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Azeotrope Enabled Anionic Polymerization of Ethylene Oxide using Initiators with different Functional groups

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**Azeotrope Enabled Anionic Polymerization of Ethylene Oxide
using Initiators with different Functional groups**

Dronareddy Madugula

Integrated M.Sc., Kakatiya University, 2012

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

At the

University of Connecticut

2016

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2016

APPROVAL PAGE

Master of Science Thesis

**Azeotrope Enabled Anionic Polymerization of Ethylene Oxide
using Initiators with different Functional groups**

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2016

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ABSTRACT

Poly(ethylene oxide) (PEO) is a nonionic hydrophilic polymer having the same repeat unit as poly(ethylene glycol) (PEG). It is of interest in both biology and materials science. PEO surfaces demonstrate a unique lack of protein adhesion, and PEO block copolymers are widely used in applications such as drug delivery. Unfortunately, the synthesis of PEO homopolymers and block copolymers can be experimentally challenging, with a typical method involving air sensitive organometallics and the removal of compounds such as naphthalene from the final product. Here we report a synthetic route that avoids these difficulties by using azeotropic distillation to remove water from the equilibrium reaction of an alkyl hydroxide and potassium hydroxide reacting to form water and a potassium alkoxide. Removing the water right side of the reaction drives the equilibrium to the right, towards the potassium alkoxide, avoiding the use of pyrophoric organometallics. GPC and NMR are used to characterize the PEO polymers made from various alcohols, polystyrene end capped with ethylene oxide single monomer unit and initiators containing amine and amide functional groups.

CHAPTER ONE

Introduction

Poly(ethylene oxide) (PEO), also known as poly(ethylene glycol) (PEG), is a water soluble,¹ nonionic semi-crystalline polymer² that is biocompatible³, nontoxic⁴, and chemically stable.³ Due to PEO's ability to inhibit the adhesion of proteins, block copolymers containing PEO have a range of applications including: polymeric surfactants,⁵ emulsifiers,⁶ drug carriers,⁷⁻¹¹ and as anti-fouling coatings for medical implants^{12,13} and on ship hulls,¹⁴ The synthesis of these materials, however, requires the use of moisture sensitive, pyrophoric organometallics in order to convert hydroxyl functional groups into the metal alkoxides required for the polymerization of ethylene oxide (EO). In this article we introduce a new mechanism for the creation of the necessary alkoxides from alcohols and hydroxyl functionalized polymers: the use of azeotropic distillation to dehydrate the reaction mixture and drive the alcohol/alkoxide equilibrium towards the alkoxide, as illustrated in **Scheme 1**. This approach uses KOH as the source of potassium cation, avoiding the use of moisture sensitive reagents that often need to be synthesized immediately prior to use.

Industrially, PEO homopolymers are synthesized at high temperatures and pressures (100-200 °C and 520 kPa) by adding ethylene oxide (EO) to an alcoholic aqueous solution containing a caustic.¹⁵ For the synthesis of block copolymers, the anionic ring-opening polymerization (ROP) of EO is typically employed, with the initiator often being a potassium alkoxide polymer end group.^{3,16} Potassium rather than lithium is normally used due to the strong association between the lithium cation and the propagating oxygen anion,^{17,18,19} that results in tight ion pairs and no chain propagation.^{18,17} This inability of lithium cations to propagate the growth of PEO from alkoxide chain ends means that

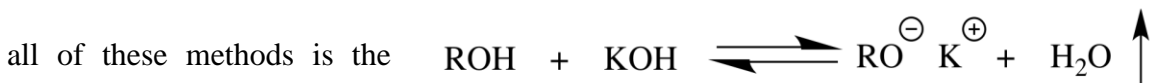
adding EO to a carbon anion with a lithium counter ion results in only one monomer unit being added to the chain. This is a useful approach to forming hydroxyl-terminated polymers, and is often used as a route to the hydroxyl terminated polymers from which PEO is subsequently grown.

Growing PEO block copolymers typically begins by reacting a hydroxyl group on a polymer chain with an alkyl or aromatic potassium organometallic to form a potassium alkoxide. The compounds most frequently used are cumylpotassium,^{20,21} diphenylmethyl potassium (DPMK),²²⁻²⁴ benzyl potassium,^{1,25,26} α -phenyl ethyl potassium,²⁷ and potassium naphthalenide.^{6,28} Examples include work by Allgaier *et al.*, where cumylpotassium was added to hydroxyl terminated polymers to initiate the polymerization of EO to form poly[1,4-isoprene-*b*-(ethylene oxide)] (PI-PEO) and poly[ethylene-*co*-propylene-*b*-(ethylene oxide)] (PEP-PEO) block copolymers.²⁰ As is common for potassium reagents, the cumylpotassium had to be synthesized and used within a short period of time.²⁰ Castle *et al.* synthesized block copolymers containing norbornene derived polymer blocks with a PEO block using DPMK,²³ and as is often the case, homopolymer of PEO was found as an impurity in the synthesized poly(styrene)comb-*b*-poly(ethylene oxide)combs.²² Benzyl potassium has also been used for the polymerization of EO in the synthesis of PEO homopolymers, PS-*b*-PEO, and for PI-*b*-P2VP-*b*-PEO copolymers.¹ α -phenyl ethyl potassium has been used to synthesize PS-*b*-PEO and PS-*b*-PEO-*b*-PS copolymers²⁷ with high conversion of EO (95%), but purification of the final product was necessary to remove PS and PEO homopolymers. Lastly, potassium naphthalide has been used in the synthesis of polyolefin-PEO block copolymers⁶ by forming the potassium alkoxide of hydrogenated polydienes containing hydroxyl end groups. Although this does not represent an exhaustive coverage of PEO block copolymer synthesis, the investigations are representative of the typical current approaches.

Other approaches have also been used, although they are not as common. Potassium methoxide was used to synthesize PS-*b*-PEO block copolymers,²⁹ requiring a reaction time of 11 days, heating gradually from 30 °C to 70 °C for 7 days followed by holding the reaction at 70 °C for another 4 days followed by the removal of PS and PEO homopolymers. Potassium metal has also been used directly to create potassium alkoxide initiators. In one example, potassium metal was added piecewise to a reaction mixture containing dimethylaminoethanol to form the potassium alkoxide.³⁰ The addition of ethylene oxide was then followed by butylene oxide to produce a copolymer after 20 days. Another example of using potassium metal is the use of a potassium mirror to synthesize PS-*b*-PEO copolymers from hydroxyl terminated PS.³¹

Methods for growing PEO that do not involve potassium have been reported, but they are the exception. One route to PEO containing block copolymers allows for the use of lithium as a counterion by adding a phosphazene base.^{18,32} The phosphazene base complexes with the lithium counterion and allows for the propagation of EO. Polybutadiene-PEO (PBd-PEO) and PI-PEO block copolymers have been synthesized using this approach.¹⁸ Another route used a lithium alkoxide with small amounts of a potassium alkoxide in a benzene/DMSO mixture. PEO homopolymer was found in the final block copolymer product but using other alkoxides, such as potassium 2,6-di-*t*-butylphenoxide, produced less PEO homopolymer.³³ Finally, to avoid the presence of potassium in the final material, a N-heterocyclic carbene was used to initiate EO polymerization, followed by the sequential polymerization of ϵ -caprolactone.³

