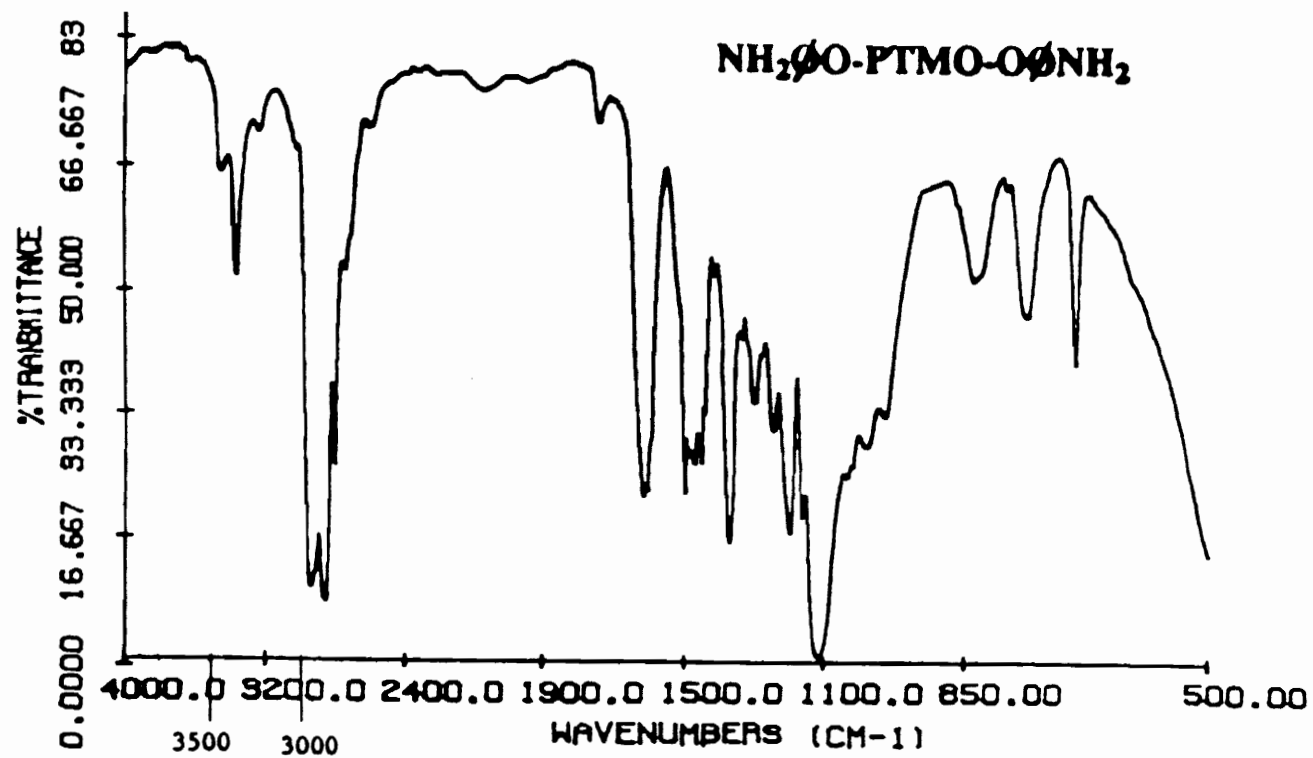
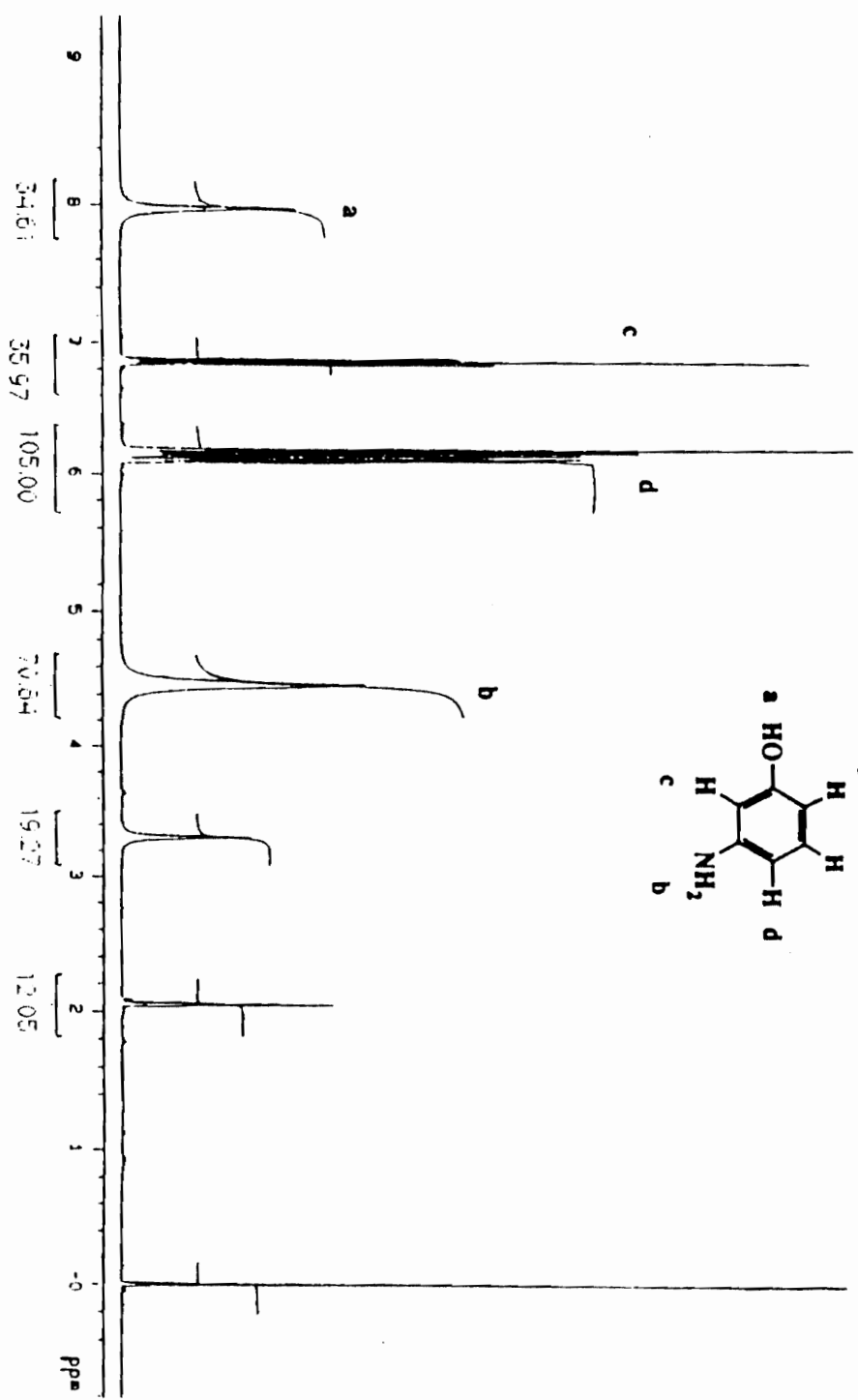
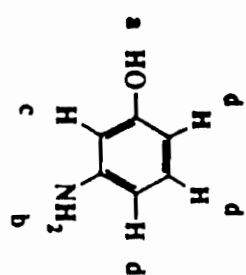


Figure 3  
IR Spectrum of m-Aminophenoxide Functionalized PTMO

### 4.3 $^1\text{H}$ NMR Spectroscopy Results

The  $^1\text{H}$  NMR spectrum for the initial starting material, sublimed m-aminophenol, is shown in figure 4. The  $^1\text{H}$  NMR spectra of linear aromatic amine telechelic PTMO (samples WLC-0067,  $M_n = 2600$  and WLC-0085,  $M_n = 1500$ ) are shown in figure 5 and figure 6. A peak was not discernible around 8 ppm in the  $^1\text{H}$  NMR spectrum of the functionalized PTMO, even when the amplitude was increased. This indicated that the PTMO did not contain an appreciable amount of aromatic hydroxy end groups. An integrated expansion of the aromatic amine telechelic PTMO  $^1\text{H}$  NMR spectrum is shown in figure 7.  $M_n$  values were determined algebraically from the ratios of the aromatic end group protons to the methylene protons in the repeating units of the PTMO samples (table 2). The calculation for determining  $M_n$  from the  $^1\text{H}$  NMR spectra is shown on pages 46 and 47 (see figure 7 for proton designations).



