

Synthesis and Characterization of Poly(propylene oxide) and its Copolymers

by

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(ABSTRACT)

The synthesis of molecularly designed poly(propylene oxide) was accomplished by using aluminum porphyrin initiator/catalysts to prepare controlled molecular weights, narrow molecular weight distributions, topologies and functionalities. Poly(propylene oxide) has been an important intermediate in macromolecular synthesis. However, lack of control via the conventional potassium hydroxide initiated synthetic method limits the applications of this polymer. In the synthesis of poly(propylene oxide) by using aluminum porphyrin catalyst system, polymerization occurred by exclusive cleavage of the epoxide methylene oxygen bond via nucleophilic attack. This type of ring opening polymerization yields to head to tail configuration with asymmetric monomers. The aluminum porphyrin allowed the synthesis of poly(propylene oxide) with a high molecular weight of ca. 100,000 g/mole and narrow molecular weight distribution, indicating a living nature of this system. A variety of reactive functional end groups, including both primary and secondary hydroxyl and amine could be incorporated in the polymer chains through the modification of the original catalyst with chain transfer agents such as bisphenol A or p-nitro phenol. These reagents also permitted very significant reductions in the required concentration of the catalyst.

The well defined poly(propylene oxide)s allowed the systematic study of effects of functional end groups on thermal degradation behavior. Interestingly, aromatic amine and aromatic nitro end groups significantly improved the thermal stability, whereas the presence of unsaturated end groups caused very adverse effects. Some of the functionally

terminated poly(propylene oxide)s were utilized in the synthesis of block and segmented copolymers to examine the well defined structures as characterized by spectroscopic analysis. The aluminum porphyrin catalyst system was also used to produce statistical copolymers of propylene oxide and allyl glycidyl ether or caprolactone.

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Table of Contents

CHAPTER I. INTRODUCTION	1
I.1. RING OPENING POLYMERIZATION OF ALKYLENE OXIDE	2
I.2. HYBRID POLYMERS	3
I.3. RESEARCH OBJECTIVES	4
I.4. FORMAT	6
CHAPTER II. LITERATURE REVIEW	8
II.1. OVERVIEW	8
II.1.1. Polyethers	8
II.1.2. Propylene Oxide	10
II.1.3. Poly(propylene oxide) and Its Copolymers	12
II.2. RING OPENING POLYMERIZATION OF CYCLIC ETHERS	15
II.2.1. Mechanism of Cationic Polymerization	16
II.2.2. Anionic Polymerization by Alkali Metal Catalysts	20
II.2.3. Coordination Polymerization	24
II.2.4. Metalloporphyrin Catalyst	30
II.2.5. Free Radical Polymerization of Cyclic Ether	42

II.2.6. Stereochemical Aspects	43
II.3.THERMAL DEGRADATION OF POLY(PROPYLENE OXIDE)	46
II.3.1. Introduction	46
II.3.2. Influence of Polymer Structure on Thermal Degradation	47
II.3.3. Stabilization of Polymers	50
II.4. POLYMER HYBRIDS	63
II.4.1. Block Copolymers	63
CHAPTER III. EXPERIMENTAL	74
III.1. GENERAL CONSIDERATION	74
III.2. PURIFICATION	75
III.2.1. Monomers and Catalyst	75
III.2.2. Solvents	79
III.2.3. Initiators and Other Reagents	82
III.3. SYNTHESIS OF MOLECULARLY DESIGNED POLY(PROPYLENE OXIDE)	86
III.3.1. Synthesis of Aluminum Porphyrin Catalysts	86
III.3.2. Monofunctional Hydroxyl Terminated Polymer	87
III.3.3. Synthesis of End Reactive Poly(propylene oxide)	91
III.4. MODIFICATION OF HYDROXYL TERMINATED POLY(PROPYLENE OXIDE)	98
III.4.1. Conversion of Hydroxyl to Carboxylic Acid	98
III.4.2. Conversion of Hydroxyl to Amine Group	99
III.5. SYNTHESIS OF COPOLYMERS	102
III.5.1. Block Copolymers of Propylene Oxide and Caprolactone	102
III.5.2. Synthesis of Statistical Copolymers	103
III.6. CHARACTERIZATION	104
III.6.1. Gel Permeation Chromatography (GPC)	104

III.6.2. Fourier Transfer Infrared Spectroscopy (FT-IR)	104
III.6.3. Intrinsic Viscosity	105
III.6.4. Nuclear Magnetic Resonance Spectroscopy (NMR)	105
III.6.5. Titration	106
III.6.6. Differential Scanning Calorimetry (DSC)	106
III.6.7. Thermomechanical Analysis (TMA)	107
III.6.8. Thermogravimetric Analysis (TGA)	107
III.6.9. Dynamic Mechanical Thermal Analysis (DMTA)	107
III.6.10. Tensile Test	108
III.6.11. Sample Preparation	108
CHAPTER IV. RESULTS AND DISCUSSION	110
IV.1. SYNTHESIS OF POLY(PROPYLENE OXIDE)	110
IV.2.1. Synthesis of Aluminum-Porphyrin Catalyst	110
IV.1.2. Synthesis of Poly(propylene oxide)	113
IV.1.3. Kinetic Studies	123
IV.1.4. Isolation of Polymer and Regeneration of Porphyrin	138
IV.1.5. Control of Functionality	142
IV.2. THERMAL DEGRADATION BEHAVIOR OF POLY(PROPYLENE OXIDE)	194
IV.2.1. Introduction	194
IV.3.2. Variables Affecting Thermal Degradation	194
IV.2.3. Effect of Functional Groups on Thermal Degradation	201
IV.2.4. Concentration Effect	209
IV.2.5. Stabilization of Poly(propylene oxide)	209
IV.3. COPOLYMERS OF POLY(PROPYLENE OXIDE)	216
IV.3.1. Poly(propylene oxide)-Poly(caprolactone) Block Copolymers	216

IV.3.2. Poly(propylene oxide) Based Polyurea Segmented Copolymers	226
IV.3.3. Statistical Copolymers	232
CHAPTER V. CONCLUSIONS AND SUGGESTED FUTURE STUDIES	245
CHAPTER VI. BABLIOGRAPHY	250
Vita	261

List of Illustrations

Figure 1. Mechanism of anionic polymerization [34]	22
Figure 2. Coordination polymerization by organozinc catalyst [84]	28
Figure 3. Synthesis of metalloporphyrin catalysts [38]	34
Figure 4. Proton-NMR of growing polymeric species [115]	38
Figure 5. Exchange of alkoxides observed from proton-NMR [123]	41
Figure 6. Thermal degradation mechanisms of poly(ethylene oxide) and polyethylene [173]	59
Figure 7. Schematic representation of block copolymer architectures [178]	65
Figure 8. Thermomechanical behavior of copolymers	67
Figure 9. Reaction apparatus for polymerization	88
Figure 10. High pressure reactor apparatus[99]	89
Figure 11. Pressure reactor	90
Figure 12. Proton-NMR spectra of tetraphenyl porphyrin and its aluminum coor- dinated derivative	112
Figure 13. Typical time vs conversion plot for the polymerization of propylene oxide by aluminum porphyrin catalysts	116
Figure 14. Molecular weights and molecular weight distributions vs conversion ..	117
Figure 15. FT-IR spectrum of poly(propylene oxide) in absorbance mode	120
Figure 16. A typical proton-NMR spectrum of poly(propylene oxide)	121
Figure 17. Fluorine-NMR spectra of derivatized end group of isopropanol and poly(propylene oxide) by trifluoroacetic anhydride	122

Figure 18. Conversion vs time at various initial monomer concentrations	126
Figure 19. Zeroth order plot of monomer concentration	127
Figure 20. First order plot of monomer concentration	128
Figure 21. Conversion vs time at various catalyst concentrations	130
Figure 22. Time vs $-\ln(1-x)$ at various catalyst concentrations	131
Figure 23. Log-log plot of polymerization rate vs catalyst concentration	132
Figure 24. Conversion vs time at various reaction temperatures	134
Figure 25. Differential method in evaluation of activation energy	135
Figure 26. $-\ln(1-x)$ vs time at various reaction temperatures	136
Figure 27. Arrhenius plot for the calculation of activation energy	137
Figure 28. Proton-NMR spectrum of regenerated tetraphenyl porphyrin by a pseudo two phase reaction	141
Figure 29. Modification of aluminum porphyrin catalyst system	143
Figure 30. Reaction scheme for difunctional hydroxyl terminated poly(propylene oxide) with bisphenol A modified catalyst	149
Figure 31. Kinetic effect of chain transfer agent concentrations	152
Figure 32. GPC trace of typical difunctional hydroxyl terminated poly(propylene oxide)	153
Figure 33. FT-IR spectrum of poly(propylene oxide) prepared from TPPAlEt/Bis A system	154
Figure 34. Proton-NMR spectrum of poly(propylene oxide) prepared from TPPAlEt/Bis A system	155
Figure 35. Polymerization of propylene oxide with DGEBA prereacted catalysts .	157
Figure 36. Synthesis of poly(propylene oxide) with primary hydroxyl end group(s)	164
Figure 37. Difunctional primary hydroxyl terminated poly(propylene oxide) by coupling with terephthaloyl chloride	165
Figure 38. Proton-NMR spectra of benzyl terminated poly(propylene oxide) before and after hydrogenolysis	167
Figure 39. Fluorine-NMR analysis of end groups of poly(propylene oxide) after derivatization by trifluoroacetic anhydride	168

Figure 40. FT-IR spectra of poly(propylene oxide) before and after hydrogenolysis of benzyl ether group	169
Figure 41. GPC traces of benzyl ether terminated poly(propylene oxide) and its hydrogenated product	170
Figure 42. FT-IR spectrum of difunctional benzyl ether terminated propylene oxide oligomer	171
Figure 43. Reaction scheme for the synthesis of aromatic amine terminated poly(propylene oxide)	173
Figure 44. Hydrogenation of aromatic nitro group monitored by proton-NMR ..	175
Figure 45. Synthesis of aromatic amine terminated poly(propylene oxide) monitored by FT-IR	176
Figure 46. Model reaction for the modification of hydroxyl to aromatic amine by isatoic anhydride	179
Figure 47. Proton-NMR spectrum of butane diamine from model reaction	180
Figure 48. Proton-NMR spectrum of modified poly(propylene oxide) by isatoic anhydride	181
Figure 49. FT-IR spectra of hydroxyl terminated PPO(A) and after modified with p-fluoro nitrobenzene(B)	185
Figure 50. Reaction scheme for star-like post coupling by DGEBA	187
Figure 51. GPC trace of poly(propylene oxide) before(b) and after(a) coupling ..	188
Figure 52. FT-IR spectrum of carboxylic acid terminated poly(propylene oxide) .	191
Figure 53. Reaction scheme for synthesis of methacrylate terminated poly(propylene oxide)	192
Figure 54. FT-IR spectrum of methacrylate terminated poly(propylene oxide) ...	193
Figure 55. Effect of molecular weight on isothermal degradation of poly(propylene oxide) at 180°C	197
Figure 56. Effect of molecular weight of poly(propylene oxide) observed by dynamic TGA thermogram	198
Figure 57. Mass spectrum of volatile fragments of commercial poly(propylene glycol) exposed at 185°C in air	199
Figure 58. Effect of atmosphere on thermal degradation of commercial poly(propylene glycol)	200