A common theme in nearly



conversion of an alcohol to a

Scheme 1. Equilibrium responsible for forming potassium alkoxide initiator. The removal of water drives the equilibrium to the right.

metal alkoxide by way of a

reactive organometallic. In our approach³⁴, rather than adding a reactive and often air sensitive pyrophoric compound to form the necessary potassium alkoxide, we add potassium hydroxide without any need for moisture free conditions or prior synthesis of the organometallic. Additionally, at the end of the reaction, there are no compounds such as naphthalene that must be removed. The formation of the initiating species is based on the equilibrium between an alcohol and alkoxide, as shown in **Scheme 1**. As examples of this approach, we discuss growing PEO off a small molecular weight alcohol, extending the chain length of a PEO homopolymer, and synthesizing a block copolymer of polystyrene and PEO (PS-*b*-PEO) from a hydroxyl terminated PS.

1.1 Synthesis of Poly (ethylene oxide) using 1-Octanol as initiator

1.1.1 Materials:

Cyclohexane, benzophenone, and tetrahydrofuran (THF) were purchased from Fisher. 0.1 N potassium hydroxide in methanol, 1.3 M *sec*-butyllithium in cyclohexane/hexane (92/8), 1,1-diphenylethylene (98%), styrene (99.5%), calcium hydride (93%), N,N-dimethylacetamide (99%), and chloroform-*d* (99.8 atom %D, 1 v/v% TMS) were purchased from Acros Organics. Methanol ($\geq 99.8\%$), toluene ($\geq 99.5\%$), and diethyl ether ($\geq 99.0\%$) were purchased from Sigma Aldrich. Dimethyl sulfoxide was purchased from J. T. Baker and 1-octanol from Fisher Science Education. Ethylene oxide gas was purchased from Praxair, condensed into a schlenk flask, and distilled into a vacuum flask containing calcium hydride. It then was distilled into a round-bottom flask containing a sodium mirror,

and finally distilled into a vacuum flask with a stir bar and stored in an explosion proof freezer. Prior to its use in a polymerization, it was again distilled onto a sodium mirror before addition to the reaction vessel. All other solvents and reagents were used as received from Fisher unless otherwise mentioned.

1.1.2 Instrumentation

Gel permeation chromatography (GPC) was used to determine the molecular weight and polydispersity of the PEO polymers. A Waters GPC-1, 1515 HPLC Pump and Waters 717Plus Autoinjector was used. The instrument contains Jordi Gel fluorinated DVB columns (1-100,000, 2-10,000, 1-500Å) and a Varian 380-LC Evaporative Light Scattering Detector (ELSD). THF was used as the mobile phase. Empower 1, Waters software, was used to run the samples and analyze the data. Proton NMR was obtained on a Bruker DMX 500MHz High Resolution Nuclear Magnetic Resonance (NMR) Spectrometer with Bruker Topspin 1.3 software. MestReNova software was utilized to analyze the spectra. For the homo PEO, five PEO standards were used to construct a calibration curve, 10.6K, 23.5K, 36K, 56K, and 93,750, all run in THF, using the same GPC instrument that was used for analyzing the PEO polymer samples.

1.1.3 Synthesis of alkoxide by atmospheric distillation with and without DMSO

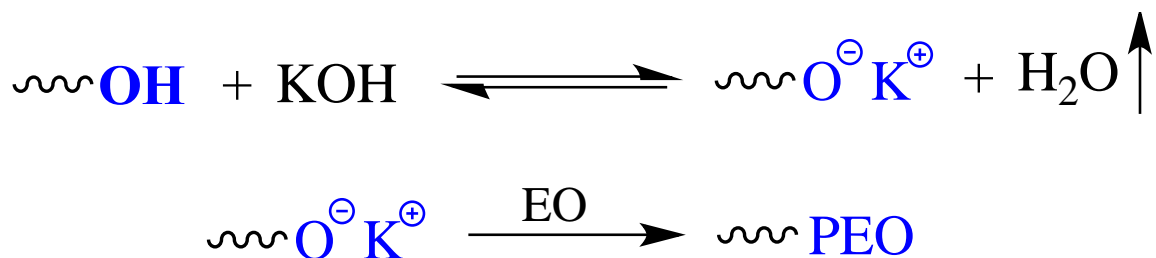
The polymerization of the Ethylene Oxide was performed by the following general procedure that varies slightly depending on the starting alcohol. The atmospheric distillation method was used to synthesize PEO from 1-octanol using a Dean-Stark apparatus to perform an azeotropic distillation of toluene and water to create the alkoxide from an alcohol and KOH in methanol. Two reactions were run simultaneously under the same conditions, with one reaction in the presence of DMSO. In a 1L vacuum flask, equipped with a stir bar, approximately 300 ml toluene, 50 ml of DMSO, 0.1N KOH in methanol, and 1-octanol were added. The Dean-Stark apparatus had a ground-glass joint

thermometer and a water condenser connected to it. The 1L flask was placed in an oil bath on a hot/stir plate and then connected to the Dean-Stark apparatus, leaving the Teflon valve open. The mixture was allowed to go overnight and once the alkoxide had formed, with the color of the reaction mixture with DMSO changing from clear to yellow, the Teflon valve was shut above 100°C. The reaction flask was allowed to cool to room temperature, fixed to a vacuum line and degassed.

1.1.4 Polymerization of Ethylene Oxide using alkoxide from 1-Octanol and KOH:

Dried and degassed THF, about 200 ml, was back-distilled into the flask followed by the addition of ethylene oxide by way of vacuum distillation. The flask was then removed from the line under vacuum by closing the Teflon stopcock and placed in an oil bath. The reaction mixture was heated to 60 °C for 5-7 days, then quenched with degassed methanol. The polymer solution was filtered and then precipitated by pouring into cold diethyl ether. The solid was collected and placed in a vacuum oven at ambient temperature to dry. GPC and ¹H NMR were used to characterize the molecular weight and polydispersity of the PEO polymers.