**Figure 4**  
**<sup>1</sup>H NMR Spectrum of m-Aminophenol**

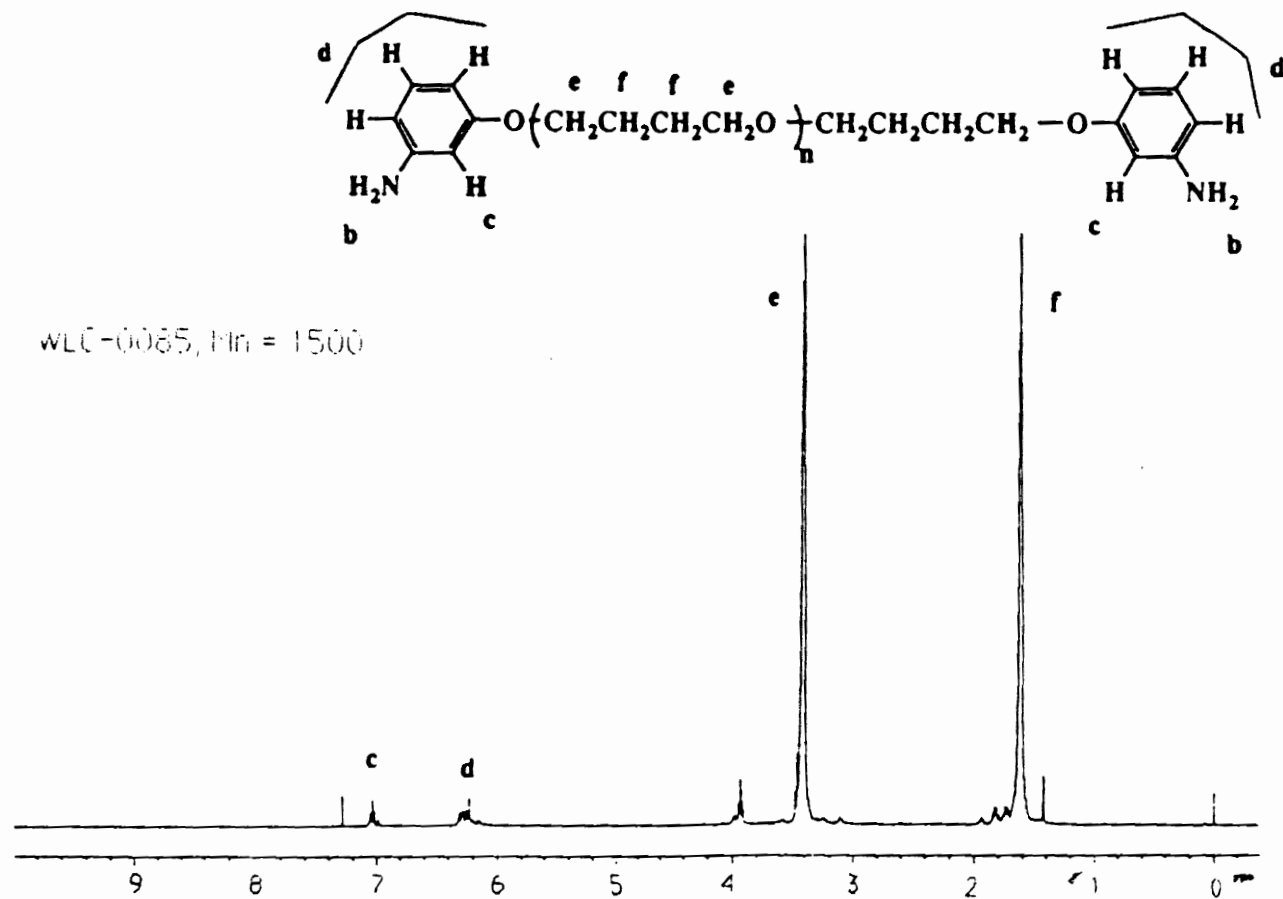
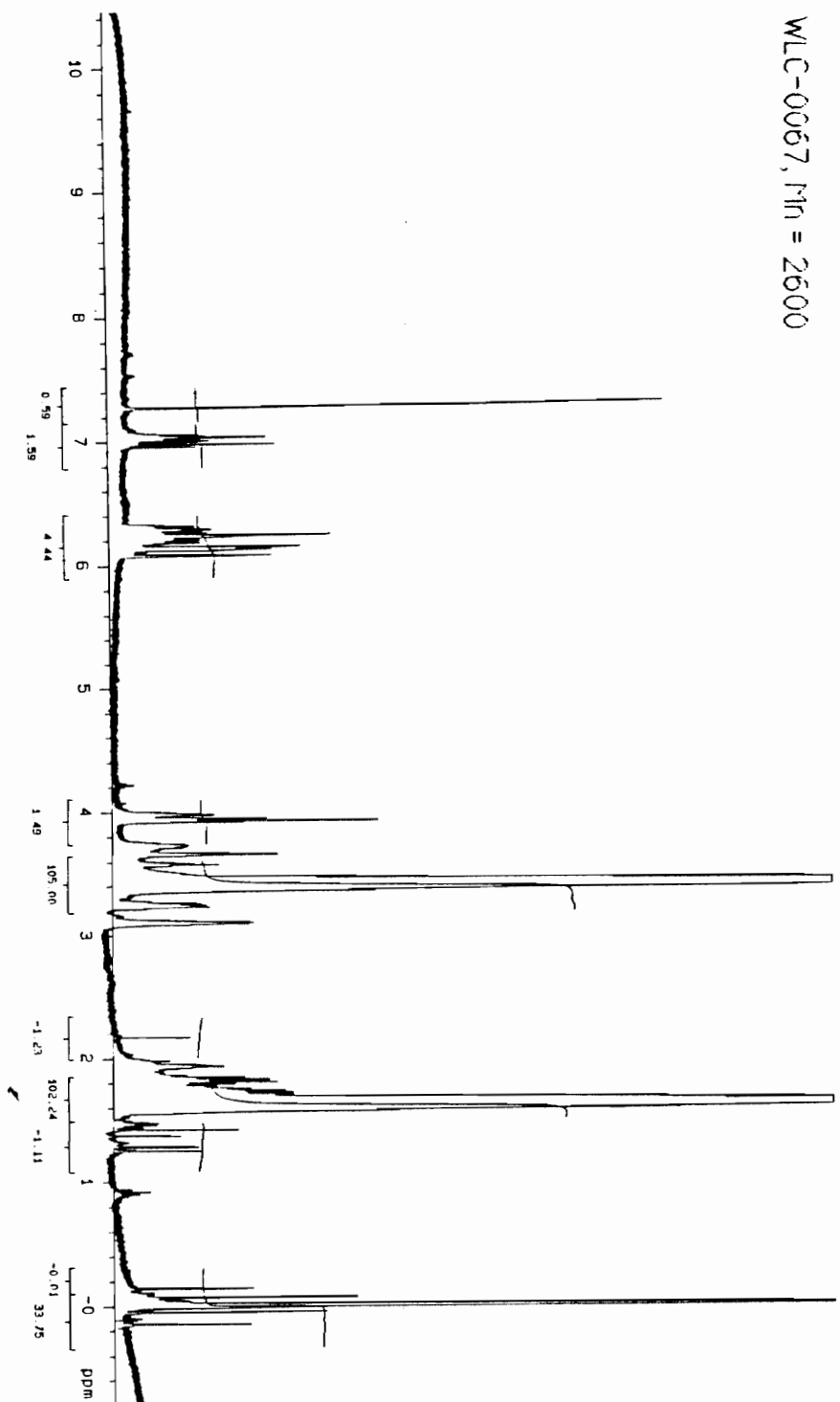
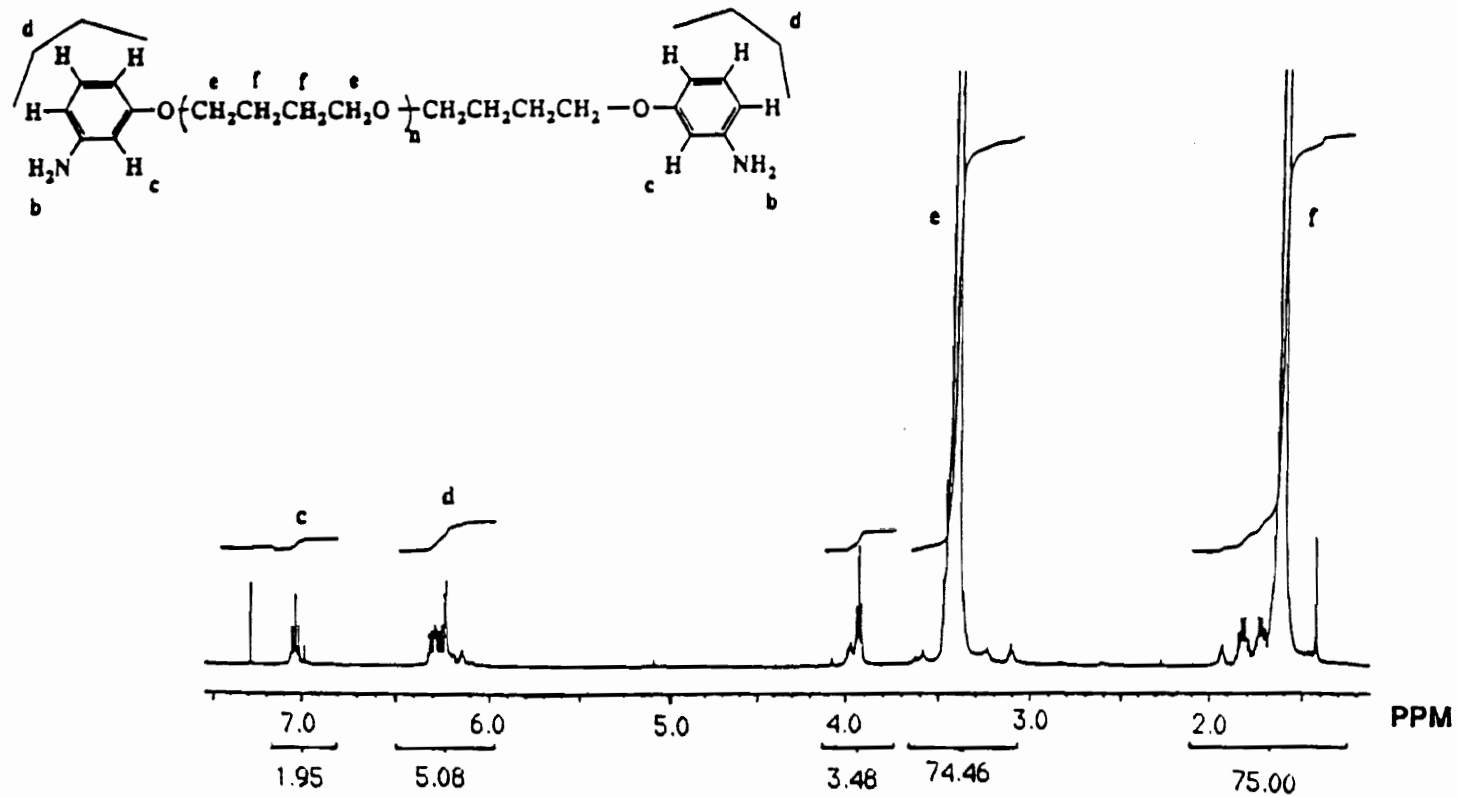