Figure 59. Dynamic TGA diagrams of poly(propylene oxide)s with various end groups	204
Figure 60. Dynamic thermal degradation of commercial PPO and aromatic nitro terminated PPO under air and nitrogen	206
Figure 61. TGA diagram of an equimolar mixture of commercial PPO and aromatic nitro terminated PPO	207
Figure 62. Isothermal TGA diagram of aromatic amine terminated poly(propylene oxide) at 225°C in air	208
Figure 63. Effect of poly(propylene oxide) molecular weight and aromatic amine end group concentration on thermal stabilization	210
Figure 64. Dynamic TGA diagram of physical mixture of p-nitro phenol and commercial poly(propylene glycol)	211
Figure 65. Synthesis of thermally stable poly(propylene oxide) via grafting anti-oxidant moiety in the polymer chain	214
Figure 66. Dynamic TGA thermogram of stabilized poly(propylene oxide) with pendant nitro group	215
Figure 67. Synthesis of triblock copolymers of propylene oxide and caprolactone	218
Figure 68. Stress-strain behavior of triblock copolymers of propylene oxide and caprolactone	221
Figure 69. DMTA of triblock copolymers of propylene oxide and caprolactone ..	222
Figure 70. Differential scanning calorimetry of triblock copolymers of propylene oxide and caprolactone	223
Figure 71. Small angle X-ray scans of triblock copolymers	225
Figure 72. Reaction scheme for the synthesis of poly(propylene oxide) based polyurea	229
Figure 73. Differential scanning calorimetry of poly(propylene oxide)s and polyureas	230
Figure 74. Typical GPC trace of statistical copolymers of PO and AGE prepared by aluminum porphyrin catalysts	236
Figure 75. FT-IR spectra of statistical copolymers of PO and AGE with various compositions	237
Figure 76. A calibration curve for the determination of copolymer composition .	238
Figure 77. Mole fraction of AGE in initial charge vs in copolymer	239

Figure 78. Mole fraction of M2 in initial charge vs. in copolymer 243

Figure 79. Proton-NMR spectrum of an attempted statistical copolymer of PO(20 mole%) and caprolactone(80 mole%) 244

List of Tables

Table 1. Structures and nomenclature of various epoxides[2]	9
Table 2. Physical properties of propylene oxide [10]	13
Table 3. Cationic initiators [38]	17
Table 4. Ring strain of cyclic ethers (kJ/mole)[38]	19
Table 5. Reactivity ratios of various monomers in aluminum-porphyrin catalyst system(TPPAlCl) using propylene oxide as M1 [122]	39
Table 6. Dissociation energy of various chemical bonds [142]	48
Table 7. Influence of molecular weight on overall energy of activation and on heat of decomposition [174]	60
Table 8. List of some differential and integral methods [175-177]	62
Table 9. Types of caprolactone polymerization [198]	71
Table 10. Results of mono-hydroxyl terminated poly(propylene oxide) synthesis by aluminum porphyrin catalysts	114
Table 11. Experimental conditions for the synthesis of hydroxyl terminated poly(propylene oxide)	150
Table 12. Calculated and observed molecular weights of difunctional hydroxyl terminated poly(propylene oxide)s	151
Table 13. Molecular structure of di-, trifunctional secondary hydroxyl terminated poly(propylene oxide)	156
Table 14. Reaction of aluminum porphyrin catalysts with DGEBA	158
Table 15. Experimental results of DGEBA prereacted catalyst system	159
Table 16. Reaction conditions and results of benzyl ether terminated poly(propylene oxide) synthesis	166

Table 17. Experimental results of amine terminated poly(propylene oxide) synthesis	174
Table 18. Experimental results of modification by p-fluoro nitrobenzene	186
Table 19. Effect of various reactive end groups on thermal stability of poly(propylene oxide)	205
Table 20. Experimental conditions for the synthesis of triblock copolymers of propylene oxide and caprolactone	219
Table 21. Experimental results of triblock copolymer synthesis	220
Table 22. Summary of thermal analysis	224
Table 23. Properties of poly(propylene oxide) based polyureas	231
Table 24. Experimental conditions and results for the synthesis of statistical copolymers of PO and AGE	235
Table 25. Reactivity ratios of propylene oxide and allyl glycidyl ether	240

CHAPTER I. INTRODUCTION

Polymers are macromolecules formed by linking together a large number of smaller molecules by covalent bonds[1]. Extensive applications for polymeric materials have become important in almost every aspect of human life because of their unique properties. The chemical structure of polymers comprises the nature of the repeating units, the composition of possible branches and crosslinks, etc.. The molecular weight distribution tells us about the average molecular size and its regularity[2].

Polymers containing flexible chemical structures, such as ether(C-O-C) bonds in the backbone, have received a great deal of attention due to their inherent characteristics. For example, the ether linkage has both low polarity and van der Waals interaction. The carbon-oxygen bond has a lower barrier to rotation than the carbon-carbon bond and thus provides a low barrier to coiling and uncoiling of chain-like molecules. Moreover, an ether oxygen has a small excluded volume, which is another factor allowing great chain flexibility. Nevertheless, the carbon-oxygen bond has comparable bond energy to the carbon-carbon bond, which contributes to hydrolytic stability[31].

These remarkably useful features have led to extensive commercial development and use of a variety of polyethers. Consequently, polymeric derivatives of propylene oxide

and other epoxides has become the basis of wide range of polymeric materials. The low molecular weight homopolymers of propylene oxide and copolymers of propylene oxide and ethylene oxide are principal components of thermosetting polyurethanes[4-6]. In addition, they are also utilized as surfactants, hydraulic fluids, lubricants and chemical intermediates in many applications. Vulcanizable copolymers of propylene oxide and unsaturated allyl glycidyl ether has been commercialized. Its heat and ozone resistance are superior to those of poly(chloroprene) or natural rubber[7,8].

I.1. RING OPENING POLYMERIZATION OF ALKYLENE OXIDE

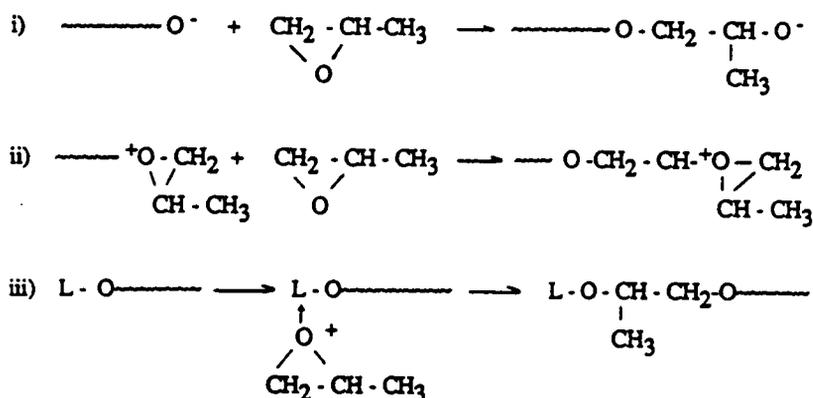
Wurtz was the first to synthesize a three-member epoxide in 1863[32]. The polymerization of propylene oxide was reported by Levene in 1927[33]. As the importance of poly(propylene oxide) in polyurethanes was recognized, propylene oxide became a leading industrial chemical. At present, major chemical companies supply bulk propylene oxide by either the chlorohydrin process or the peroxide process[34a].

Since the polymerization of propylene oxide was reported by Levene, ring opening polymerization of three member cyclic ethers has been extensively investigated. As a result, many new approaches have been developed, all of which fall into following three categories[35].

- (i) Anionic(base catalyzed)
- (ii) Cationic(acid catalyzed)
- (iii) Coordination

The third one essentially combines the features of the first two opposite categories, because it involves the coordination of the monomer oxygen at a Lewis acid catalyst site,

followed by an attack on this activated monomer by an alkoxide already bound to that site or another. The basic chemistry may be illustrated by the following equations:



Despite considerable efforts on the investigation of cyclic ether polymerization, there is a great deal of potential further applications from well defined polymers. Though the anionic route has been commercialized to produce polyether polyols, some serious side reactions limit its application for higher molecular weight materials[34b]. With the advance of coordination chemistry, certain metalloporphyrin compounds have been recently recognized as new initiators. The novel function of this metalloporphyrin as a catalyst affords the polymerization of three membered cyclic ether in a highly controlled manner[38]. Therefore, one can now prepare poly(propylene oxide) with high molecular weight and even remarkably narrow molecular dispersity which reflects the living nature of the polymerization.

I.2. HYBRID POLYMERS

The polymers are commonly used as homopolymers. However, sophisticated applications are continuously developed that demand combinations of properties not attain-

able with simple homopolymers. As a result of this development, several techniques for producing polymer "hybrids" have arisen[182]. There are essentially two general ways of forming polymer hybrids. The first is the physical blending of two polymers. The second approach is via formation of copolymers (thermoplastic) or multiphase network system(thermosetts).

The category of thermoplastic elastomers includes graft, block and random copolymers having a combination of soft segments, usually an amorphous polymer, and a hard segment, typically a glassy or crystalline polymer. Elastomeric feature of copolymers may be attributed to the reversible intermolecular association of hard segments, so called "physical crosslinking". Morphological studies often reveal domain formation, or phase separation of two or more components in the material.

Thermoplastic elastomers are important materials which display dissociation of the physical crosslink and become processable at certain temperatures and pressures. Surprisingly, poly(propylene oxide) has not been widely used as a soft segment for thermoplastic elastomers inspite of its remarkably useful features. This fact may due to the lack of controlled synthesis of this polymer in terms of chain length and functionalities and inability to stress-crystallize. Rather, it has been utilized in thermosetting polyurethane elastomers and for the toughening of epoxy cured networks, since the thermosetting system may tolerate a relatively less controlled molecular structure.

I.3. RESEARCH OBJECTIVES

The principal objective of this research was directed toward achieving molecularly designed poly(propylene oxide) through coordination polymerization. In addition, it was

anticipated that one may obtain a better understanding of the phenomena and mechanism of anionic coordination catalyst system through this study.

The synthesis of poly(propylene oxide) with controlled chain length and narrow molecular weight distribution has been the primary goal of this research. Also, the control of polymer functionalities, which has not yet been achieved in an extensive manner, has been particularly emphasized. End group control of poly(propylene oxide) will permit new engineering applications, since some functional groups may be capable of undergoing desirable chemical reactions, leading to thermoplastic or thermosetting elastomers or elastoplastics.

Currently available anionic routes only provide poly(propylene oxide) with limited molecular weight and functionalities. Cationic polymerization of three member epoxide is even less favored due to the significant side reactions caused by inherent coordinating tendency of polyethers toward Lewis acid type catalyst. Therefore, the research in this regard will focus on establishing the synthesis of the polyethers with specific goals. The First goal was concerned with the control of molecular weight of the polymer over the range of 1,000-100,000 g/mole with a narrow molecular weight distribution. Secondly, a variety of terminal functional groups will be introduced including hydroxyl (primary, secondary), amine, acrylate, allylic and carboxylic acid. The average number of functional groups per chain may be controlled from mono to even multifunctional.