1.1.5 General synthetic scheme of azeotrope enabled PEO:



1.1.6 ^1H NMR of 1- Octanol initiated PEO:

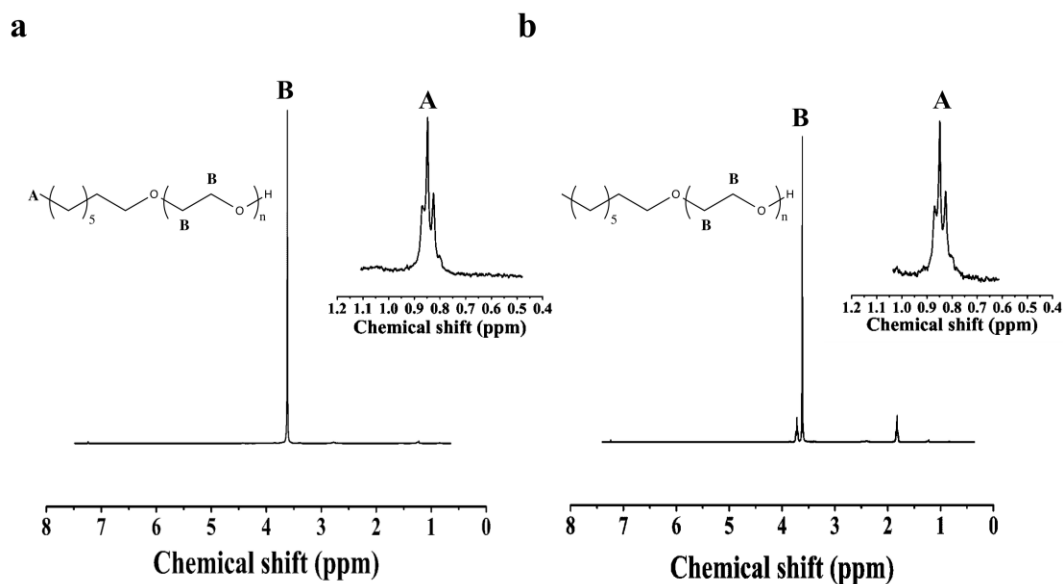


Figure 1: (a) ^1H NMR of PEO homopolymer from 1-octanol initiator with DMSO

(b) ^1H NMR of PEO homopolymer from 1-octanol without DMSO

1.1.7 SEC of 1-Octanol initiated PEO:

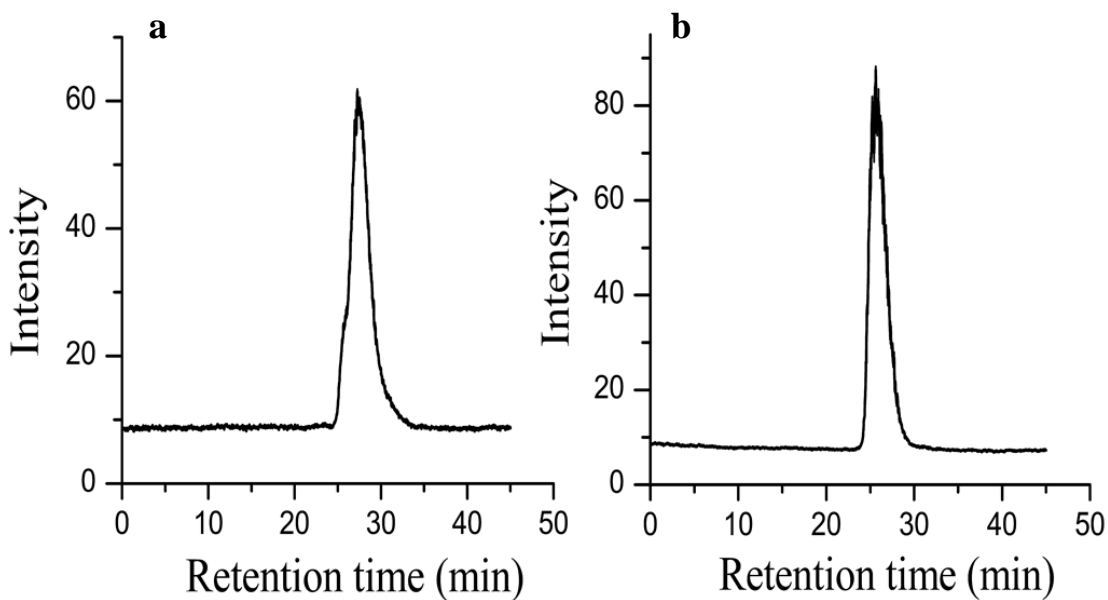


Figure 2: (a) GPC trace of PEO homopolymer from 1-octanol initiator with DMSO

(b) GPC trace of PEO homopolymer from 1-octanol without DMSO.

1.1.8 Results and discussion:

The equilibrium between alcoholic potassium hydroxide and a potassium alkoxide, shown in **Scheme 1**, normally lies far to the left, on the side of the hydroxide and alcohol. However, by Le Chatelier's principle, removing the water from the right hand side drives the equilibrium towards the potassium alkoxide, without the need for the addition of organometallic reagents or potassium metal. A typical reaction starts by dissolving the hydroxyl-containing molecule in toluene and adding a stoichiometric amount of KOH dissolved in methanol. The toluene is then partially distilled off, observing the boiling temperature of the toluene. Initially, the boiling temperature is far lower than the literature value for toluene, as first the methanol, then the water in the form of an azeotrope, are removed. Once all the water in the system is removed, the boiling temperature reaches its literature value. After complete removal of the water, dry THF is added to provide a polar solvent for chain propagation, followed by the addition of the EO monomer.

Toluene is our solvent of choice, as it forms an azeotrope with both water and methanol, solubilizes a variety of polymers, has a reasonably low boiling temperature, and has fewer health concerns than benzene. The binary positive azeotrope between methanol and toluene distills at 63.8 °C, with the vapor containing 0.883 mole fraction methanol, or 72.4 wt% methanol. The azeotrope with methanol is convenient, as we typically add the KOH by way of a 0.1 N standard solution of KOH in methanol. The positive binary azeotrope between water and toluene distills at 84.1 °C, with the vapor containing 0.444 mole fraction of water, or 13.5 wt% water.³⁵ The differences between the boiling temperature of the azeotropes and of pure toluene (110.6 °C) are large enough to clearly distinguish them during the distillation.

To demonstrate the growth of PEO from a small molecular weight alcohol, we use 1-octanol, an alcohol with sufficiently low vapor pressure to remain in solution while the

water is removed by azeotropic distillation with the toluene co-solvent. A PEO polymer with a target MW of 10K is synthesized in solution of toluene and THF, both with and without DMSO. The use of DMSO as a co-solvent is studied based on literature reports that it aids in the polymerization of EO.³³ During the reaction, the reaction mixture with DMSO turned yellow once the alkoxide had formed, indicating an anion was present. The reaction mixture in the absence of DMSO remained clear.

The PEO homopolymer thus synthesized from 1-octanol is analyzed with ¹H NMR and GPC, using PEO standards to calibrate the GPC. The peak average molecular weight (M_p) and polydispersity index (PDI) determined by GPC for the polymer made with DMSO present is 6.4 kg/mole with a PDI of 1.21. Without DMSO, the GPC shows the MW to be 13.1 kg/mole with a PDI of 1.19. The GPC chromatograms of the PEO homopolymers from 1-octanol with and without DMSO are shown in **Figures 2a and 2b**. The lower MW of the PEO with DMSO corresponds with a lower yield, and indicates that the polymerization did not consume all of the monomer. This result is likely due to EO being less soluble in the reaction mixture containing DMSO. The nearly identical PDI with and without DMSO argues against a termination event, and the polar character of DMSO would suggest the rate of propagation is not adversely affected by its presence.