Figure 5  
 $^1\text{H}$  NMR Spectrum of m-Aminophenoxide  
 Functionalized PTMO

WLC-0067, Mn = 2600

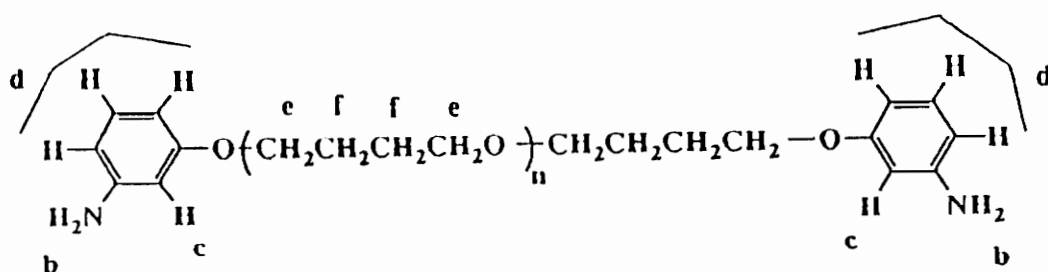


**Figure 6**  
**1H NMR Spectrum of m-Aminophenoxide**  
**Functionalized PTMO**



**Figure 7**  
**Expanded  $^1\text{H}$  NMR Spectrum of m-Aminophenoxide**  
**Functionalized PTMO**

**Table 2**  
**<sup>1</sup>H NMR Molecular Weight Data and**  
**Comparison to Titration Results**



Sample	1H Ratios	1H NMR Calc.	<MW>n (g/mole)	
			1H NMR	HBr Titr.
WLC-0067	c to <e,f>/2 d to <e,f>/2	2622 2796	2700	2500
WLC-0085	c to <e,f>/2 d to <e,f>/2	1653 1863	1800	1200

**Note:** The relative standard error is from 2 to 5 percent for  $M_n$  values using <sup>1</sup>H NMR spectroscopy. This produces an error from 54 to 135 g/mole for WLC-0067, and an error from 36 to 90 g/mole for WLC-0085.

## Calculation of $M_n$ Using Integrated $^1\text{H}$ NMR Spectrum

### Calculation Using Protons c

The ratio of protons c to an average of protons e and f is  
 $1 : 2n$ ,

where  $n$  = number of repeating polymer units.

Integration of the spectrum gives a ratio of 1.95 for the c protons to 74.73 for the average of e and f protons, which can be simplified to  $1 : 38.32$ .

Now,  $n$  may be determined algebraically from the  
 $1 : 2n$  ratio.

$$1 : 2n \text{ is to } 1 : 38.32$$

$$2n = 38.32$$

$$\text{Therefore, } n = 19.16$$

The repeat unit of PTMO has a molecular weight of 72.11 g/mole, so the molecular weight of the PTMO portion of the sample is

$$72.11 \text{ g/mole} * n = 72.11 \text{ g/mole} * 19.16 = 1381 \text{ g/mole}$$

The molecular weight of the telechelic m-aminophenoxide functionalities are 272 g/mole, so the total  $M_n$  of the sample is

$$1381 \text{ g/mole} + 272 \text{ g/mole} = 1653 \text{ g/mole}$$

## Calculation Using Protons d

The ratio of protons d to an average of protons e and f is  $1 : (2/3)n$ . Integration of the spectrum gives the ratio of 5.08 for the d protons to 74.73 for the average of e and f protons, which can be simplified to  $1 : 14.91$ .

Now, n may be determined algebraically from the  $1 : (2/3)n$  ratio.

$$1 : (2/3)n \text{ is to } 1 : 14.91$$

$$(2/3)n = 14.91$$

$$\text{Therefore, } n = 22.07$$

Multiplication by the molecular weight of the repeating PTMO unit and addition of the molecular weight of the telechelic m-aminophenoxide functionalities gives a total  $M_n$  of 1758 g/mole.

The relative standard error was from two percent to five percent for  $M_n$  values determined from  $^1\text{H}$  NMR spectroscopy using the Varian 400 MHz instrument. The  $M_n$  values determined by both HBr titration and  $^1\text{H}$  NMR spectroscopy gave good agreement for sample WLC-0067 and fair agreement for sample WLC-0085 (table 2). For sample WLC-0085, a  $M_n$  of 1000 g/mole was desired, and a  $M_n$  of approximately 1500 g/mole was produced.

#### 4.4 $^{19}\text{F}$ NMR Spectroscopy Results

In  $^{19}\text{F}$  NMR spectroscopy, a small change in electronic environment causes a significant chemical shift.  $^{19}\text{F}$  NMR spectra of the fluorine tagged PTMO samples WLC-0067 and WLC-0085 are shown in figure 8, figure 9 and figure 10. The peaks are presented in tabular form in table 3. The peak at -68.3 ppm in the m-aminophenoxide functionalized PTMO spectra did not correlate well with the organic molecules investigated in the article by H. Dorn, et al.<sup>11</sup> m-Phenetidine, designated Model NH<sub>2</sub>, and 3-dimethylaminophenol, designated Model OH, were chosen as model compounds. The electronic environment of the fluorine tagged model compounds should have been very similar to any possible fluorine tagged functionalities of the m-aminophenoxide functionalized PTMO (scheme 3 and scheme 4).

From  $^{19}\text{F}$  NMR spectroscopy, the trifluoroacetic anhydride used in this experiment was determined to be 91 % pure, with 9 % trifluoroacetic acid present ( figure 11). Since the trifluoroacetic anhydride was added in large excess to the samples, this should not have affected the results. The  $^{19}\text{F}$  NMR spectrum of fluorine tagged m-aminophenol is shown in figure 12.

The  $^{19}\text{F}$  NMR spectrum of the Model  $\text{NH}_2$  was very clean, with a strong peak at -68.6 ppm and a weaker peak at -70.8 ppm (figure 13 and figure 14). The peak at -68.6 ppm corresponded to the fluorine tag of the primary amine; the peak at -70.8 ppm was probably due to the trifluoroacetic anhydride reacting further with the fluorine tagged amine group (table 3).

The  $^{19}\text{F}$  NMR spectrum of the Model OH was not as clean (figure 15 and figure 16). Ortho and para compounds appeared to be present, as determined both by  $^1\text{H}$  NMR spectroscopy and  $^{19}\text{F}$  NMR spectroscopy. The peak at -71.4 ppm was a strong peak corresponding to the fluorine tag of the hydroxy group. The weaker peaks at -68.3 ppm and -68.2 ppm may have corresponded to impurities of methylaminophenol present in the sample (table 3).

$^1\text{H}$  NMR spectra of the model compounds were obtained after the  $^{19}\text{F}$  NMR experiment was completed (figure 17 and figure 18). No cross contamination of the model compounds occurred. The 3-dimethylaminophenol (Model OH) was not as pure as would have been desired. A more definitive experiment would entail further purification of the 3-dimethylaminophenol before performing the  $^{19}\text{F}$  NMR experiment.

The  $^{19}\text{F}$  NMR spectra of the m-aminophenoxide functionalized PTMO corresponded well with the Model  $\text{NH}_2$   $^{19}\text{F}$  NMR spectrum. Even when the amplitude was increased, no peaks were discernible in the region from -70.6 ppm to -72.5 ppm of the m-aminophenoxide functionalized PTMO spectra. A peak in this region would have corresponded to the Model OH  $^{19}\text{F}$  NMR spectrum.