After establishing the synthesis of molecularly designed poly(propylene oxide)(PPO) in terms of chain length, polydispersity and functional group, this research progressed in two separate directions. Thermal degradation behavior of the polymer with well defined structures was investigated. PPO has been widely used due to its reasonably good hydrolytic stability and balanced properties, but application has been still very much limited because of its low thermal stability. In this thermal degradation study, the effect

of molecular weight, environment and functional group was studied. The information obtained from the study premitted the design of thermally stable polymers.

Secondly, poly(propylene oxide) with controlled chain lengths and functionalities were incorporated into various polymer hybrid systems such as block copolymers and crosslinked networks. Well defined structure of poly(propylene oxide) may allow one to prepare well defined copolymeric materials, which may eventually provide a better understanding in structure-property relationships. The research in this area included the synthesis of poly(caprolactone)-poly(propylene oxide) block copolymers, which fall into the category of amorphous/crystalline block copolymers, as well as polyurea segmented copolymers. Polymer structure has been identified by spectroscopic analysis, such as FT-IR, proton-NMR and fluorine-NMR. Thermal analysis techniques such as TGA(thermogravimetric analysis), DSC(Differential Scanning Calorimetry) and DMTA(Dynamic Mechanical Thermal Analysis) were utilized to characterize the thermal behavior of the polymers.

I.4. FORMAT

This thesis is composed of six chapters. In Chapter I, an Introduction of the thesis will describe the brief background and objectives of this research. Chapter II is devoted to the review of previous efforts in the related areas including ring opening polymerization of alkylene oxide, thermal degradation behavior of polymers and multi-phase polymers. This chapter will provide the basic knowledge and justification of the thesis. Chapter III describes the experimental details for the purification of reagents, the synthesis and characterization of various homo- and copolymers. Results and discussions of the experiments are presented in Chapter IV along with characterization by

various techniques. Moreover, some kinetic experiments of the coordinate anionic polymerization are also discussed in this chapter. The latter part of this chapter will be devoted to the thermal degradation studies of poly(propylene oxide) and synthesis and characterization of copolymeric materials containing polyether segments. Finally, in Chapter V some conclusions will be given suggesting future studies in this area of polymer science.

CHAPTER II. LITERATURE REVIEW

II.1. OVERVIEW

II.1.1. Polyethers

Polyethers are composed of flexible ether and hydrocarbon groups in the backbone and are of great interest to both academia and industry. Polyethers usually derived from cyclic ether monomers via ring opening polymerization. Monomers which have a three-membered ring structure with one oxygen are termed epoxides or oxiranes[1]. The chemical structures of representative three membered epoxides are illustrated in Table(1).

Propylene oxide(PO) and ethylene oxide(EO) are widely utilized monomers to prepare low molecular weight homopolymers of propylene oxide and copolymers of ethylene oxide and propylene oxide which are major ingredients for polyurethane arti-

Table 1. Structures and nomenclature of various epoxides[2]

Structure	Monomer name	
	Common	CA
	propylene oxide	methyloxirane
	1-butene oxide	ethyloxirane
	<i>cis</i> -2-butene oxide	<i>cis</i> -2,3-dimethyloxirane
	<i>trans</i> -2-butene oxide	<i>trans</i> -2,3-dimethyloxirane
	1-hexene oxide	<i>n</i> -butyloxirane
	<i>tert</i> -butylethylene oxide	(1,1-dimethylethyl)oxirane
	cyclohexene oxide	7-oxabicyclo[4.1.0]heptane
	1-octene oxide	<i>n</i> -hexyloxirane
	cyclohexylethylene oxide	cyclohexyloxirane
	styrene oxide	phenyloxirane
	phenyl glycidyl ether	phenoxy methyloxirane
	allyl glycidyl ether	(2-propenyloxy)methyloxirane
	1-decene oxide	octyloxirane
	1-octadecene oxide	hexadecyloxirane
	isobutylene oxide	2,2-dimethyloxirane
	epichlorohydrin	chloromethyloxirane

cles, such as rigid or flexible foams, coatings, elastomers and adhesives. These polyethers range in molecular weight from about 250 to 7,000 g/mole[3-6]. Another group of applications for these materials includes surfactants, lubricants, hydraulic fluids, cosmetics and pharmaceuticals as well as many smaller volume products[7,8]. Some typical features of propylene oxide and polymers derived from the monomer will be briefly outlined in the following section.

II.1.2. Propylene Oxide

Propylene oxide is a three-membered ring compound containing one oxygen atom. This cyclic ether is the first member of a homogenous series of alkyl substituted derivatives of ethylene oxide called oxiranes or epoxides. The strain of the three-membered ring imparts unusual chemical properties and reactivity. Although cyclic ethers have many of the properties of ethers, they are much more reactive and are usually considered as a separate class of compound[9-12].

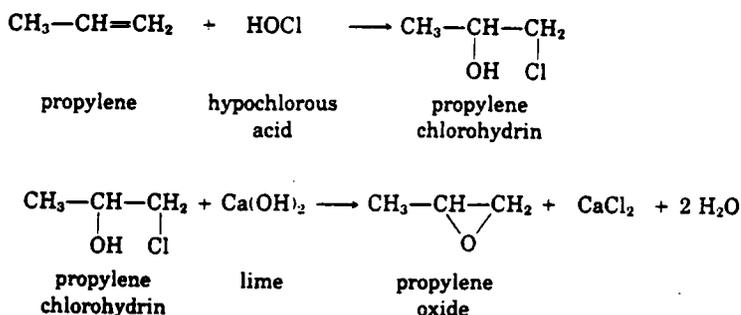
According to the IUPAC and Hantzsch-Widman nomenclatures[11], oxirane is the formal name for the three-membered ring containing the oxygen atom and the propylene oxide is called methyl-oxirane, but the common name for three-membered ring is an epoxide.

II.1.2.1. Synthesis

Ethylene oxide and propylene oxide were first prepared in Wurtz's Laboratory[17]. At present, propylene oxide is produced by two major processes, which are described below;

(a) Chlorohydrin process

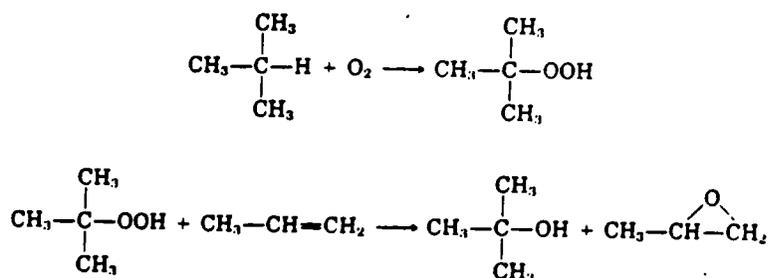
In the chlorohydrin process, chlorine and propylene react in excess water to afford chlorohydrin. The mechanism is thought to involve chloronium ion formation, followed by reaction with water to give a mixture of chlorohydrins. The propylene chlorohydrin is then treated with slaked lime (or caustic soda) to form the oxide[10,18].



The main disadvantage of this process is that most of the chlorine employed becomes waste. If sodium hydroxide is used, the sodium chloride formed can be recycled to the chlorine-generating unit and the organic by-products would include 10 wt% propylene chloride and a small amount of dichloroisopropyl ethers, the overall yield is about 80%.

(b) Oxirane process (peroxide process)

In this oxidation process, propylene is oxidized with a hydroperoxide in the presence of a catalyst. The metal catalyzed homolytic decomposition is a competing reaction, but with proper choice of catalysts, the epoxidation proceeds almost quantitatively[21]. The catalysts include molybdenum(VI) compounds, tungsten(VI), vanadium(V) and titanium(IV)[19,21]. In the first commercial process, tert-butyl hydroperoxide was used, which was obtained from isobutane[19]. Alternatively, ethylbenzene is another source of the peroxide[22]. The latter process can produce styrene as well as propylene oxide.



II.1.2.2. Physical and chemical properties

Propylene oxide is a colorless flammable liquid which is miscible with a wide variety of organic solvents. Although soluble in water, it is not completely miscible and may form two phases. Some of physical properties are listed in Table(2)[10].

In general, epoxides are highly reactive and their chemistry is dominated by ring opening reactions. Typically, the reactions of propylene oxide involve a ring-opening addition of a polar bond(O-H, N-H, etc.) to form a substituted hydroxyl group. Examples are the reactions with water, alcohols and ammonia with ethylene oxide to produce ethylene glycol ethers and ethanol amine, respectively[23]. The driving force for these ring-opening reactions is the relief of the strain energy of the three-membered ring. This strain energy is primarily angle strain but also contains an element of torsional strain due to the eclipsing interactions of the planar ring structure. The strain energy in propylene oxide is estimated to be 123.7 kJ/mole(29.6 kcal/mole) from the heat of combustion data[24].

II.1.3. Poly(propylene oxide) and Its Copolymers

The presence of the ether linkage is responsible for the unique properties of these polymers. The carbon-oxygen bond energy of an ether is similar to the carbon-carbon

Table 2. Physical properties of propylene oxide [10]

Property	Value
molecular weight	58.08
freezing point, °C	-112.0
boiling point, °C	34.2
critical pressure, MPa*	4.92
critical temperature, °C	209.15
explosive limits in air, vol %	
upper	37.0
lower	2.3
flash point, calculated, °C	< -20.0

* To convert MPa to atm, multiply by 9.87.

bond of a hydrocarbon. However, the barrier to rotation around a carbon-carbon bond in a hydrocarbon is about 3 kcal/mole, whereas the barrier to rotation around carbon-oxygen bond of aliphatic ether is only 1.2 kcal/mole[12].

The electron rich oxygen atoms in the backbone structure of the polymers offers a site for coordination. In the case of poly(ethylene oxide), the solubility in water is a result of hydrogen bonding. This water solubility and ability of other electron poor groups to associate with these polymers are critical elements in many applications[8].

The physical properties of these polyethers provide the basis for their utility. Physical properties are affected by the initiator moiety, the functional groups as well as type of monomers present in the polymer molecule[25]. The properties that are influenced by these parameters may include viscosity, solubility and surface activity. However, specific gravity, refractive index and heat capacity may vary relatively little on those factors.

Polymers prepared from propylene oxide are soluble in many organic solvents. Polymers of very low molecular weight or high "hydroxyl number" are relatively polar and are not soluble in non-polar solvents such as hexanes. Instead, these polymers are soluble in water in all proportions. As ethylene oxide is introduced into copolymers of propylene oxide, the solubility in water increases[27]. However, in polyethers containing more than 15 wt% ethylene oxide, the viscosity increases dramatically and certain "gel-like" properties are even observed[28]. This fact has been attributed to hydrogen bonding between water and the ether linkages.

The viscosity of poly(propylene oxide) increases with molecular weight as with other macromolecules. However, the behavior of branched polyethers, initiated with compounds having more than two active hydrogens, shows somewhat different behavior. As soon as propylene oxide are added, the viscosity may increase, but from that point the viscosity falls rapidly until a minimum viscosity is reached. Beyond the minimum,

the bulk viscosity increases as molecular weight increases[26]. No doubt this is related to variations in the radius of gyration in such star oligomers/polymers.