¹H NMR MW results agree with those from the GPC. **Figure 1** shows the spectra. Assigning the singlet at 3.62 ppm to the methylene protons in the backbone of the PEO chain, and the triplet at 0.85 ppm to the terminal methyl group of the 1-octanol chain, integration of the peak areas gives M_n values of 6.5 kg/mole for the polymer grown with DMSO and 10.0 kg/mole for the polymer synthesized without DMSO. The agreement of the NMR and GPC measured molecular weights provides evidence that the PEO chains are indeed initiated from the alcohol, as the presence of PEO chains not initiated from the alcohol would result in ¹H NMR results, which are based on the peak areas associated with

the alcohol, being very different from the GPC results. The presence of free alcohol is unlikely due the precipitation of the polymer during workup. Looked at a different way, this means that there was no significant amount of PEO “homopolymer”, or polymer initiated without the intended initiator. As our approach works by removing the water present in the system, no water is available to initiate polymerization and produce unfunctionalized homopolymer.

1.2 Synthesis of Poly (ethylene oxide) using propargyl alcohol as initiator:

1.2.1 Polymerization of Ethylene Oxide using propargyl alkoxide by vacuum distillation:

In addition to 1-octanol, propargyl alcohol was used to grow PEO with a target of 5K. Due to its thermal sensitivity, vacuum distillation was used to form the alkoxide and no DMSO was present in the system. In a 500 mL round-bottom single-necked flask equipped with a magnetic stir bar and a high vacuum Teflon valve, was placed propargyl alcohol. To this was added approximately 300 ml toluene. Next, an equimolar amount of KOH was added. The reaction flask was attached to a vacuum line and the toluene slowly removed by vacuum distillation, with the flask removed from active vacuum when the solution froze. After the toluene was removed, degassed THF dried over sodium/benzophenone was added by vacuum distillation, followed by the addition of ethylene oxide by way of vacuum distillation.

The flask was then removed from the line under vacuum by closing the Teflon stopcock and placed in an oil bath. After back-distilling THF, the solution turned cloudy, white before heating at 60°C for 7 days. The anion did not turn color (slight yellow) until after ~2 hours of heating and the color intensified slowly throughout the reaction time. The reaction mixture was heated to 60 °C for 5-7 days, then quenched with degassed methanol. The polymer solution was filtered and then precipitated by pouring into cold diethyl ether. The

solid was collected and placed in a vacuum oven at ambient temperature to dry. GPC and ^1H NMR were used to characterize the molecular weight and polydispersity of the PEO polymers. Once the alkoxide had formed, a colorless liquid remained with a ring of potassium salts inside the flask.

1.2.2 Characterization of Propargyl alcohol initiated PEO by ^1H NMR and SEC:

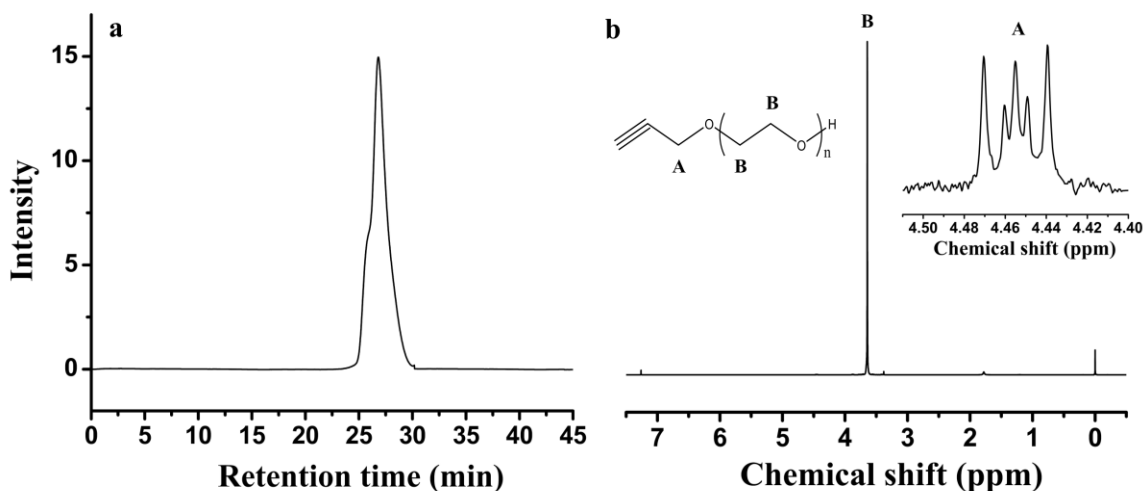


Figure 3: (a) SEC of PEO homopolymer from propargyl alcohol initiator (b) ^1H NMR of PEO homopolymer from propargyl alcohol.

The PEO homopolymer synthesized from propargyl alcohol is analyzed with ^1H NMR and GPC, using PS standards to calibrate the GPC and N,N-Dimethylacetamide (DMAc) as the mobile phase. The peak average molecular weight (M_p) and polydispersity index (PDI) determined by GPC for the polymer is 5.5 kg/mol and 1.37. **Figure 3** shows the GPC chromatogram and ^1H NMR spectrum for the homopolymer. The chemical shift value at 4.45 ppm corresponds to the methylene group in the initiator. The methylene group in the backbone of the polymer chain is shown as a singlet at 3.60 ppm. Comparing the integration of the peak areas, the calculated M_n from ^1H NMR was 6.8 kg/mol. The molecular weight calculated from NMR is slightly higher than the target MW due to a

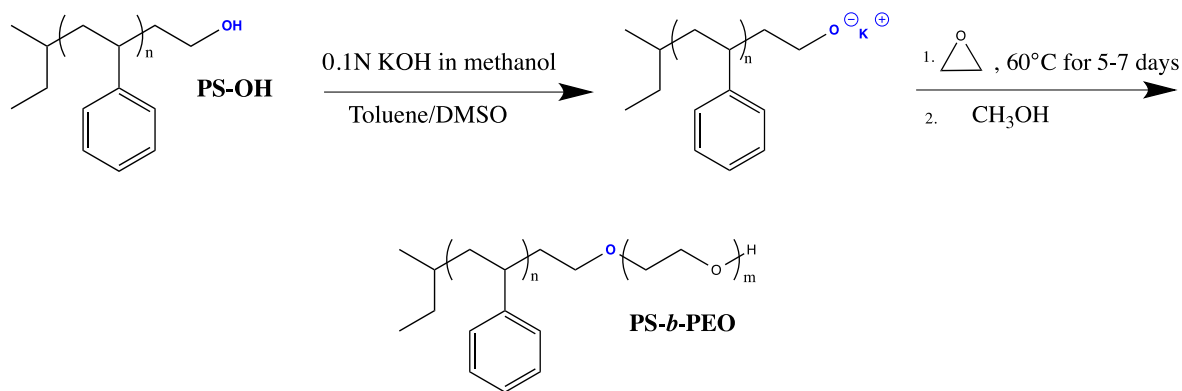
possible reason that not all of the propargyl initiator was either converted or participated in the polymerization of EO. The yield of the reaction was 96%.