## List of Abbreviations for $^{19}\text{F}$ NMR Spectroscopy Data

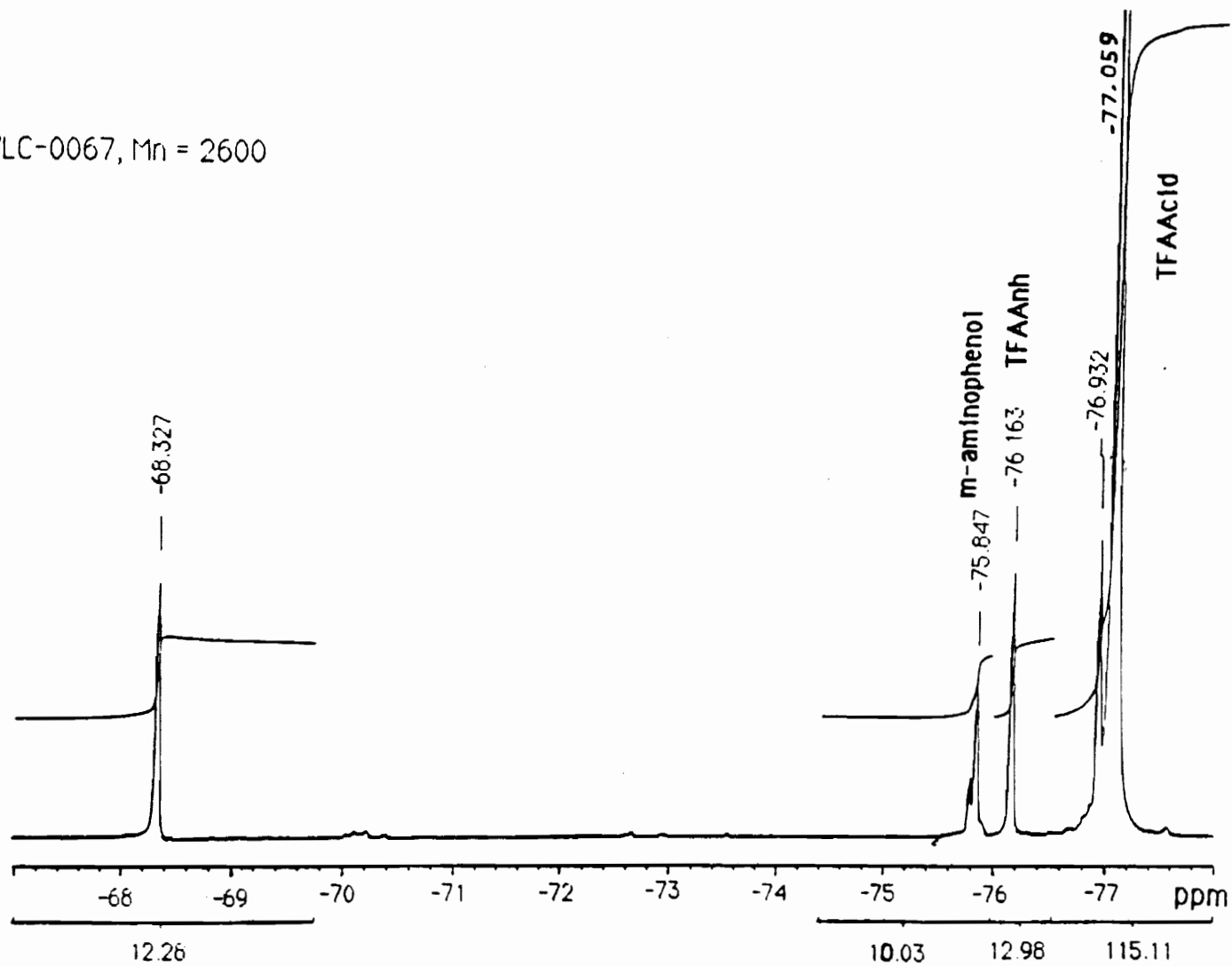
TFAAnh = trifluoroacetic anhydride

TFAAcid = trifluoroacetic acid

MAP = m-aminophenol

MAPoxide = m-aminophenoxide

WLC-0067, Mn = 2600



**Figure 8**  
**19F NMR of Derivatized MAPoxide Functionalized PTMO**

Spiked with TFAAnh

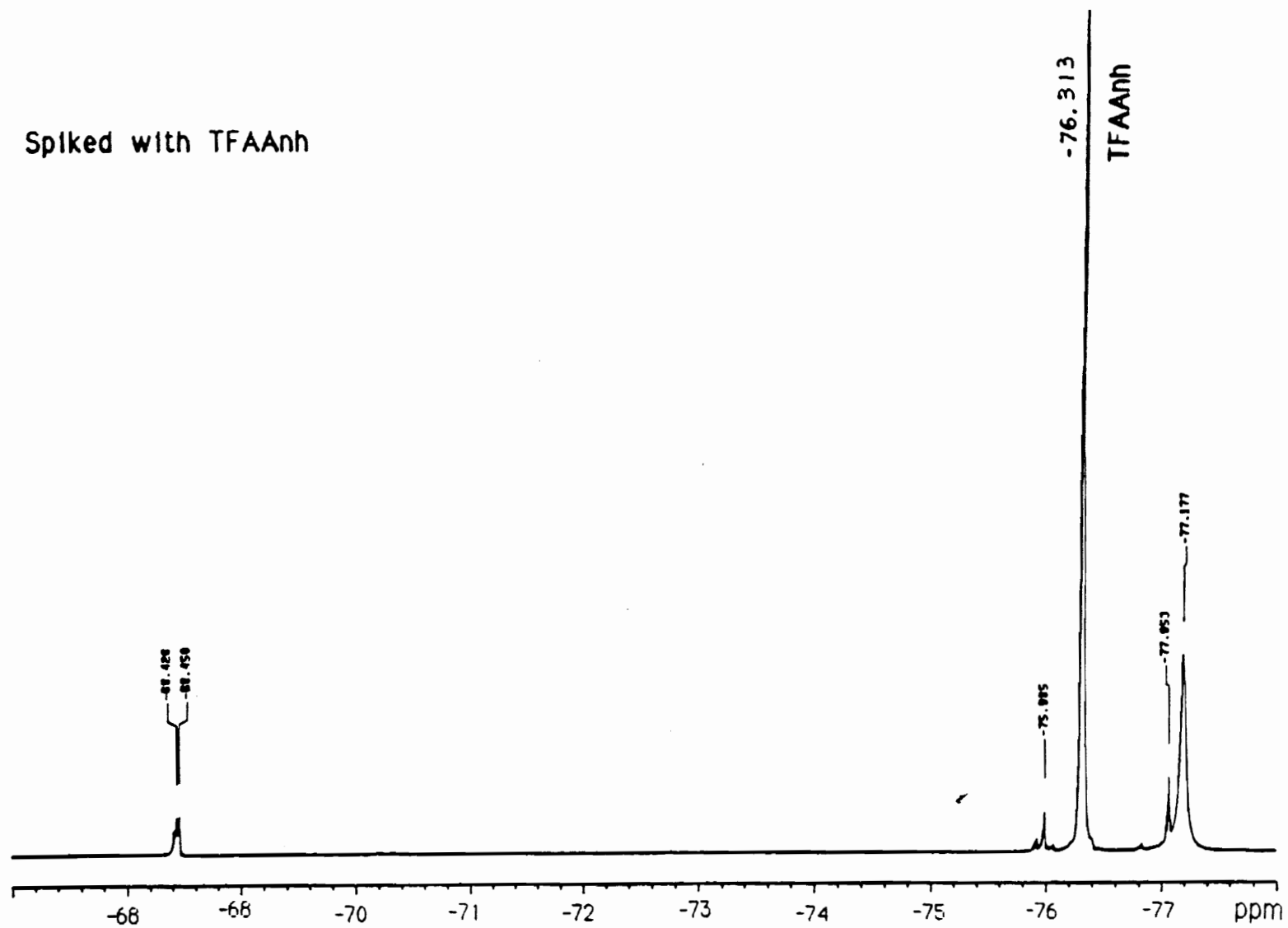
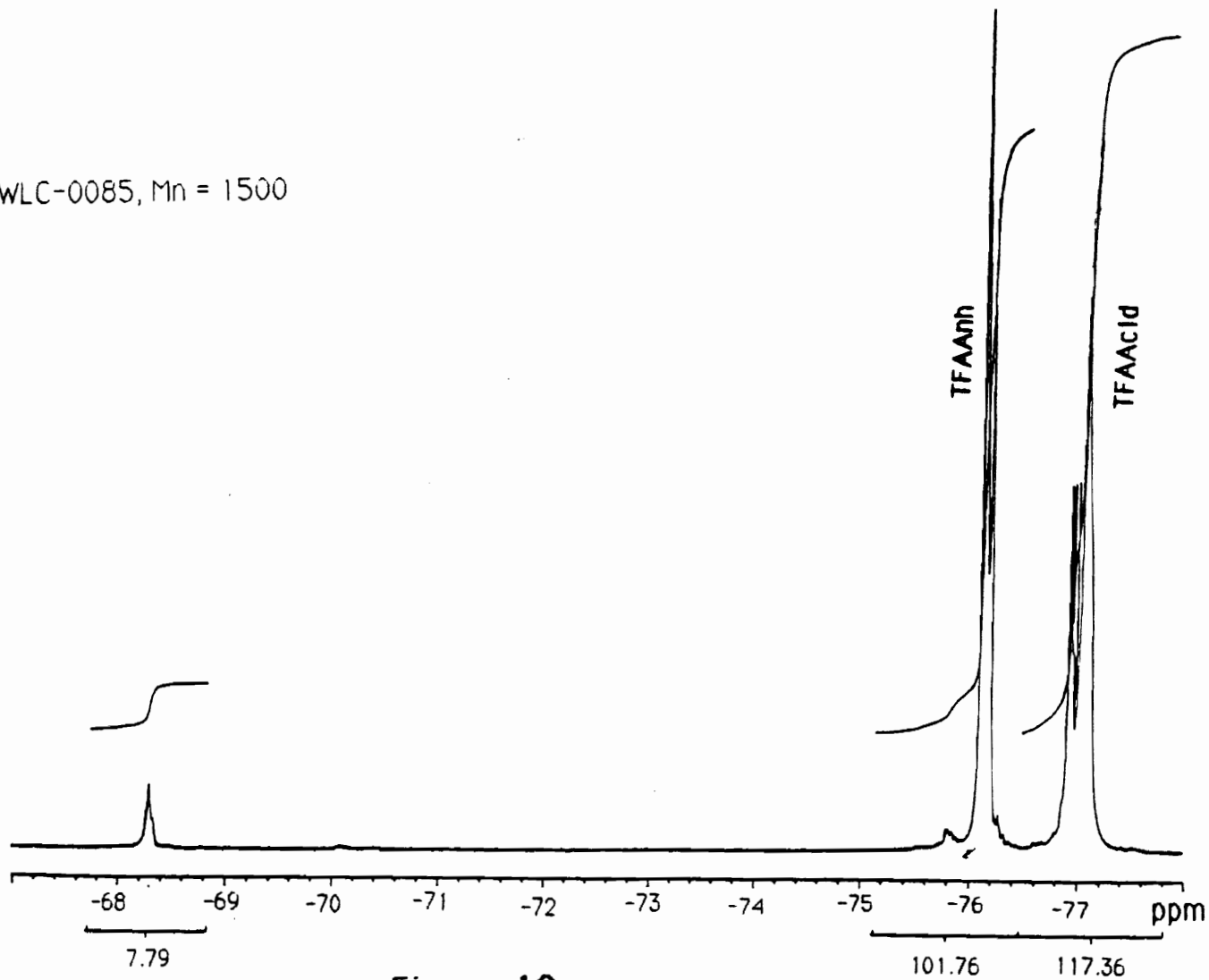