II.2. RING OPENING POLYMERIZATION OF CYCLIC ETHERS

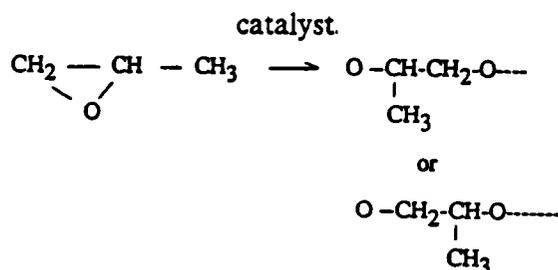
A number of systematic studies have been conducted on the polymerization of cyclic ethers during the last few decades. Recent remarkable improvements in catalysis and analytical techniques have enabled significant progress in the mechanistic views of these polymerizations. The three-membered epoxides have been investigated most extensively due to the unusual structure of the strained ring, which allows polymerization by both anionic and cationic mechanisms.

In anionic polymerization, a base or a nucleophile attacks the epoxide to open the ring in the initiation step. A typical example is the polymerization of ethylene oxide by sodium or potassium hydroxide. The reaction proceeds stepwise by the repeated addition of the epoxide to sodium or potassium alkoxide and molecular weight increases with the extent of polymerization[37]. Cationic polymerization of epoxide can be brought about by Lewis acids such as BF_3 , AlCl_3 , or FeCl_3 and propagation occurs through the cyclic oxonium ionic species[38], although cyclic formation can be a major side reaction.

In this section, mechanistic and stereochemical aspects of these two categories of ring opening polymerization will be reviewed. Also, recent developments with the metalloporphyrin type catalysts will be introduced, which was essentially the basis of this dissertation.

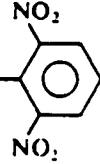
II.2.1. Mechanism of Cationic Polymerization

In cationic polymerization, the principal reaction to form the polymer chain is achieved through the formation of an oxonium ion. However, the actual mechanism may be more complicated due to the high basicity of linear ether groups in the polymer chain compared to those of the epoxide monomers. Consequently, the formation of a cyclic dimer, tetramer, or cyclic oligomer is observed during the cationic polymerization[39]. Recently, Penczek has shown these can be minimized by continuously feeding the monomer and maintaining low monomer concentration[92]. In the cationic polymerization of propylene oxide, the ring opening takes place almost equally at both the methylene-oxygen and methine-oxygen linkages[40].

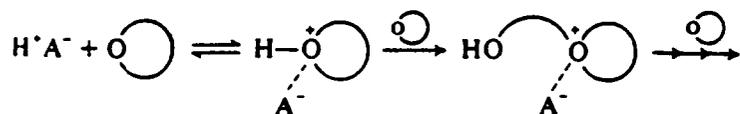


The cationic initiators may be classified as listed in Table(3). In Group A and Group B, a proton or a group from the initiator adds directly to the monomer, whereas in Group C, initiators act by hydride transfer from the monomer. In Group D, the reactions to form reactive species are more complicated. In cationic polymerizations with Group A initiators, a protonic acid reacts with cyclic ethers to form a secondary oxonium ion which is subsequently attacked by other monomer molecules to generate a tertiary oxonium ion. Thus, a growing polymer with a hydroxyl end group may be formed[38].

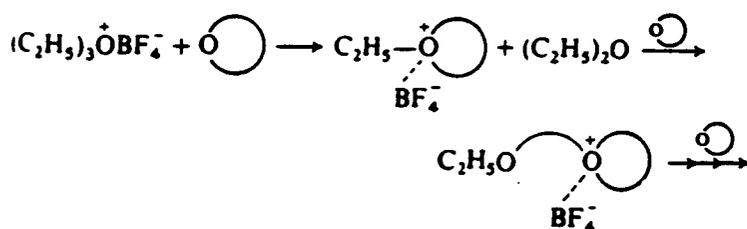
Table 3. Cationic initiators [38]

Group A	Protonic acids	$H^+ A^-$
Group B	Direct addition type initiators	
	B-1	$(C_2H_5)_3O^+ A^-$
	B-2	 $R A^-$
	B-3	$R-C \equiv O^+ A^-$
	B-4	$ROSO_2CF_3, ROSO_2F, ROSO_2Cl, R-OSO_2-$  NO_2
		$((CF_3SO_2)_2O, (FSO_2)_2O, (ClSO_2)_2O)$
Group C	Hydride transfer type initiators	
	B-5	$(C_6H_5)_2C^+H A^-$
	C-1	$(C_6H_5)_3C^+ A^-$
	C-2	$(C_6H_5N_2)^+ A^-$
Group D	Others	
	D-1	Friedel-Crafts type
	D-2	organometallic systems
	D-3	electron transfer type

A^- : complex anion (SbF_6^- , AsF_6^- , PF_6^- , $SbCl_6^-$, BF_4^- , $AlCl_4^-$, etc.); non-complex anion (CF_3COO^- , ClO_4^- , $CF_3SO_3^-$, FSO_3^- , $ClSO_3^-$, etc.).



In case of Group B initiators, various functional groups originating from the initiators may be introduced as an end group. The following is an example of this case where a triethyl oxonium salt is used as an initiator.



II.2.1.1. Reactivity of growing species

The reactivity of the growing polymer chain in a cationic polymerization mechanism is a function of both the counter ion(X-) and the ring size of the monomer. This is because the enthalpy of the growing oxonium ion and the basicity of monomer depends mainly on the ring size of the monomer[41]. The estimated ring strain of various cyclic ethers are tabulated in Table(4). The more reactive oxonium ion pair results from the less stable cyclic ether which has more exothermic enthalpy(- H). However, rather unreactive and stable oxonium ions may still propagate without appreciable chain transfer or termination. The stability of the monomer usually indicates that there is only a small change in free energy(ΔG) during polymerization and consequently the monomer has a low ceiling temperature. The ceiling temperature of a given monomer is that temperature where polymerization and depolymerization rates are in equilibrium[41]. Essentially, the enthalpy term is balanced by the T ΔS term in the Gibb's equation, as summarized below.

Table 4. Ring strain of cyclic ethers (kJ/mole)[38]

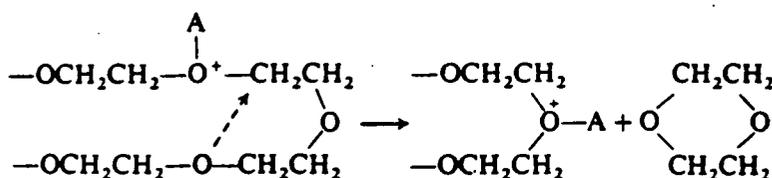
					
114	107	23	5	33	42

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = 0, T = T_{\text{ceiling}} = \Delta H / \Delta S$$

If ΔH is small, then T_{ceiling} is low.

For example, in the polymerization of tetrahydrofuran, the ceiling temperature is only 85°C [42]. Also, the basicity of the ether group of the monomer or polymer chain plays an important role in the mode of the reaction of the growing species, since these nucleophiles participate in various side reactions.



II.2.2. Anionic Polymerization by Alkali Metal Catalysts

Anionic polymerizations are those which are initiated by an alkali metal or its derivatives. Initiation of the polymerization has been reported to be a reaction of the cyclic ethers (propylene oxide, ethylene oxide) with, for example, the hydroxide of the alkali metal to generate the anion of ethylene or propylene glycol. This anion can react with the monomers in a propagation step to afford a long polymer chain [37,43]. The product from the anionic polymerization of ethylene oxide with alkali metal catalysts exhibits a narrow molecular weight distribution.

At present, the mechanism of the anionic polymerization of epoxides is fairly well established. The complete chemical reaction may be broken into the classical steps, i.e., initiation, (the attack of a nucleophile on the epoxide), propagation (the growth of the polymer chain by successive addition of epoxide monomer to the alkoxide anion) and

possibly chain transfer (the transfer of a proton from the hydrogen donating species to the growing chain resulting in a new anion that is generated more rapidly than the chain propagation step). Each step is described by a chemical equation in Figure(1)[34].

II.2.2.1. Nature of the growing species and reaction kinetics

Reactivity of the anionic growing species is strongly dependent upon the type of initiator and catalyst. Higher reactivity is observed with the more basic alkoxide and the order of basicity is as follows[48];



Kinetic studies of epoxide anionic polymerization have been extensively investigated. A kinetic study of the polymerization of propylene oxide[47] using sodium methoxide as the initiator found that the rate of monomer consumption could be expressed by an equation which was the first order in both alkoxide and monomer concentrations.

$$-d[\text{PO}]/dt = k [\text{I}] [\text{PO}]$$

In another study by Ishii[48] using sodium alkoxide and a solvent consisting of a mixture of chlorobenzene and dichlorobenzene, the rate expression contained a first order term in initiator, monomer and alcohol, for the case where a high concentration of alcohol was employed. However, in most of the systems the order of alcohol concentration in the kinetic expression was negative when used as a chain transfer agent. The kinetics of the base catalyzed polymerization of an alkylene oxide is complicated by the fact that reaction involves ionic species. These species can exist as nearly covalent, as associated ion pairs, or in a variety of ionized forms[49]. Each of these different forms may react with an epoxide at its own unique rate. Any outside influence, such as sol-