1.3 Synthesis of amphiphilic diblock copolymers:

1.3.1 Synthesis of Macroinitiators: Polystyrene end capped with EO

The synthesis of PS-OH was performed in a glove box. The solvent, cyclohexane, was previously dried over *sec*-butyllithium and 1,1-diphenylethylene on a vacuum line. Cyclohexane was then distilled into a vacuum flask and brought into the glove box. The initiator, *sec*-butyllithium, was then added to the dried cyclohexane. Styrene was added and the reaction allowed to stir overnight. The color of the solution turned deep orange. Excess ethylene oxide was then added and the color of the solution faded. The vacuum flask was removed from the glove box and degassed methanol was added to terminate the reaction. The cloudy solution was allowed to stand overnight. The polymer solution was filtered followed by precipitation in excess methanol. The resulting solid was dried under vacuum for several days. GPC and ^1H NMR were used to characterize the molecular weight and polydispersity of the polymer.

1.3.2 Synthetic scheme of PS-*b*-PEO diblock co-polymers:



1.3.3 Table 1: Summary of PS-*b*-PEO diblock copolymers synthesized:

Polymer ^{a,b}	Experimental Yield (%)	¹ H NMR M _n (g/mol)	SEC		
			M _n (g/mol)	M _w (g/mol)	Polydispersity
3k PS	93	2624	2731	2954	1.08
3k PS-EO	96	2770	2714	2907	1.07
3k PS- <i>b</i> -PEO	85	6792	7174	7901	1.1
5k PS	99	5300	4381	4914	1.12
5k PS-EO	98	5119	4216	4513	1.07
5k PS- <i>b</i> -PEO	88	9102	10166	10579	1.04
10k PS	97	9073	11174	14151	1.26
10k PS-EO	95	9360	10748	12676	1.17
10k PS- <i>b</i> -PEO	>99	17616	19581	22861	1.16

- a. The copolymers are synthesized by keeping 5k PEO block as constant in all the three diblocks.
- b. All the three copolymers were synthesized in the (4:1) THF: DMSO solvent system

1.3.4 Characterization of PS-*b*-PEO copolymer by ^1H NMR and SEC:

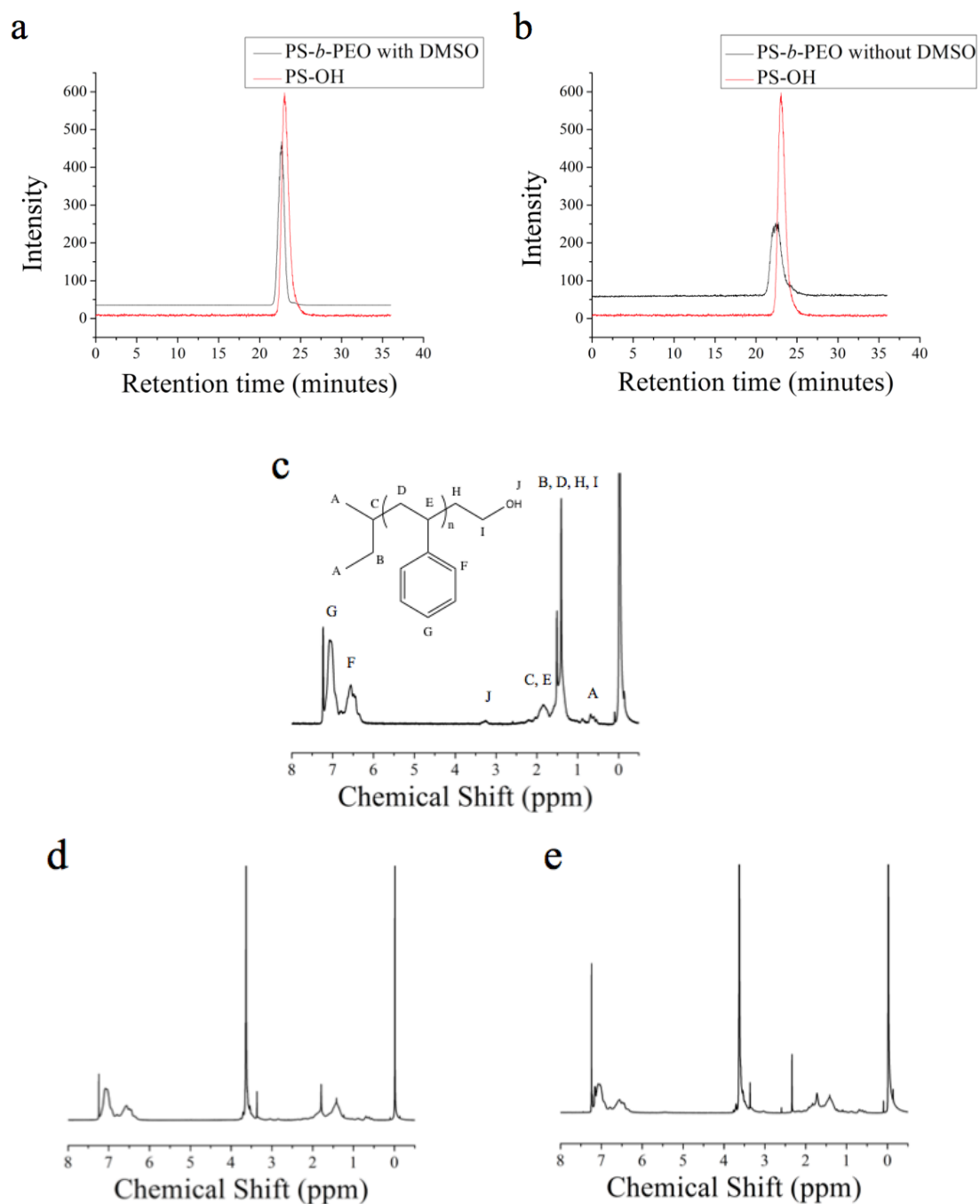


Figure 4. (a) Overlapping GPC traces of PS-OH and PS-*b*-PEO with DMSO (b) Overlapping GPC traces of PS-OH and PS-*b*-PEO without DMSO (c) ^1H NMR of PS-OH (d) ^1H NMR of PS-*b*-PEO with DMSO (e) ^1H NMR of PS-*b*-PEO without DMSO

1.3.5 Results and discussion:

While there appears to be no advantage to using DMSO for the growth of PEO from 1-octanol, the PDI does not appear to suffer from its use, suggesting the mechanism of propagation is not significantly affected by its presence. The molecular weights are consistently lower in the presence of DMSO for the same reaction times and temperatures, however, possibly resulting from EO being less soluble in the reaction mixture containing DMSO. Slower rates of reaction due to lower concentrations of EO dissolved in the reaction mixture are supported by several observations. The first is that the isolated yield of the reaction with DMSO is 77%, and the measured molecular weight was roughly 70 % of the target. This suggests the lower observed MW was due to low conversion rather than termination or chain transfer. The second observation is that using a 1:1 ratio of DMSO:THF results in PEO with a MW roughly 10% of the of the target. Changing the ratio to 1:4 DMSO:THF results in PEO with a MW 70% of the target, with all other reaction conditions held constant. Without any DMSO at all, the yield is 99.5%.