Figure 9  
 $^{19}\text{F}$  NMR of Derivatized MAPoxide Functionalized PTMO

WLC-0085, Mn = 1500



**Figure 10**  
 **$^{19}\text{F}$  NMR of Derivatized MAPoxide Functionalized PTMO**

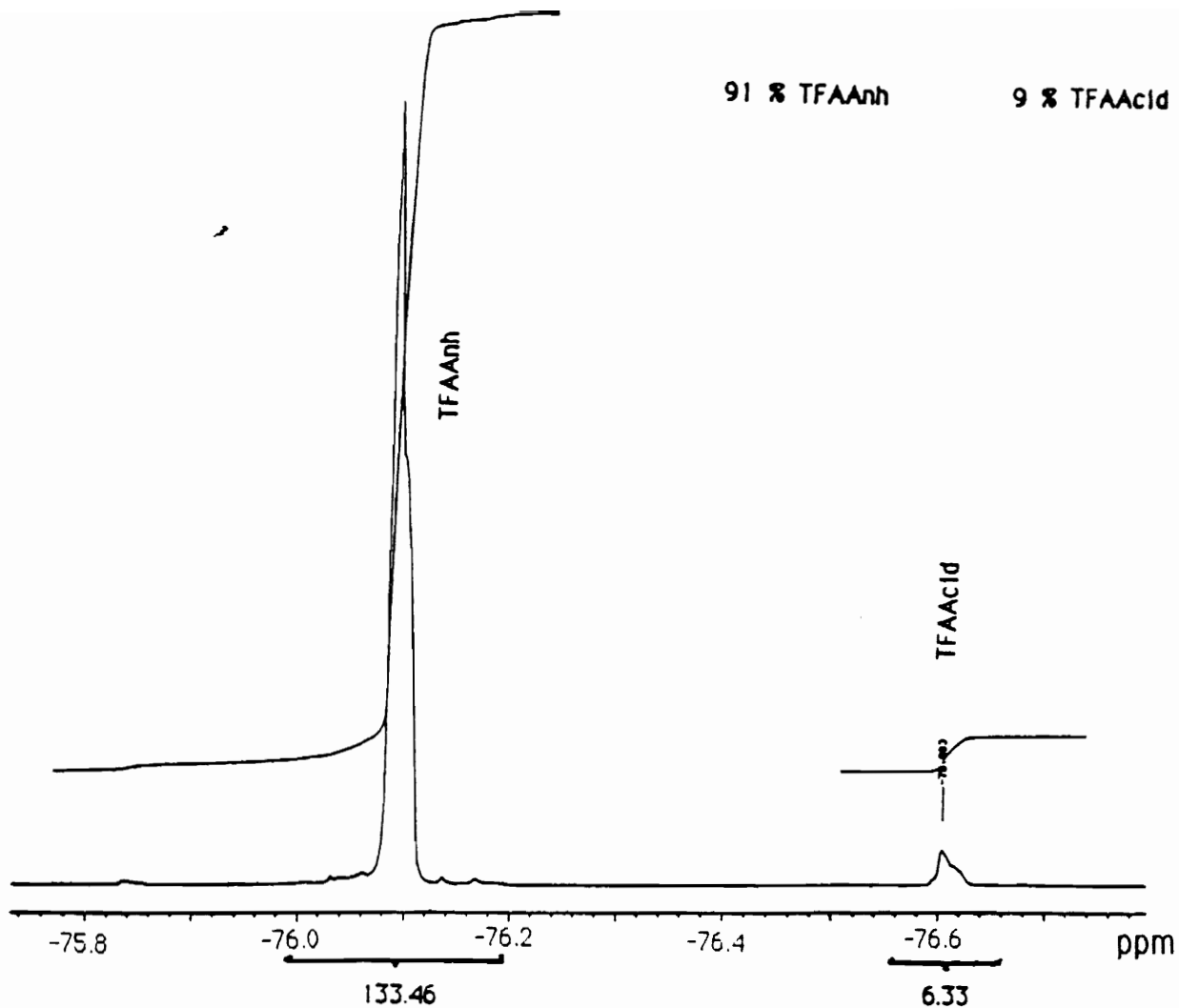
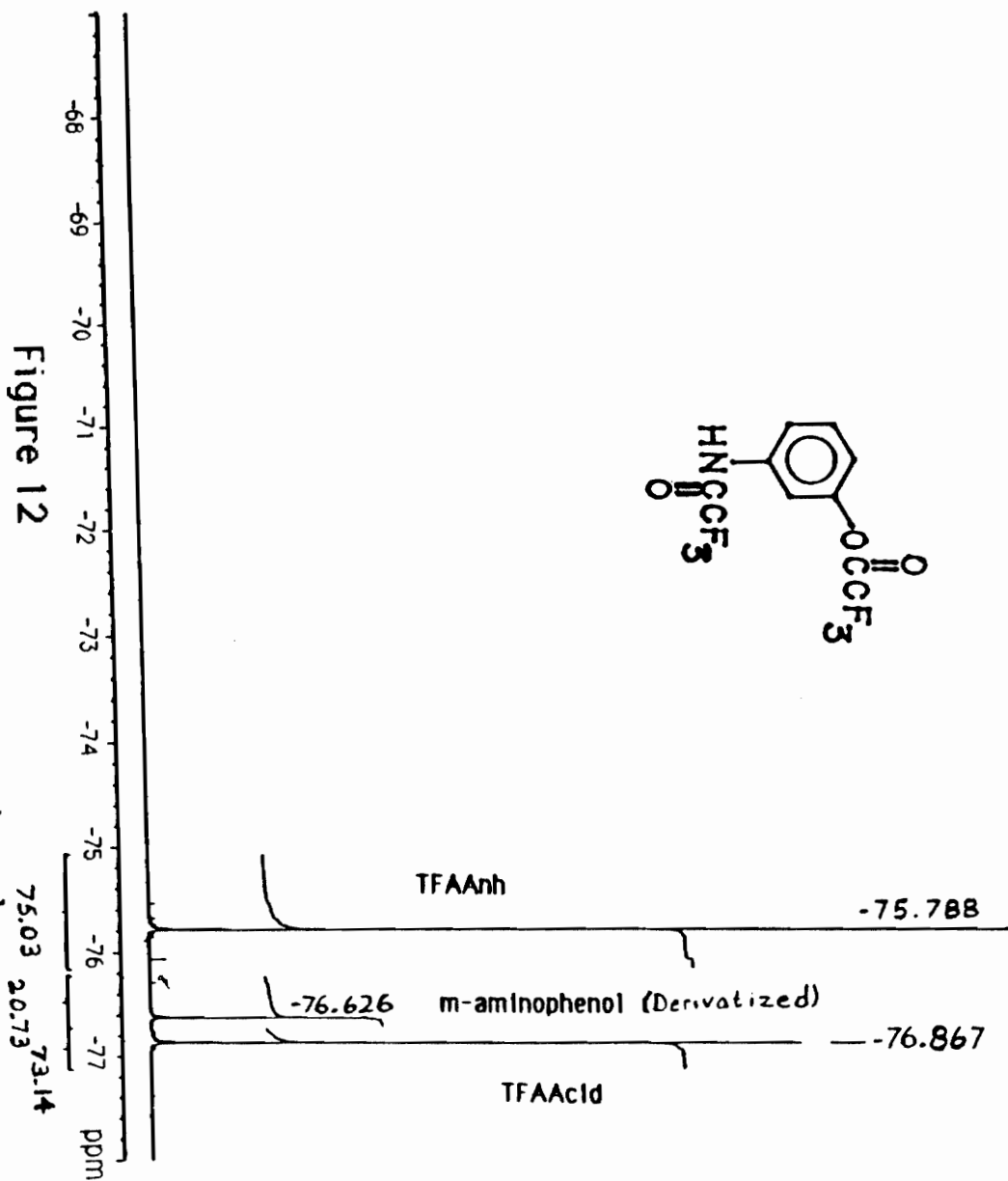
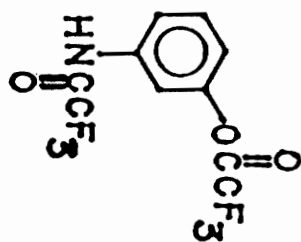