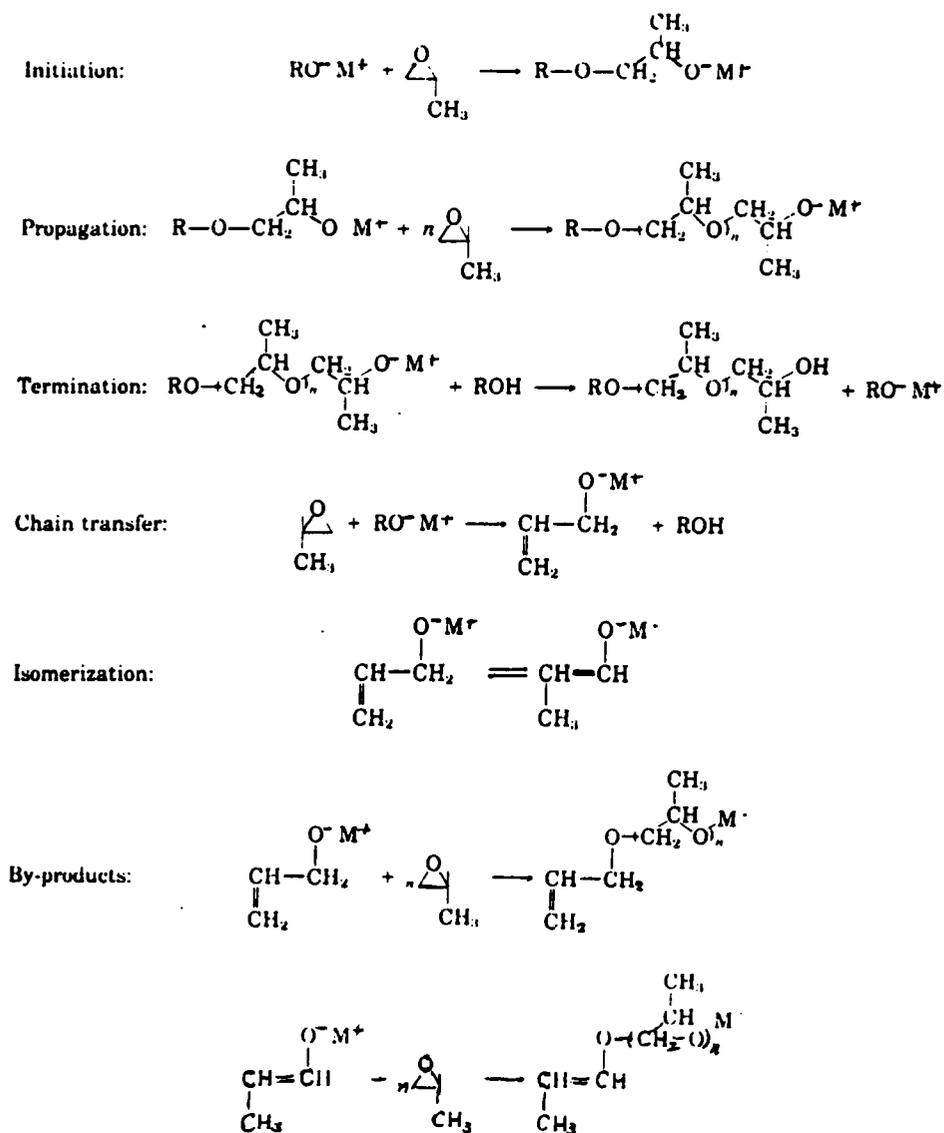
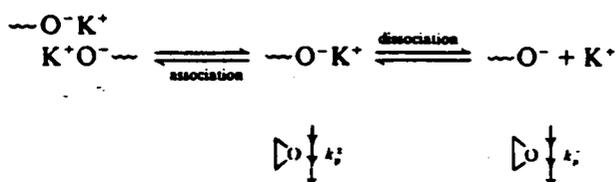


Figure 1. Mechanism of anionic polymerization [34]

vent, which changes the distribution of ionic forms, can thus change the rate at which the epoxide is consumed. Thus, different degrees of solvation of the various forms by the excess alcohol usually can also have an impact on the rate. The effect of different ionic forms has been studied. Dissociated methoxide ions have been reported to open the epoxide ring ten times faster than sodium methoxide ion pairs [44,45]. Also dilution of reaction mixture with more solvent generally favors dissociation.

Boileau[46] has used highly polar solvents or complexation agents such as cryptates to study the differences in reactivity between tight ion pairs and free ions. In those systems, the free ions react with ethylene oxide 50-100 times faster than the tight ion pairs. However, some investigators argue that the association of ion pairs takes place even in highly polar solvents such as DMSO, which makes it difficult to measure reliable rate constants of propagation via ion-pairs(k_p^\pm) and free ions(k_p^-)[50].



Deffieux et.al.[51] claimed that this association may be negligible at very dilute ion pair concentration (up to 0.0003 mole/liter). The reactivity of free alkoxide anion can be determined to be 66 times higher than that of the tight ion pair. The following equation shows how each reaction constant is related to the apparent reaction constant.

$$k^{app} = (1 - \alpha) k_p^\pm + \alpha k_p^-$$

II.2.2.2. Side reactions in anionic polymerization

It has been well recognized that alkali alkoxide initiated anionic polymerizations generate a considerable amount of allyl groups via deteriorious side reactions. It was proposed previously that the formation of the unsaturation units could be due to a cyclic mechanism to give either allyl or propylene groups[53]. The observation that unsaturation occurs only during the addition of propylene oxide argues against this mechanism[52]. Heating the growing active polymer does not increase unsaturation, however, as soon as propylene oxide is added, unsaturation is observed to rise[54]. The effect of the metal counter ion has been studied by Furukawa et.al.[55,56]. They found that the tendency for rearrangement of propylene oxide to allyl alcohol is greatest with lithium hydroxide and decreases in the following order:

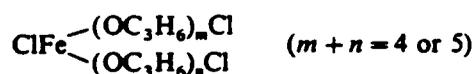


Also, the effect of alcohols as chain transfer agent was examined[57]. It was claimed that because of the interaction between the growing alkoxide and the alcoholic hydroxyl group, the rate of allyl formation may be reduced as the alcohol concentration increases. The activation energy for the ring-opening polymerization of propylene oxide has been reported to be 17.4 kcal/mole, while the rearrangement of propylene oxide to allyl alcohol has an activation energy of 25.1 kcal/mole. This difference in activation energy may account for the increase in the formation of unsaturation with temperature[58].

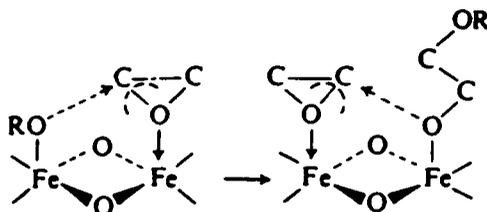
II.2.3. Coordination Polymerization

Some alkylene oxides such as ethylene oxide and propylene oxide can be polymerized to very high molecular weight under moderate reaction conditions. This

type of polymerization has historically been called "coordinated anionic polymerization" or simply "coordination polymerization", since its mechanism is characterized by the fact that the monomer first coordinates at a catalyst site prior to propagation, and that the propagation species, which may be essentially anionic (e.g., metal alkoxide), then attacks the coordinated monomer [59-85]. This is almost the same mechanism that is believed to occur during the polymerization of olefins by Ziegler-Natta catalysts. The coordination of monomer serves two functions, which include the activation of monomer and potentially, stereo-control of the propagation. Activation of monomer through coordination allows for propagation even with relatively low nucleophilicity of the growing alkoxide, thus avoiding the side reactions. Thus, the production of high molecular weight stereoregular polymers such as poly(propylene oxide) and polypropylene are illustrative of these types of polymerization [59]. The coordination polymerization of alkylene oxides originated in an experiment by Pruitt and Baggett [60] who synthesized a very high molecular weight polymer of propylene oxide using a catalyst consisting of the product of FeCl_3 with propylene oxide as shown in the following formula:



Price [61] first used the name "coordinate anionic polymerization" in order to distinguish it from conventional anionic and cationic polymerization. A simplified mechanism was proposed for the polymerization with this type of catalyst.



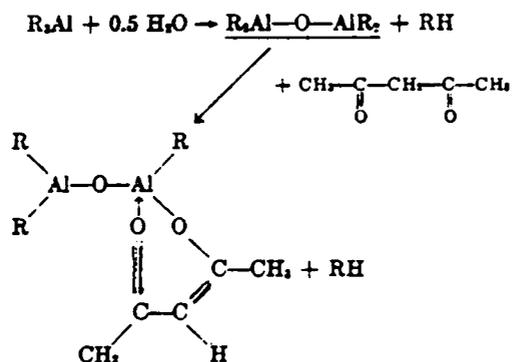
In the above mechanism, propylene oxide monomer is activated toward polymerization by the coordination to the ferric center, which is attacked by the neighboring alkoxide group of the catalyst (for initiation) or the growing alkoxide chain propagation end (for propagation). This mechanism has several important features; first, coordination of epoxide and growth of polymer on one metal atom; second, ring opening at the secondary carbon atom of the epoxide; third, retention of configuration of the asymmetric carbon atom because of a front side attack; fourth, a possible racemization of the asymmetric carbon atom during ring opening due to free carbene-like ion formation under some conditions to explain the amorphous optically inactive fraction[60].

After the discovery of Pruitt and Baggett, many related catalytic or initiator systems were also discovered. For example, partly hydrolyzed ferric alkoxide[80], $\text{ZnEt}_2/\text{H}_2\text{O}$ [71,72], ZnEt_2/ROH [73], $\text{AlR}_3/\text{Zn Cl}_2$ [75,76] and $\text{Et}_2\text{AlCl}/\text{porphyrin}$ [64,66,74] were utilized for the polymerization of epoxides. The propagating polymeric species in all cases is believed to be an alkoxide[77-79]. Ethylene oxide can also be polymerized to extremely high molecular weight polymer by the carbonates of alkaline earth metals (Ca, Sr, Ba)[81]. In addition to the carbonates, other compounds of alkaline earth metals such as oxides, alkoxides and amides have been shown to induce polymerization of ethylene oxide[82]. The amides of alkaline earth metals polymerize ethylene oxide to high molecular weight at the temperature as low as -33°C [42]. This type of coordination catalyst is effective for the production of high molecular weight polymer. Such a result cannot, in general, be achieved by using alkali metal salts, indicating that the rate of propagation is probably much higher than that of termination. However, it is rather difficult to in-

investigate the structure of the active site, because of its heterogeneous nature and extremely low effective concentration (0.05-1 mole% of total catalyst)[38].

A linear increase in the viscosity average molecular weight with conversion was observed in the polymerization of propylene oxide with $\text{ZnEt}_2 / \text{H}_2\text{O}$. In conformity with this observation, the addition of more monomer to the reaction mixture after the completion of the polymerization cause an increase in the molecular weight and yield of the resulting polymer. However, the molecular distribution of polymer is not narrow (MWD=3), which is typical of polymerization of epoxides with coordination catalysts[83]. Similarly, in the polymerization of propylene oxide with ZnEt_2 /pyrogallol (2:1) system in dioxane at 35°C, the intrinsic viscosity of the polymer increased with increasing conversion at a given catalyst concentration. Further addition of the monomer to the reaction mixture of the first stage of polymerization results in the formation of polymer with higher intrinsic viscosity than the initial one. The structure and mechanism of this catalyst is postulated in Figure(2)[84].

Along with organozinc and organomagnesium catalysts, alkyl aluminum based catalysts were frequently utilized in the ring opening polymerization of propylene oxide for high molecular weight polymers. Like other organometallic catalysts, water was used a co-catalyst, e.g. $\text{Et}_3\text{Al}-0.5\text{H}_2\text{O}$, $\text{Et}_3\text{Al}-0.5\text{H}_2\text{O}-0.5$ Acetyl acetone. In the latter case, acetyl acetone served as a chelating agent for the aluminum atom. Vanderburg[85] found that by utilizing these ratios of components, a very effective and commercially attractive catalyst was generated. However, the ratios of these ingredients can be varied over a wide range and the best composition will depend on the conditions and the specific epoxide being polymerized thus, these two types of alkyl aluminum catalysts demonstrated different performances. The fundamental reactions postulated and basic structures thus formed in preparation of alkyl aluminum catalysts are presented in the following equation[86].



With the alkyl aluminum- H_2O catalyst, water reacts at both of active hydrogens to form a bis(dialkylaluminum) oxide species and releases a hydrocarbon. This is fact was confirmed by Vanderberg and Furukawa[87] by employing tritiated water in the re- actions and showing that the final catalysts did not retain appreciable (< 1% of initial concentration) radioactivity.