Comparing the molecular weight distributions of the two chemically identical block copolymers, the one without DMSO has a broader distribution. The only difference between the two polymerizations is the presence of DMSO in one of the reactions. The presence of the DMSO helped control the polymerization to give a more narrow molecular weight distribution, which has been seen before by Quirk & coauthors.³³ Hence, while synthesizing the three diblock amphiphilic copolymers, DMSO was used as a co-solvent to prevent the formation of any PEO homopolymer.

1.4 Table 2: Summary of PEO polymers and copolymers discussed :

Alcohol	Target M_n (g mol ⁻¹)	¹ H NMR M_n (g mol ⁻¹)	SEC		Isolated Yield (%)
			M_n (g mol ⁻¹)	Polydispersity	
1-Octanol w/ DMSO	10000	6510	5847	1.21	77
1-Octanol w/o DMSO	10000	10042	9970	1.19	>99
Propargyl alcohol	5000	6820	5603	1.37	96
3k PS-OH	3k- <i>b</i> -5k	6792	7174	1.1 (1.07) ^a	85
5k PS-OH	5k- <i>b</i> -5k	9102	10166	1.04 (1.07) ^a	88
10k PS-OH	10k- <i>b</i> -5k	17616	19581	1.16 (1.17) ^a	>99

^a Dispersity of macroinitiator prior to synthesis of PEO block

1.5 CONCLUSION:

We have demonstrated the synthesis of a PEO homopolymer from two small molecular weight alcohols and the formation of block copolymers containing PEO, all using this azeotropic distillation approach. Two methods were shown and the only difference was the way in which the alkoxide was formed. The presence of a co-solvent, DMSO, in the formation of the alkoxide was also studied. In the 1-octanol initiator system, the addition of DMSO did not help to increase the conversion of the homopolymer and did not affect the polydispersity. In the case of the block copolymer, PS-*b*-PEO, when DMSO was added, a more narrow molecular weight distribution was found. A disadvantage was that the addition of DMSO created a difficult workup of the polymer. In the absence of DMSO, a broader molecular weight distribution was determined but the workup of the reaction was easier. The addition of DMSO did not have an affect on the conversion in the synthesis of the PEO containing block copolymers.

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CHAPTER TWO

PEO Synthesis using initiators with amine and amide functional groups

After successful study of initiators with hydroxyl groups for the azeotrope enabled polymerization of ethylene oxide, we wanted to extend the technique by using initiators with amine and amide functional groups¹⁻⁴. The selection of amine and amide group containing initiators was considered by taking into consideration all the essential factors like the boiling point of initiators, their thermal stability and accordingly suitable azeotropic distillation was performed.

2.1 Synthesis of Poly(ethylene oxide) using hexadecyl amine (HDA) as initiator

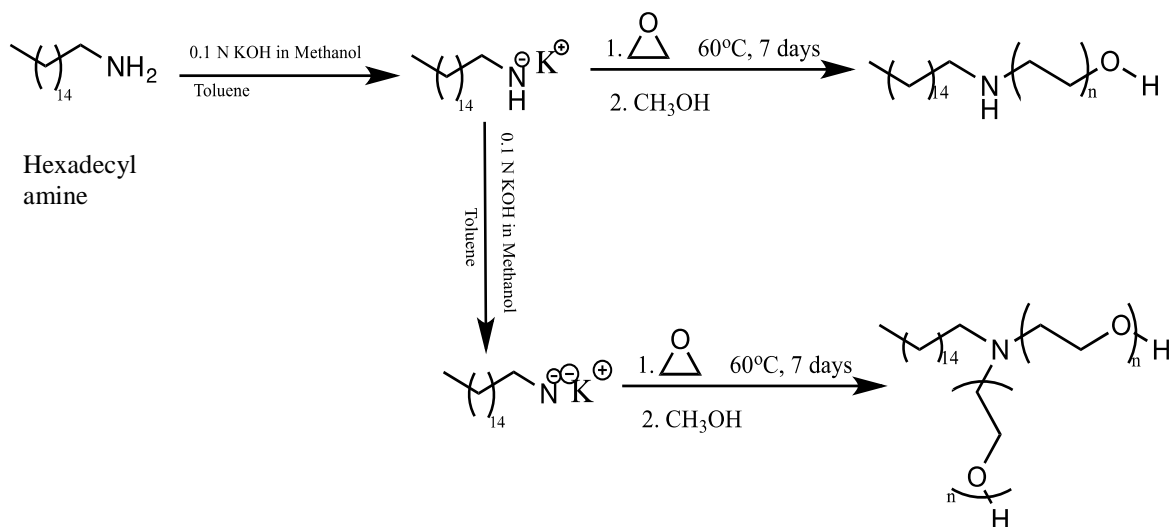
2.1.1 Materials

Benzophenone, and tetrahydrofuran (THF) were purchased from Fisher. 0.1 N potassium hydroxide in methanol, N,N-dimethylacetamide (99%), and chloroform-d (99.8 atom %D, 1 v/v% TMS) were purchased from Acros Organics. Methanol ($\geq 99.8\%$), toluene ($\geq 99.5\%$), and diethyl ether ($\geq 99.0\%$) were purchased from Sigma Aldrich. Dimethyl sulfoxide was purchased from J. T. Baker. Hexadecyl amine and acrylamide was purchased from Fisher Science Education. Ethylene oxide gas was purchased from Praxair, condensed into a schlenk flask, and distilled into a vacuum flask containing calcium hydride. It then was distilled into a round-bottom flask containing a sodium mirror, and finally distilled into a vacuum flask with a stir bar and stored in an explosion proof freezer. Prior to its use in a polymerization, it was again distilled onto a sodium mirror before addition to the reaction vessel. All other solvents and reagents were used as received from Fisher unless otherwise mentioned.

2.1.2 Instrumentation

Gel permeation chromatography (GPC) was used to determine the molecular weight and polydispersity of the PEO polymers. A Waters GPC-1, 1515 HPLC Pump and Waters 717Plus Autoinjector was used. The instrument contains Jordi Gel fluorinated DVB columns (1-100,000, 2-10,000, 1-500Å) and a Varian 380-LC Evaporative Light Scattering Detector (ELSD). THF was used as the mobile phase. Empower 1, Waters software, was used to run the samples and analyze the data. Proton NMR was obtained on a Bruker DMX 300MHz High Resolution Nuclear Magnetic Resonance (NMR) Spectrometer with Bruker Topspin 1.3 software. MestReNova software was utilized to analyze the spectra. For the homo PEO, five PEO standards were used to construct a calibration curve, 10.6K, 23.5K, 36K, 56K, and 93,750, all run in THF, using the same GPC instrument that was used for analyzing the PEO polymer samples.