Figure 11  
 $^{19}\text{F}$  NMR Spectrum of TFAAnh Stored in Freezer



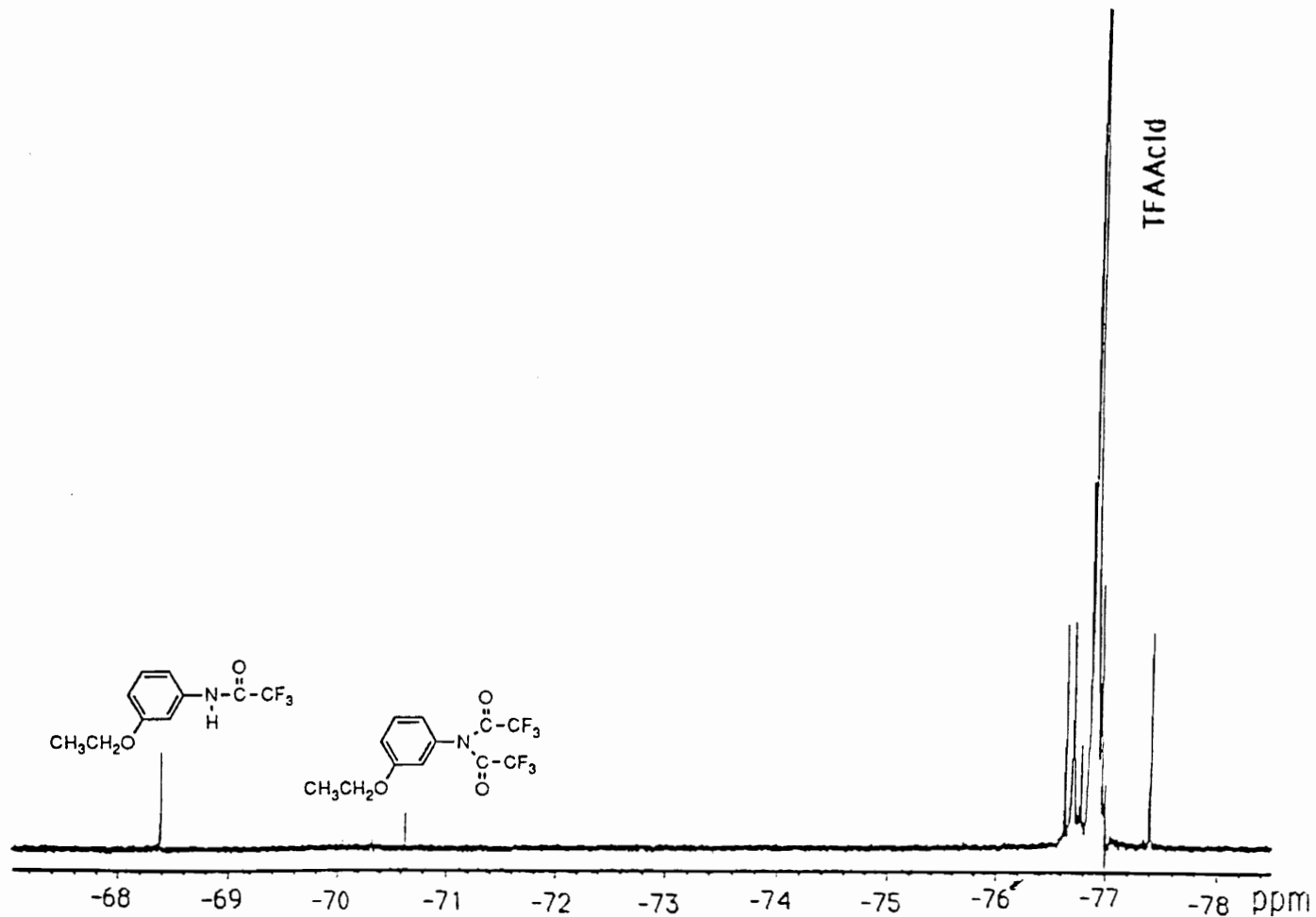


Figure 13  
 $^{19}\text{F}$  NMR of Derivatized Model  $\text{NH}_2$

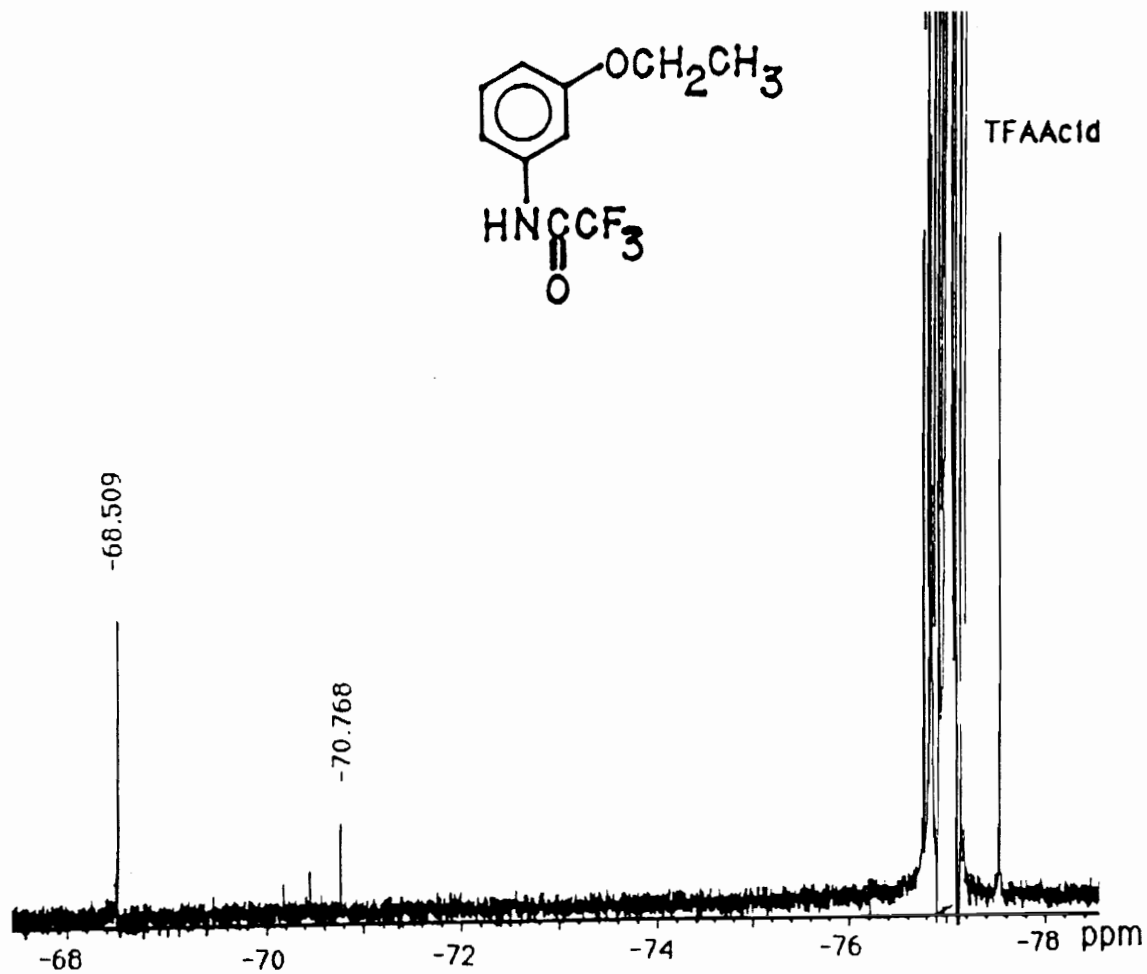


Figure 14  
Expanded  $^{19}\text{F}$  NMR of Derivatized Model  $\text{NH}_2$

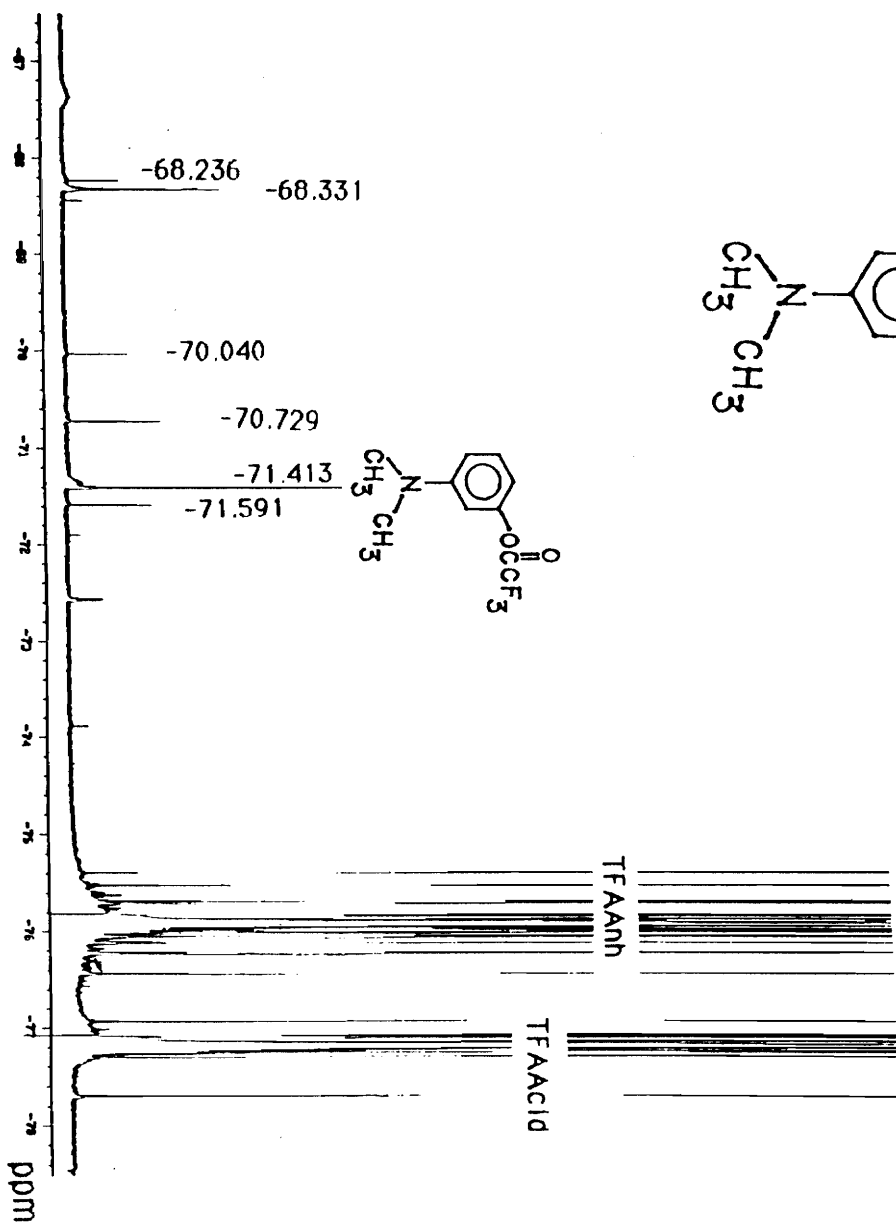
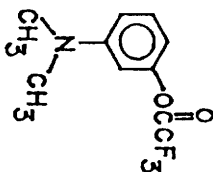
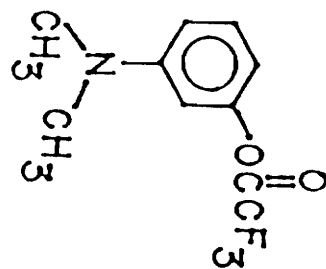


Figure 15  
 19F NMR of Derivatized Model OH

Spiked with TFAAnh

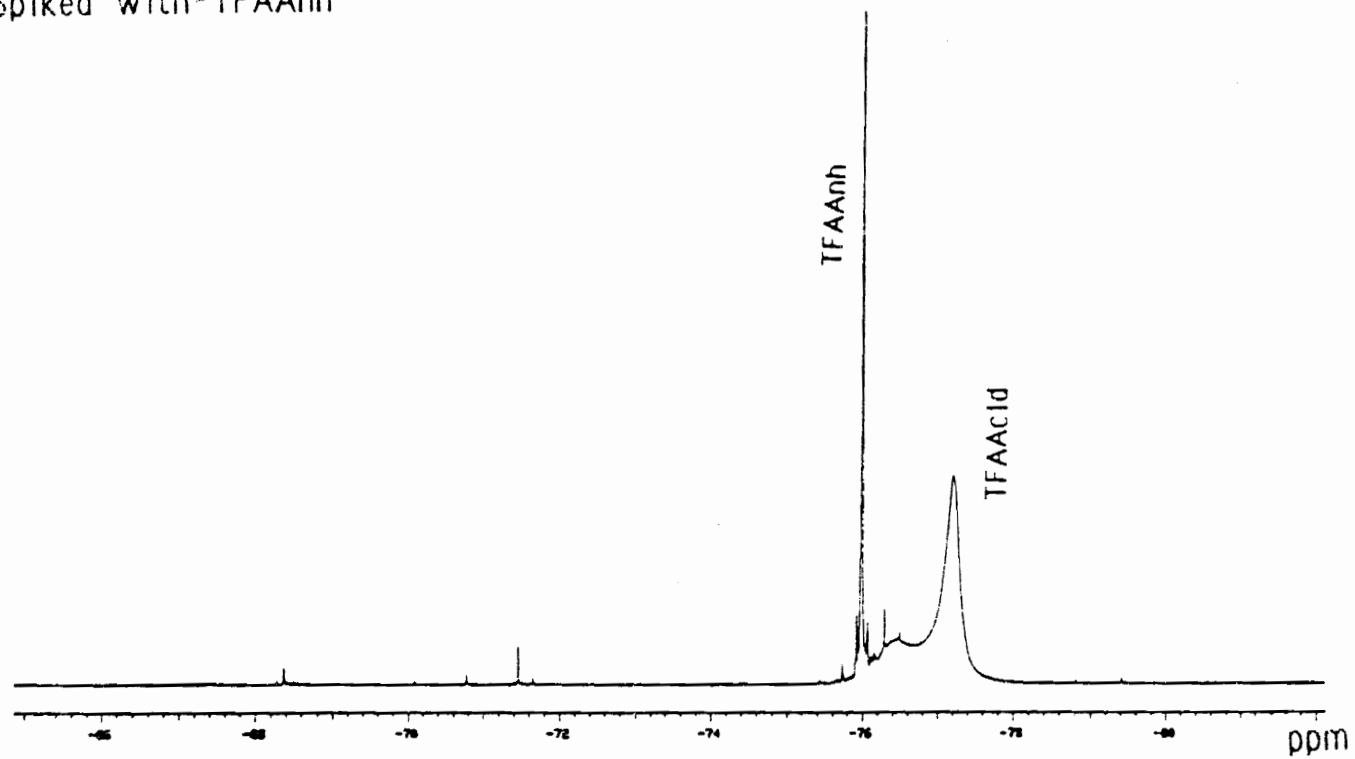
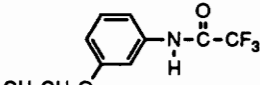
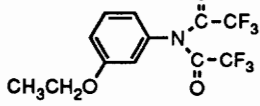
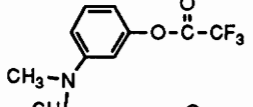
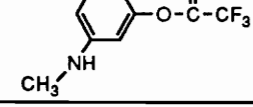


Figure 16  
 $^{19}\text{F}$  NMR of Derivatized Model OH

Table 1: Results of  $^{19}\text{F}$  Experiment

Sample	Shift (ppm)
TFAAnh	-75.8 --> -76.3
TFAAcid	-75.8 --> -78.7
MAP (derivitized)	-75.8 --> -78.6
MAPoxide Terminated PTMO, Mn = 2500 TFAAnh TFAAcid MAP Functionality	-76.2 -77.1 -75.8 -68.3
MAPoxide Terminated PTMO, Mn = 1200 TFAAnh TFAAcid Functionality	-76.1 -77.0 -68.3
Model NH2 TFAAcid	-77.0
	-68.6 (strong)
	-70.8
Model OH TFAAnh TFAAcid	-76.1 -77.1
	-71.4 (strong) -70.7, -71.6
	-68.3, -68.2

Note: No discernible peaks from -70.6 ppm to -72.5 ppm in MAPoxide Terminated PTMO samples