In the formation of acetylacetonone-modified catalyst, acetylacetonone reacts further with organoaluminum intermediate to liberate another mole of hydrocarbon and form chelated species. Kambara and coworkers[88] also synthesized epoxide catalysts based on the combination of alkylaluminums with transition metal chelate compound (as acetylacetonates). Since Sartori et.al.,[89] previously showed that triethyl aluminum and chromium triacetylacetonate interact to form alkyl aluminum acetyl acetone type species, Kambara's catalyst merely offer an alternative way of the process. Acetylacetonone chelated catalysts were compared in terms of their performance, which showed that direct synthesis method employed by Vandenberg demonstrated more ef- fectiveness in the polymerization of epoxides. The role of the coordinating chelating agent has been speculated that it may minimize an ordinary cationic polymerization of the Lewis acid type catalyst by blocking the fourth coordinate position of aluminum and

allowing the fifth and/or sixth coordinate positions of aluminum to function in a coordination propagation step[90].

In addition, the presence of metal-oxygen-metal grouping in the catalysts are considered to be important in the polymerization of epoxides. A variety of other reactive additives, such as polyols, amine, hydrogen sulfide may be utilized to join together organometal groups to form active catalysts. Useful additives may vary considerably depending on the starting organometallic compound[91].

Vandenberg proposed a mechanism of coordination polymerization with alkyl aluminum based catalyst[92]. In this mechanism, the coordination bonds in the catalyst structure are needed to move the growing polymer chain from one metal to an adjacent one without altering the valence of the metal. Although two four-coordinate aluminum atoms are shown in the following equation, one may imagine more aggregated structures of catalysts can be formed and the fifth and sixth coordination are also involved in the polymerization.

Coordination catalysts are not always favored for the synthesis of polymers with controlled chain length, since the catalyst tends to be highly aggregated and different catalyst sites may have different reactivities, which produce a continuous initiation step. This may be the major reason for the broad molecular weight distributions often observed in these polymerizations.

II.2.4. Metalloporphyrin Catalyst

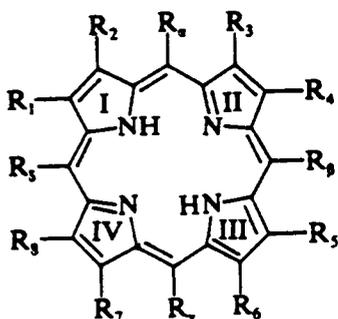
II.2.4.1. Coordination compounds of porphyrin

Metalloporphyrins including chlorophyll and heme components of blood represent a unique group of intercomplex compounds. A central metal atom displaces two hydrogen atoms from the porphyrin ligand, thus forming a symmetrical electrostatic field of

four nitrogen atoms, which may form four almost equivalent coordinate donor-acceptor bonds. If the electrostatic interaction involves the filling of vacant orbitals of the central metal atom by the electrons of the donor N atoms of the porphyrin ligand, then stable porphyrin complexes of predominantly a covalent type complexes will be formed, which includes the complexes of Fe^{2+} , Fe^{3+} , Co^{2+} , Zn^{2+} , Al^{3+} , Si^{4+} , etc. However, if the electrostatic interaction occurs alone, labile ionic complexes are formed. These include the complexes of Na^+ , K^+ , Ba^+ , Ca^+ and other cations[102].

The specific features of metalloporphyrins as intercomplex compounds are due not only to the polydentate nature of the ligand but also to its rigidity, which is determined by the planar and conjugated structure of large ring porphyrin structure. The strong π -electron interaction may be partially responsible for this rigid structure over the entire macro- ring, also the four nitrogens facilitate the coordination of the metal atom.

Because of the high rigidity the porphyrin ligand imposes specific requirements on geometric parameters of the metal ions, forming two distinctive classes of porphyrin complexes which are stable or labile. It was postulated that direct contact of the central metal atom has a severe effect on the oxidation- reduction and acid-base characteristics of the porphyrin. Another specific feature of porphyrins is their diversity, which can be seen in the following structure[103]:



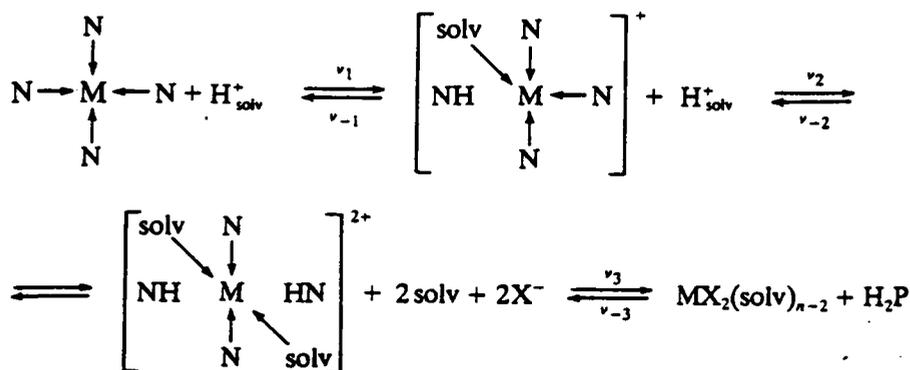
Porphyrin differs in the nature of the bridging groups occupying the meso position in the porphyrin molecule; the bridging groups may be $-\text{CH}=\text{}$, $-(\text{X})\text{C}=\text{}$, $-\text{N}=\text{}$, or their combinations. Also, it is worthwhile to note that a porphyrin molecule ceases to exist as soon as at least one double bond in the macro-ring is hydrogenated[102].

The unique characteristics and great diversity of porphyrins, particularly metalloporphyrins are responsible for their importance and extensive applications in various physical, physicochemical, biological studies as well as in the production of dyes, semiconductors and catalysts[104]. Another important feature of metalloporphyrin complexes is that they are extremely stable to dissociation. This is one of the reasons why it is difficult to quantitatively measure the equilibria of their formation in a direct manner. The coordination capacity is also a significant feature of the porphyrin complexes. It is referred to as extra coordination along the Z-axis, passing through the metal atom at a right angle to the plane of the porphyrin molecule. Extra coordination is an important nature of the porphyrin complex since this fact may allow the metalloporphyrin to be utilized as transport media for small molecules or electrons.

In this regard, metalloporphyrins of Fe show good oxygen binding, electron transport and enzymatic catalysis[104]. The porphyrin complexes of magnesium have drawn some attention due to its ability to store and convert solar energy in living cells. A variety of characteristics which metal complexed porphyrin may bring including steric hindrance, site isolation as well as transeffect by the axial coordination[105]. The phenomenon are very much related to each other. Recent advances in porphyrin synthesis has enabled molecular design of these compounds for particular purposes. Due to its steric hindrance, the metalloporphyrin complexes have been applied to epoxidation of alkene compounds by fixation of oxygen on the coordinated metal site in the form of $\text{TPPM}(\text{V})=\text{O}$, which can be transferred into $\text{TPPM}-\text{O}-\text{C}-\text{C}$ [106]. Steric hindrance is pronounced when the compound with bulk substituents approaches the porphyrin

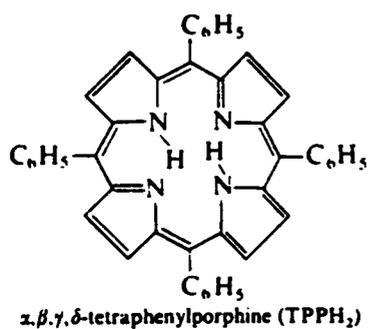
moiety. It was well recognized that steric hindrance around the porphyrin ligand tend to limit the bimolecular irreversible oxidation of the central metal atom on which the oxygen atom is attached. This is referred as the site isolation effect, which could be a significant feature when used in catalytic application since homogeneity of all reactive site may be acquired. Another feature of metalloporphyrin complexes is the facile excitation by light. An effort to design a photo galvanic cell by using this concept was made by Hoffman et.al.[104], in which photo dissociation could take place via simple excitation by light.

Kinetic studies in the dissociation of metalloporphyrin complexes have been conducted by many workers[107,108]. The metalloporphyrin complex with covalent type bond was so stable that concentrated sulfuric acid in ethanol or acetic acid medium was employed for the dissociation of the metal from porphyrin ligand. The reaction is considered to be a reversible process as described in the following:



II.2.4.2. Polymerization by metalloporphyrin initiators

Recently, some metalloporphyrins of aluminum and zinc have been discovered to be effective for the living polymerization of epoxides and other monomers to afford polymers with controlled chain lengths[109-111]. These catalysts are prepared according to the scheme shown in Figure(3).



OR

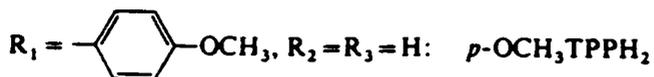
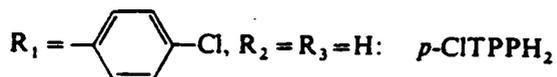
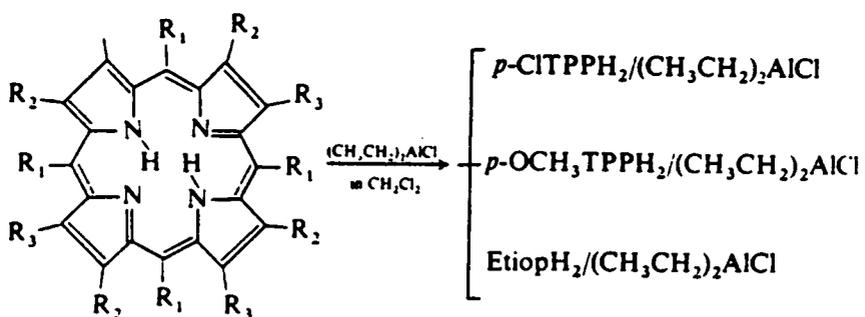
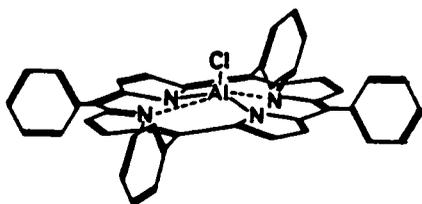
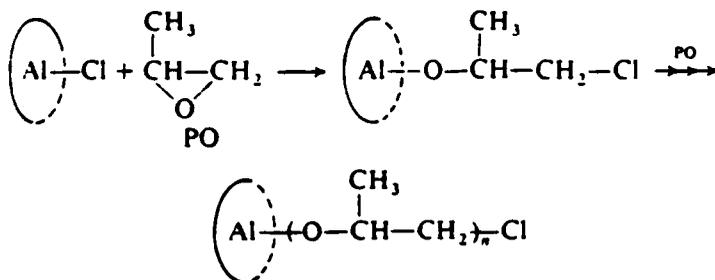


Figure 3. Synthesis of metalloporphyrin catalysts [38]

All of these complexes are able to synthesize poly(propylene oxide)s with a narrow molecular weight distribution. However, tetraporphyrinato aluminum chloride (TPPAAlCl) demonstrated the highest reactivity[112].