2.1.3 Synthetic scheme of HDA initiated PEO



2.1.4 Polymerization of EO using HDA initiator by atmospheric distillation:

The alkyl amine, hexadecyl amine (HDA) was used to grow PEO with a target of 5K by following the synthetic procedure similar to 1-octanol initiated PEO. Due to thermal stability of HDA, atmospheric azeotropic distillation was used to form the alkoxide and no DMSO was present in the system. In a 500 mL round-bottom single-necked flask equipped with a magnetic stir bar and a high vacuum Teflon valve, was placed hexadecyl amine. To this was added approximately 300 ml toluene. Next, an equimolar amount of KOH was added. After the toluene-methanol and toluene-water azeotropes were removed by atmospheric distillation, the reaction vessel is fixed to the vacuum line, degassed THF dried over sodium/benzophenone was added by vacuum distillation, followed by the addition of ethylene oxide by way of vacuum distillation. The flask was then removed from the line under vacuum by closing the Teflon stopcock and placed in an oil bath. After back-distilling THF, the solution turned cloudy, white before heating at 60°C for 7 days. The anion did not turn color (slight yellow) until after ~2 hours of heating and the color intensified slowly throughout the reaction time. The reaction mixture was heated to 60 °C for 5-7 days, then quenched with degassed methanol. The polymer solution was filtered and then precipitated by pouring into cold diethyl ether. The solid was collected and placed in a vacuum oven at ambient temperature to dry. GPC and ¹H NMR were used to characterize the molecular weight and polydispersity of the PEO polymers. Once the alkoxide had formed, a colorless liquid remained with a ring of potassium salts inside the flask.

2.1.5 Characterization of HDA initiated PEO by ^1H NMR and SEC:

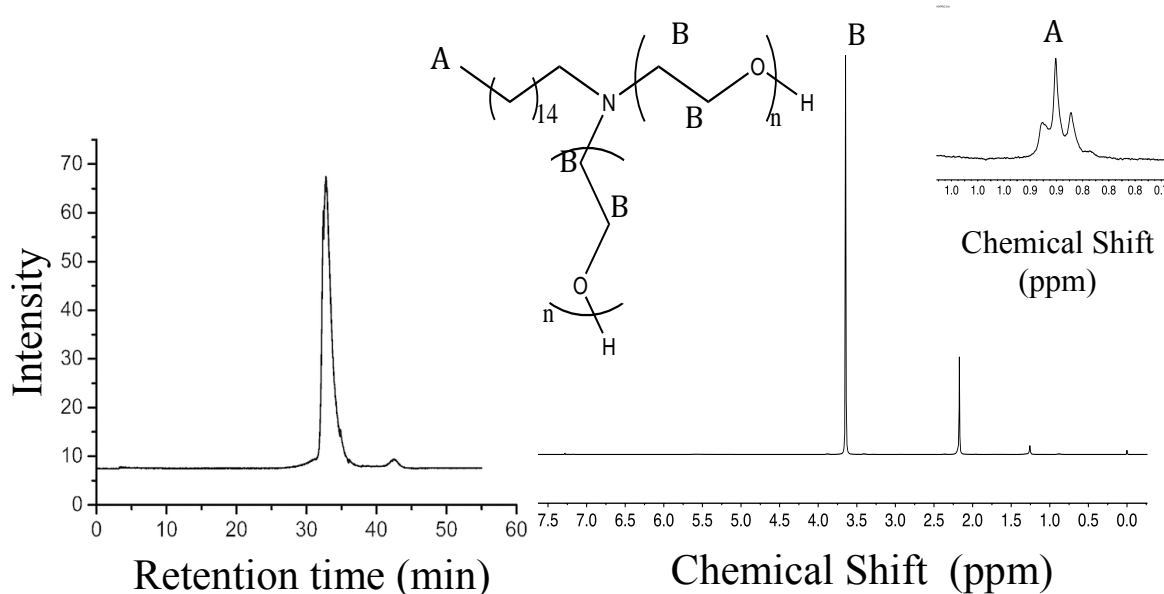
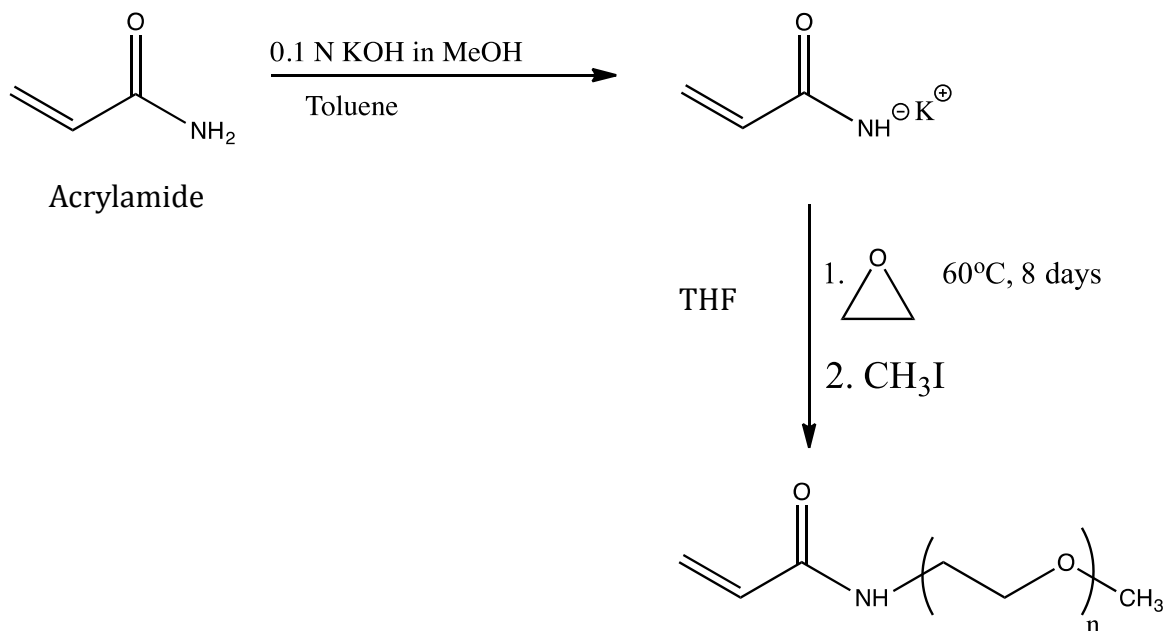


Figure 5: (left)) SEC of PEO homopolymer from hexadecyl amine initiator. (right) ^1H NMR of PEO homopolymer from hexadecyl initiator.

The PEO homopolymer synthesized from hexadecyl amine is analyzed with ^1H NMR and GPC, using PS standards to calibrate the GPC and N, N-Dimethylacetamide (DMAc) as the mobile phase. The peak average molecular weight (M_p) and polydispersity index (PDI) determined by GPC for the polymer is 4.9 kg/mol and 1.08. **Figure 5** shows the GPC chromatogram and ^1H NMR spectrum for the homopolymer. The chemical shift value at 0.9 ppm corresponds to the methyl group in the initiator. The methylene group in the backbone of the polymer chain is shown as a singlet at 3.60 ppm. Comparing the integration of the peak areas, the calculated M_n from ^1H NMR was 4.2 kg/mol. The molecular weight calculated from NMR is slightly lower than the target MW of 5 kg/mol due to a possible reason that not all of the initiator was either converted or participated in the polymerization of EO. The yield of the reaction was 88%.