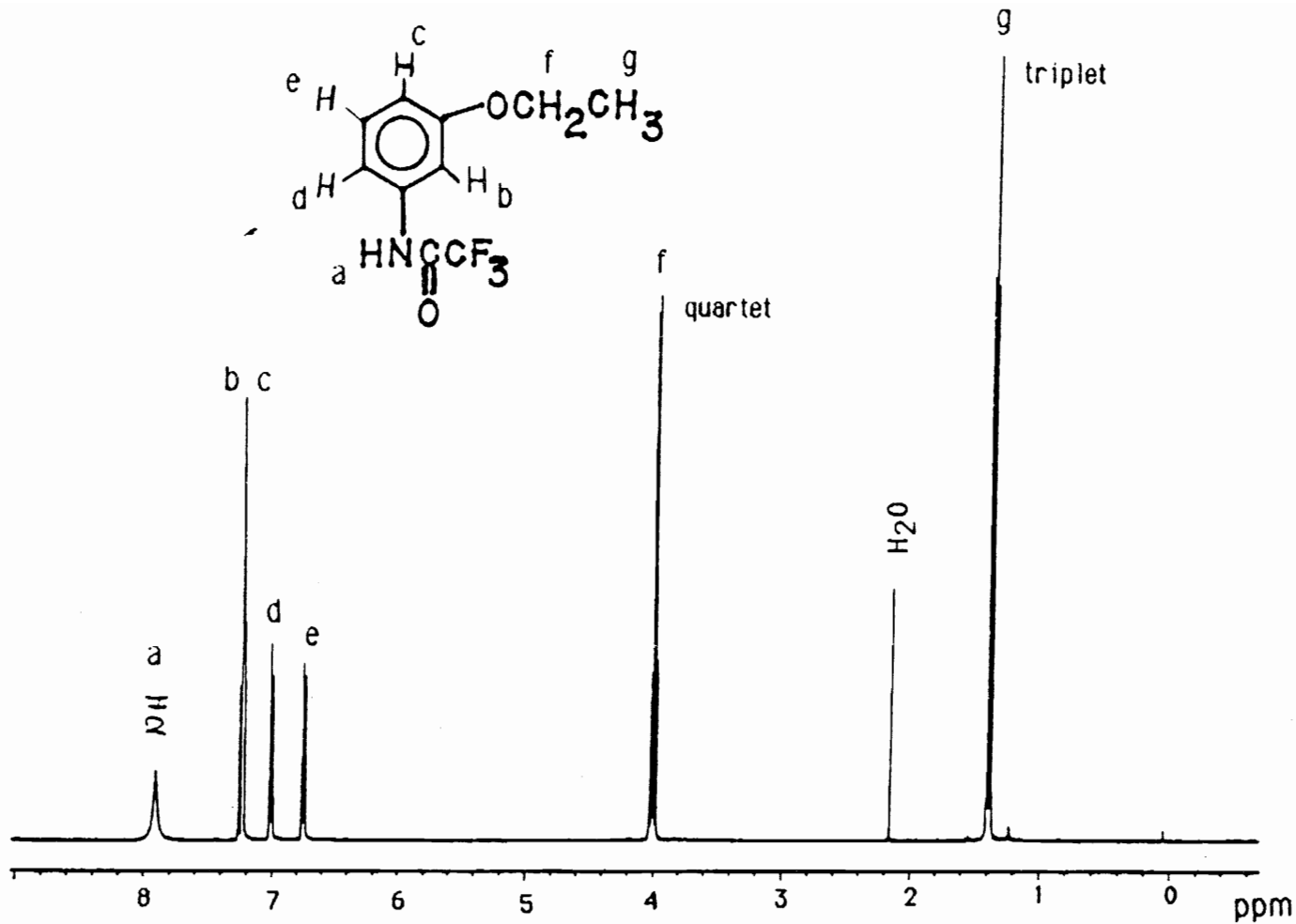


Figure 17  
 $^1\text{H}$  NMR of Derivatized Model  $\text{NH}_2$

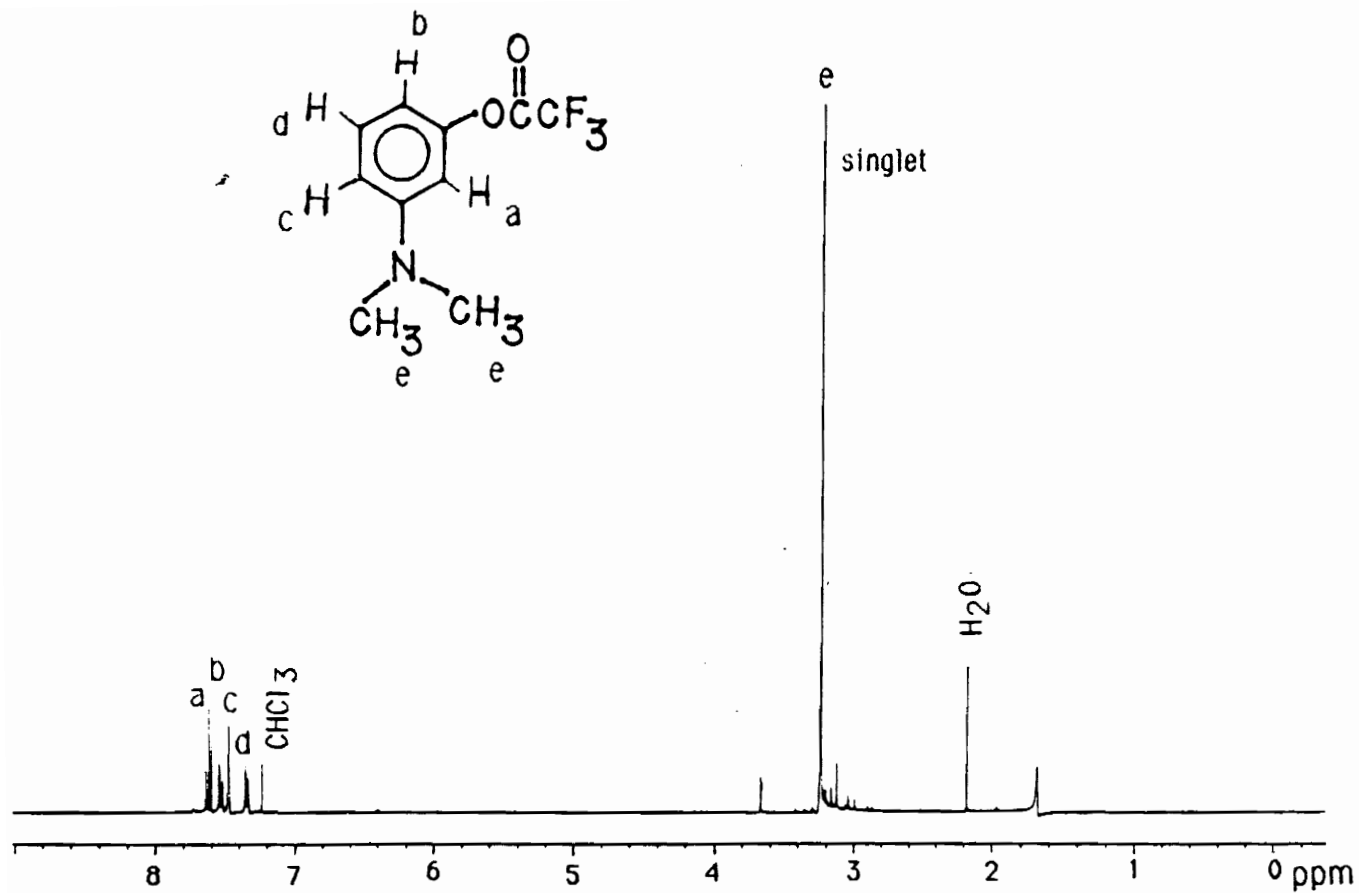


Figure 18  
<sup>1</sup>H NMR of Derivatized Model OH

## Chapter 5

### Conclusions

By using triflic anhydride to initiate the living polymerization of THF in a bifunctional manner, and then terminating the polymerization with *m*-aminophenoxide, linear aromatic amine telechelic PTMO has been obtained. The order of addition of the *m*-aminophenoxide to the bifunctional living PTMO was found to be crucial. In order to produce linear aromatic amine telechelic PTMO, the living PTMO must be charged to the *m*-aminophenoxide solution. Using *m*-aminophenoxide as the terminating agent produced PTMO consisting exclusively of aromatic amine end groups. PTMO with aromatic hydroxy end groups was either entirely absent, or in such low concentrations as to be considered negligible.

$M_n$  determination by HBr titration and  $^1\text{H}$  NMR spectroscopy gave reasonable agreement.  $^1\text{H}$  NMR spectroscopy, IR spectroscopy and HBr titration confirmed that the synthesis of aromatic amine telechelic PTMO was successful. Based on the fluorine tagging experiments and  $^{19}\text{F}$  NMR spectroscopy results, the functionality of the *m*-aminophenoxide functionalized PTMO was determined to consist exclusively of aromatic amine end groups.

This synthetic method readily produced linear aromatic amine telechelic PTMO, where the end groups were determined to consist exclusively of aromatic amine end groups. This material may be further reacted in a step growth polymerization to form segmented block copolymers. The PTMO segments could serve as low  $T_g$  blocks between reinforcing high  $T_g$  blocks such as polyamides, polyurea copolymers and epoxies, and may act to toughen these types of materials.

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## VITA

Winola Lenore Carman Rasmussen was born in Fairfax, Virginia on January 1, 1963. She graduated from Pennsboro High School in Pennsboro, West Virginia. The author attended Virginia Polytechnic Institute and State University in Blacksburg, Virginia, graduating in May 1986 with Bachelor of Science Degrees in biochemistry and chemistry. She completed a Master of Science degree in biology, with a concentration in biophysics, at Purdue University in West Lafayette, Indiana, graduating in May 1988. At Purdue University, she began working independently on an idea that evolved into a polymer project. The author pursued a Master of Science degree at Virginia Polytechnic Institute and State University under the guidance of Professor James E. McGrath, graduating in May 1992.

The author married Dr. Henrik Torstholm Rasmussen on October 13, 1990 and was doubly blessed with the birth of their son, Paul Henrik Rasmussen, on May 6, 1991.

A handwritten signature in black ink, appearing to read "W. Lenore Carman Rasmussen". The signature is fluid and cursive, with a long horizontal line extending to the right.