Polymerization takes place rapidly even at room temperature and the polymerization of ethylene oxide, propylene oxide and 1-butene oxide have a living nature. For example, in the polymerization of 1-butene oxide, a linear increase in the molecular weight of polymer with conversion was observed[66]. The molecular weight distribution obtained from gel permeation chromatography demonstrated very narrow "Poisson" distribution throughout the polymerization. It was confirmed on the basis of the spectroscopic analysis of the propagating oligomeric species that the polymerization of epoxides by this catalyst proceeds in the following manner:



The living polymer of propylene oxide was observed by ¹H-NMR as shown in Figure(4), due to the strong shielding effect of the porphyrin ring on this catalyst. The living nature of this catalyst system may be ascribed to the separation of active group

ends from each other by a rigid and planar porphyrin ring, which is partly responsible for the uniform reactivity of all the growing species[113]. The polymerization of various mono- or di-substituted epoxide was investigated using this aluminum porphyrin catalysts system[114]. However, this catalyst was much less reactive for the polymerization of substituted epoxides with bulky pendant groups such as styrene oxide and isobutene oxide[115].

(a) Copolymerization by metalloporphyrin catalysts

1. Block copolymers

The metalloporphyrin catalyst were utilized to prepare binary or ternary block copolymers with very high blocking efficiencies via successive addition of different monomers[116-120]. The block copolymers are characterized by a narrow molecular weight distribution as well as controlled molecular weight. The block- copolymers prepared by this catalyst include poly(propylene oxide)-b-poly(ethylene oxide), poly(propylene oxide)-b-poly(epichlorohydrin), and poly(propylene oxide)-b-poly(butylene oxide), etc.. Ternary blockcopolymers were prepared by simply adding three different monomers sequentially on to this catalyst. The successful formation of block copolymers of controlled chain lengths by the successive polymerization of epoxides catalyzed by the aluminum-porphyrin catalyst may confirm the living character without chain transfer and termination.

2. Statistical polymers

In addition to homopolymers and block-copolymers, the aluminum porphyrin catalyst system was also employed for the random copolymerization of epoxides to give copolymers with controlled molecular weights. The effect of the substituent of epoxide on the reactivity of growing species, (porphinato) aluminum alkoxide seems to be more

significant than on the reactivity of the epoxide. A much higher reactivity of the primary alkoxide (TPPAI-OCH₂CH₂-) over that of secondary alkoxide, i.e., (TPPAI-O-CH(CH₃)-CH₂-) clearly demonstrated in the competitive reactions toward 3,3-dimethyl-1,2-epoxybutane having little homopolymerizability[121].

The reactivity in random copolymerization was studied by Aida et.al.[122] with propylene oxide (M₁) and other epoxide(M₂). In the copolymerization using ethylene oxide(EO), 1,2-epoxybutane, or epichlorohydrin(ECH) as a counterpart for propylene oxide(PO), the compositions of copolymers formed at the early stage is similar to those of the comonomers in the feed, indicating that copolymerizabilities of these epoxides are not much different from each other. However, when propylene oxide was copolymerized with 3,3-dimethyl epoxybutane (with 1,2- disubstitution), preferential incorporation of the propylene oxide was observed over a wide range of initial comonomer ratios. The reactivity ratios of each case was estimated by the Kelen- Tüdös model, assuming steady state with respect to the concentrations of each monomer. Table(5) summarizes the reactivity ratios obtained from this method. The value 1/r₁ represents the relative reactivity of M₂ to M₁ toward the growing species derived from M₁. It was claimed that the reactivity of the epoxide toward the growing species of this system may decrease parallel with the increasing bulkiness of the substituent on the epoxide ring. This was confirmed by the fact that even epichlorohydrin demonstrated less reactivity than propylene oxide since epichlorohydrin is highly susceptible toward nucleophilic attack, due to its electron- withdrawing substituent[122].

Polyether-polyester statistical copolymeric systems were also investigated. The polyether component usually included poly(propylene oxide) and poly(ethylene oxide) while β-lactone or phthalic anhydride formed the polyester part[123]. In the copolymerization of epoxide and β-lactone initiated by aluminum porphyrin catalysts, exchange of alkoxide or carboxylate group as the growing species on aluminum

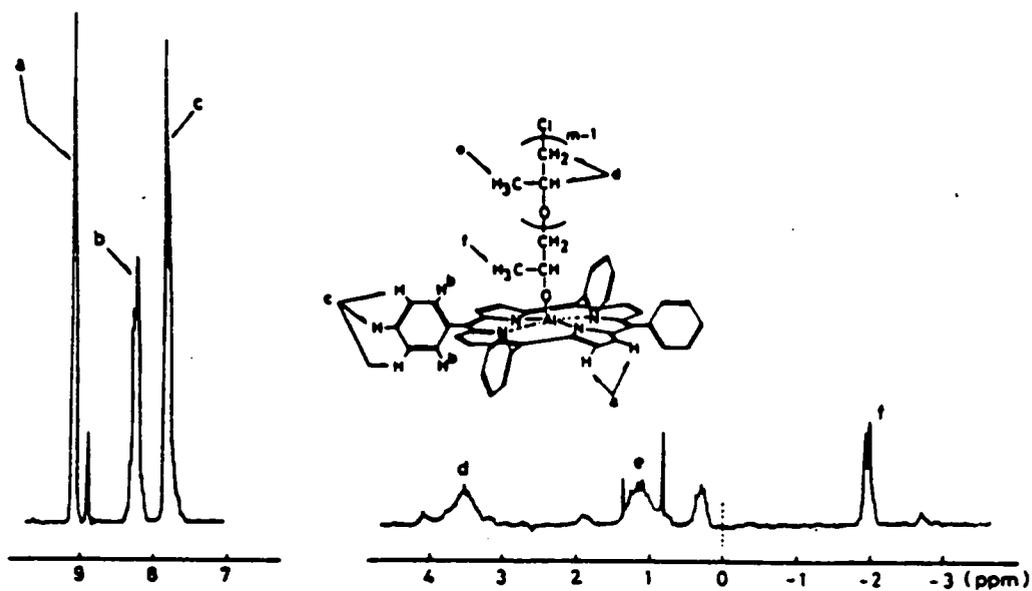


Figure 4. Proton-NMR of growing polymeric species [115]

Table 5. Reactivity ratios of various monomers in aluminum-porphyrin catalyst system(TPPAlCl) using propylene oxide as M1 [122]

M ₁ (PO)		M ₂		r ₁	r ₂	1/r ₁
R ₁	R ₂	R ₁	R ₂			
		H	H	0.5	0.3	2.0
		CH ₂ CH ₃	H	1.4	0.9	0.7
CH ₂	H	CH ₂ Cl	H	5.1	5.3	0.2
		<i>cis</i> -CH ₃	<i>cis</i> -CH ₃	1.8	a	0.6

* Very small, close to 0.

porphyrin was observed through proton-NMR analysis by mixing two types of aluminum porphyrin with alkoxide or carboxylate groups. Figure(5) shows that exchange is taking place between two types of growing species. It was postulated that fast rate of exchange of the alkoxide and carboxylate groups may be consistent with a unimodal and narrow molecular distribution of polymer formed by using the mixture of two different aluminum porphyrin catalyst with different reactivities[123,124].

When the propylene oxide was copolymerized with phthalic anhydride or carbon dioxide by the aluminum porphyrin catalyst coupled with quaternary salts, copolymerization occurred simultaneously on both sides of a metalloporphyrin, yielding copolymers with a regular alternating structure. The quaternary organic salt is activated as nucleophile by the metalloporphyrin to form a hexa-coordinated aluminum porphyrin carrying one reactive axial ligand on both sides of square planar Al-N skeleton[125]. Metalloporphyrins are regarded as a "molecular" system with two structurally isolated sites linking back to back with each other through one metal atom, so that an information at one site can be delivered to the opposite site by an electronic interaction between two isolated sites via trans effect of the metal[127]. For example, one reaction may take place at one side of the metalloporphyrin plane, while the other side of an appropriate ligand coordinates to the metal and assists the reaction by affecting the rate or equilibrium. In the copolymerization of phthalic anhydride and propylene oxide, a phosphonium salt is used as an extra ligand for porphyrinato aluminum chloride, where the chlorine is first axial ligand covalently bound to the aluminum. It was demonstrated that the copolymers with a terminal group originating from the anion of quaternary ammonium or phosphonium salt or the axial group on aluminum porphyrin were formed and that the number of copolymer molecules is twice that of the catalyst molecules[128].

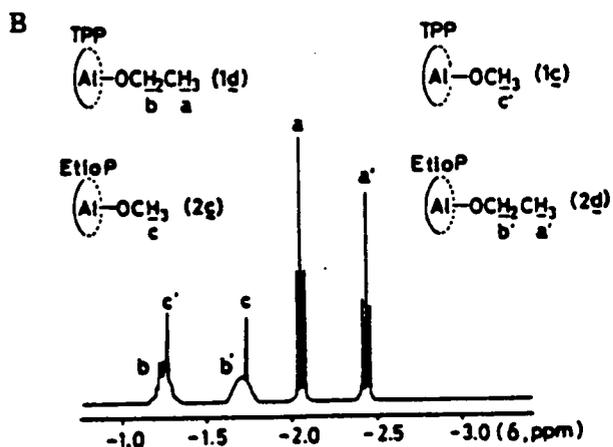
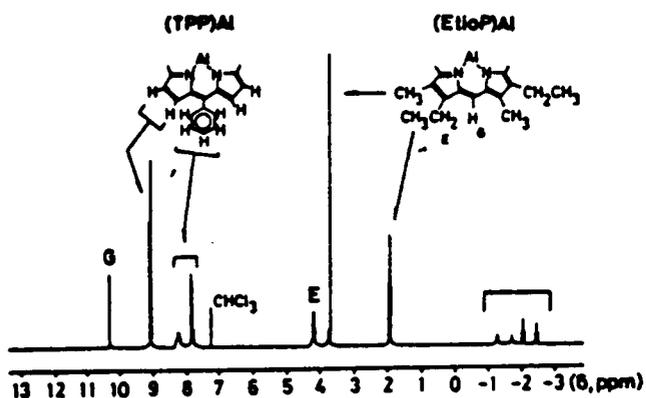


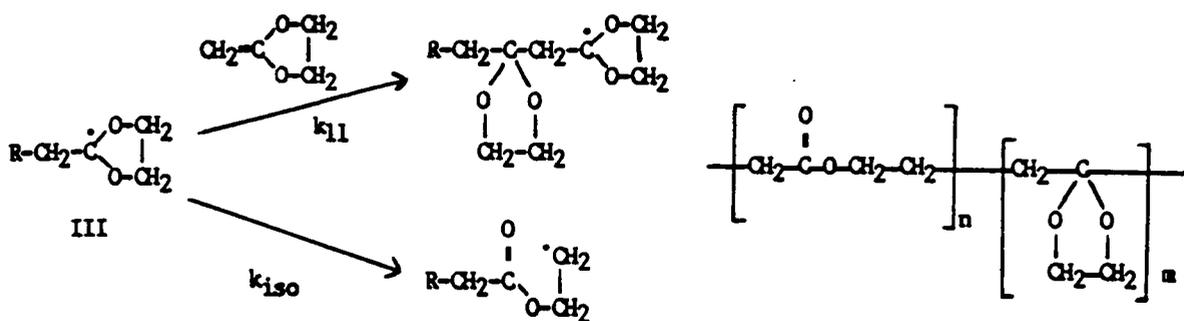
Figure 5 (A) ^1H NMR spectrum of the equimolar mixture of (TPP)AlOCH₂CH₃ (1d) and (EtioP)AlOCH₃ (2c) in CDCl₃ at room temperature after 30 min. (B) High magnetic field region. [123]

The presence of hexa-coordinated structures of aluminum porphyrin catalyst was examined via proton-NMR analysis, where β -pyrrole proton of porphyrin shifted ca. 0.7ppm by extra coordination of quaternary salt on the other side of aluminum. Interestingly, the penta-coordinate structure of aluminum-porphyrin catalysts showed much less reactivity in the copolymerization of phthalic anhydride and propylene oxide, which was ascribed to the mutual trans effect between the reactive species separated by a porphyrin planar structure[129].