2.2 Synthesis of Poly (ethylene oxide) using acrylamide as initiator

2.2.1 Synthetic scheme of acrylamide initiated PEO



2.2.2 Polymerization of EO using acrylamide by vacuum distillation:

Acrylamide³ was used to grow PEO with a target of 5K. Due to its thermal sensitivity, vacuum distillation was used to form the alkoxide and no DMSO was present in the system. In a 500 mL round-bottom single-necked flask equipped with a magnetic stir bar and a high vacuum Teflon valve, was placed acrylamide. To this was added approximately 300 ml toluene. Next, an equimolar amount of KOH was added. The reaction flask was attached to a vacuum line and the toluene slowly removed by vacuum distillation, with the flask removed from active vacuum when the solution froze. After the toluene was removed, degassed THF dried over sodium/benzophenone was added by vacuum distillation, followed by the addition of ethylene oxide by way of vacuum distillation. The flask was then removed from the line under vacuum by closing the Teflon stopcock and placed in an oil bath. After back-distilling THF, the solution turned cloudy, white before heating at 60°C for 7

days. The anion did not turn color during heating throughout the reaction time. The reaction mixture was heated to 60 °C for 5-7 days, then quenched with degassed methanol. The polymer solution was filtered and then precipitated by pouring into cold diethyl ether. The solid was collected and placed in a vacuum oven at ambient temperature to dry. GPC and ^1H NMR were used to characterize the molecular weight and polydispersity of the PEO polymers. Once the alkoxide had formed, a colorless liquid remained with a ring of potassium salts inside the flask.

2.2.3 Characterization of acrylamide initiated PEO by ^1H NMR and SEC

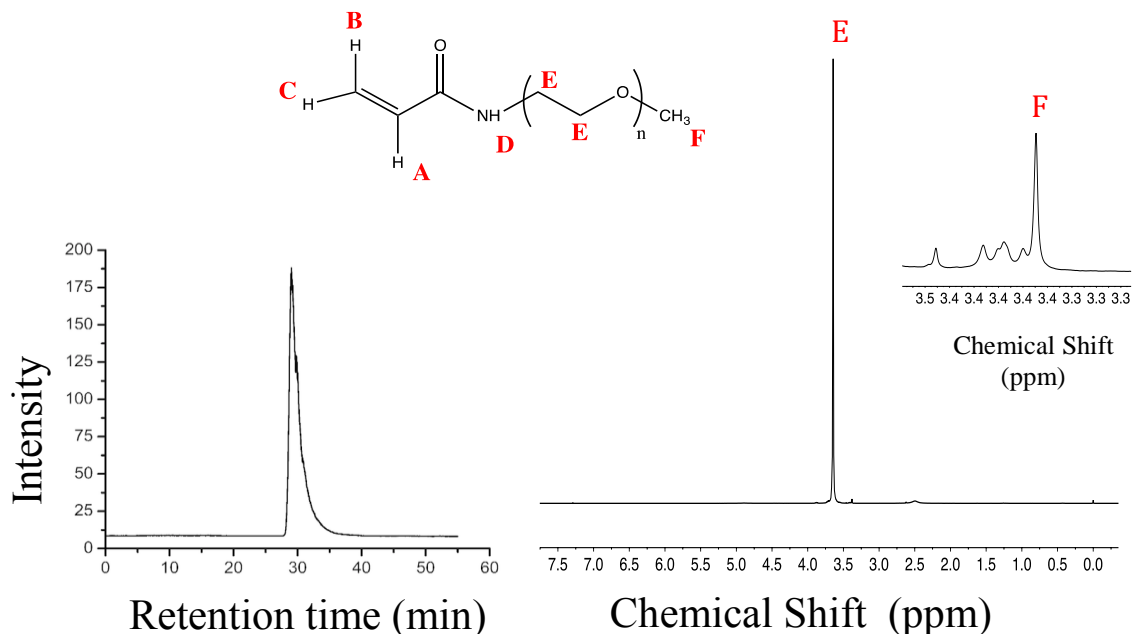


Figure 6: (left)) SEC of PEO homopolymer from acrylamide initiator. (right) ^1H NMR of PEO homopolymer from acrylamide initiator.

The PEO homopolymer synthesized from acrylamide is analyzed with ^1H NMR and GPC, using PS standards to calibrate the GPC and Tetrahydrofuran (THF) as the mobile phase. The peak average molecular weight (M_p) and polydispersity index (PDI) determined by GPC for the polymer is 4.0 kg/mol and 1.14. **Figure 6** shows the GPC chromatogram and ^1H NMR spectrum for the PEO homopolymer. The chemical shift value at 3.4 ppm

corresponds to the methoxy group which is the chain end of the polymer after terminating using methyl iodide which acts as a quencher of the living polymeric chain. The methylene group in the backbone of the polymer chain is shown as a singlet at 3.60 ppm. Comparing the integration of the peak areas, the calculated M_n from ^1H NMR was 5.9 kg/mol. The molecular weight calculated from NMR is slightly higher than the target MW of 5 kg/mol due to a possible reason that not all of the initiator was either converted or participated in the polymerization of EO. The yield of the reaction was greater than 90%.

2.3 Results and discussion:

Apart from polymerizing ethylene oxide using small molecular weight alcohols like 1-octanol, propargyl alcohol and hydroxyl terminated polystyrene, it has been demonstrated that the azeotropic distillation of PEO homopolymer can also be synthesized by employing initiators containing amine and amide functional groups. Unless selective protection of one of the NH_2 group, it was observed that both the hydrogens attached to the nitrogen in the amine group are labile and hence have initiated polymerization of ethylene oxide simultaneously even though a stoichiometric ratio of 0.1 N KOH and hexadecyl amine were used for the reaction. In case of amide group initiated polymerization of ethylene oxide, based on the interpretation of ^1H NMR spectrum, only one of the hydrogen of amide group are replaced by potassium ions thereby initiating the polymerization. One of the inferences that can be drawn is that amine functional group acts as a bi-functional initiator whereas amide functional group acting as a mono-functional initiator.

2.4 CONCLUSION:

In this part of the project, we have extended the same concept and demonstrated the synthesis of a PEO homopolymer from hexadecyl amine and acrylamide using the azeotropic distillation approach. Two methods were shown and the only difference was the atmospheric distillation for thermally stable hexadecyl amine while vacuum distillation for

thermally sensitive acrylamide to generate the initiating anions with potassium as counter cations. Based on the study of the effect of DMSO on homopolymer PEO systems using 1-octanol, DMSO was not used for amine and amide initiated PEO systems. One of the disadvantage of using thermally sensitive initiator, acrylamide forms initially an oligomer probably due to the unstable vinyl bond in its structure and produces a high molecular weight PEO. Future studies can also be extended to difunctional initiators containing two different functional groups to the study their relative reactivity in the initiation process, for example ethanol amine, thermally stable primary amide group containing initiators, initiators with secondary and tertiary amine or amide groups⁴ and the study of PEO initiated from the hydroxyl groups present on the surface two dimensional materials like reduced graphene oxide produced by modified hummer's method would be interesting to explore.

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