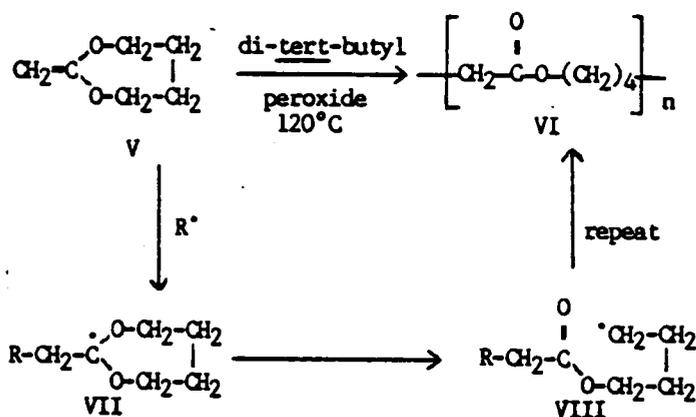
More recently, statistical copolymers and block copolymers of epoxide and carbon dioxide were synthesized by Kogima et.al.[130], where a secondary amine(dialkyl amine) was employed as extra ligand for aluminum porphyrin catalysts.

II.2.5. Free Radical Polymerization of Cyclic Ether

It has been quite rare that the ring opening polymerization occurs by a free radical mechanism. However, some cyclic hydrocarbon monomers, such as cyclopropane, vinyl cyclopropane have been ring opened to give the corresponding polymers[131,132]. Several cyclic monomers containing oxygen would undergo a ring opening polymerization in the presence of free radical catalysts. One such case is the diethyl ketene acetal which has been polymerized by Bailey et.al.[131] to give a random copolymer of the following structure;



High reaction temperature produces more ring opening of this monomer in a kinetically controlled manner, which in turn introduces more ester group in the backbone of this random copolymer. Bailey and his coworkers [133] who have pioneered this area successfully synthesized the seven membered ketene acetal, which underwent the ring opening polymerization quantitatively even at the room temperature. They postulated that the seven membered ring increased the steric hindrance in the intermediate free radical to eliminate practically all of the direct addition and also introduced a strain to accelerate the ring opening.



II.2.6. Stereochemical Aspects

In the polymerization of racemic propylene oxide by alkali catalyst, the distribution of the steric structure with respect to the asymmetric carbons of the monomer unit in the polymer chain is random and the polymer is atactic [134]. In contrast, catalyst systems such as FeCl_3/PO , $\text{ZnEt}_2/\text{H}_2\text{O}$ and $\text{AlEt}_3/\text{H}_2\text{O}/\text{acetyl acetone}$ [135-137] afford polymers with isotactic structures.

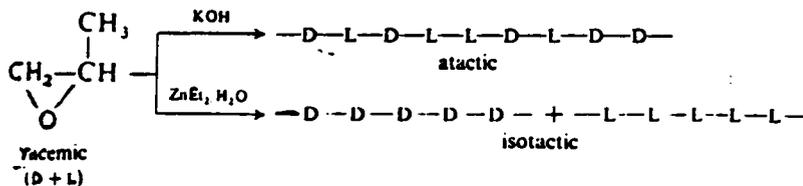
Since propylene oxide has an asymmetric carbon, the formation of isotactic polymer from racemic monomers is the result of the selective incorporation of one of the

optical antipodes of the monomer into a growing polymer molecule[138]. In principle, there are two possible mechanisms for such a stereo-selection in polymerization reaction. If a growing polymer terminal with e.g., d-configuration, reacts preferentially with the same d- configuration, an isotactic polymer will result (growing chain mechanism). On the other hand, an asymmetric structure of the catalyst, with which the monomer coordinates, may be responsible for the stereo-selection. For the formation of isotactic poly(propylene oxide) catalyzed by $ZnEt_2/CH_3OH$, the latter mechanism (enantiomorphic catalyst site control) has been suggested. More recently, the polymerization by a well defined zinc complex with an asymmetric structure has been found useful in the interpretation of this mechanism at the molecular level. On the contrary, the asymmetry of the growing polymer chain is considered to be responsible for the selection of optical antipodes observed in the polymerization of sterically hindered monomer such as t-butylene oxide with t-BuOK[139].

With a ferric catalyst system it was shown that the consumption of two antipodes of propylene oxide were due to their unbalanced coordination[140]. The reaction product of ferric chloride and propylene oxide was partly hydrolyzed in the presence of bornyl ethyl ether to produce an asymmetric catalyst. The polymerization of l-monomer was 6% higher than the d-monomer. The extent of unbalanced polymerization between two propylene oxide antipodes was the same as that of the adsorption.

Although isotactic polymers of propylene oxide prepared from the racemic monomer are optically inactive because of the equal amounts of d-d-d- and l-l-l- sequences, the synthesis of optically active polymer from racemic monomer may be realized by using an optically active catalyst system such as $ZnEt_2/t\text{-bornel}$ [141]. The selection of one of the monomer antipodes is clearly demonstrated by the fact that the unreacted monomer is rich in the antipode opposite to that incorporated into the polymer as illustrated in below. Such a partial optical resolution of monomer antipode

in the polymerization is called asymmetric-selective polymerization or stereo-elective polymerization. The isotactic poly(propylene oxide)s demonstrated a crystallization behavior with a crystalline melting point of ca. 78°C.



II.3.THERMAL DEGRADATION OF POLY(PROPYLENE OXIDE)

II.3.1. Introduction

Degradation of polymers under certain conditions has been a major factor limiting the applications of these remarkably versatile materials. All polymers are subject to eventual degradation under their service environment. Important properties such as mechanical strength and integrity are affected adversely as degradation proceeds although there is considerable variation among specific polymers' resistance to degradation. Thus, diminished properties may result in a failure during an applications[142,143].

In order to prolong the service life or enhance the use temperature stabilization of polymers has been attempted. The most favored method to improve stability has been accomplished by compounding with selected additives such as antioxidants. Another means of enhancing stability has been to alter the structure of the polymer. However, problems arise from the fact that it is extremely difficult to obtain a required level of stability while maintaining every other property within specified limits. Only limited examples of structural modifications may be considered successful, in particular, the elimination of imperfections in molecular structure and incorporation of stabilizer moieties into polymer molecules. Studies of polymer degradation behavior, along with the development of the art of stabilization perhaps originated from the discovery of Hoffman on natural rubber[143]. Many earlier investigators observed inhibition of the degradation process by the addition of phenol or amine additives[144,145]. Over several decades, it was recognized that protection provided by those additives was due to elimination of certain chemical side reactions occurring in the polymer. For instance, the term "antioxidant" was used to describe the class of stabilizers which protects against oxygen

induced degradation. As the science of stabilization developed, several other types of stabilizers appeared, each functioning at a specific stage of the degradation mechanism. Therefore, the stabilization of polymeric materials could be established only after the degradation mechanism was elucidated. In this section, a brief review of the general degradation mechanism of polymers will be discussed.

II.3.2. Influence of Polymer Structure on Thermal Degradation

Degradation of polymers is defined as an irreversible structural change, which eventually leads to a failure in service. The degradation may take place by several different mechanisms, depending on polymer structures and exposure conditions, but in most cases, the degradation occurs through chemical reactions. However, it may result from physical changes by disruption of morphology rather than by reactions on a molecular level. These changes can result in rapid and complete failure and the degradation may be monitored by changes in the mechanical strength, color, dielectric constant and molecular weight loss, etc.[146].

Degradation by oxygen is the most significant, since small amounts of oxygen may be sufficient for oxidation reactions. Pyrolysis, which could be defined as degradation without oxygen is also important. However, these reactions usually take place simultaneously with thermal oxidation. When polymers are exposed to high temperatures, energy is absorbed and distributed through the molecule and eventually the energy is concentrated at one bond, thus exceeding its dissociation energy. Consequently, the bond ruptures and irreversible changes occur. Therefore, degradation is closely related to the dissociation energy of molecular bonds. Some typical bond energies for dissociation reactions are listed in Table(6)[142].

Table 6. Dissociation energy of various chemical bonds [142]

Bond	Dissociation energy Kcal/mol
$\begin{array}{c} \quad \\ -C \text{ --- } C- \\ \quad \end{array}$	83
$\begin{array}{c} \\ -C \text{ --- } H \\ \end{array}$	91
$\begin{array}{c} \\ -CH \text{ --- } H \\ \end{array}$	95
$\begin{array}{c} \\ -CH_2 \text{ --- } H \\ \end{array}$	98
$\begin{array}{c} \\ -CH_2 \text{ --- } O- \\ \end{array}$	106
$\begin{array}{c} \\ -CH_2 \text{ --- } F \\ \end{array}$	93
$\begin{array}{c} \\ -C \text{ --- } N- \\ \end{array}$	82
$\begin{array}{c} \\ -Si \text{ --- } O- \\ \end{array}$	106
$\begin{array}{c} \\ -CH \text{ --- } Cl \\ \end{array}$	78

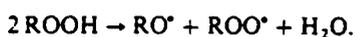
II.3.2.1. Thermal oxidative degradation

Oxygen combined with heat is a major factor in polymer degradation. Even the most inherently stable polymer undergoes thermal oxidation if exposed to sufficiently high temperatures for a long period of time. Therefore, a number of studies have been directed toward thermal oxidation of polymers. Emphasis has been placed on autoxidation, which is a thermal oxidation under mild conditions up to about 200°C. The general kinetic scheme of autoxidative degradation was proposed by Shelton[147] ,as follows.

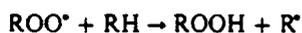
Initiation:



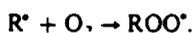
or



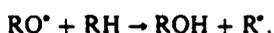
Propagation:



and



Oxidative Chain Branching



Initiation of polymer autoxidation is complicated, but generally, hydroperoxides are a major source of the radicals which initiate oxidation. However, various additives may be involved in the initiation step. Propagation occurs via chain transfer of radicals to a number of other molecules.

The chemical structure of the hydrocarbon polymer plays a significant role in oxidative degradation. This is evident from the fact that polyethylene, branched polyethylene and polypropylene show different degradation rates. In branched polymers, a hydrogen atom attached to a tertiary carbon atom has a lower dissociation energy than that between hydrogens and carbons in the methylene groups along the chain. Therefore,

these labile hydrogens are likely the points for initiation of thermal oxidation. Accordingly, branched polyethylene(PE) is less stable than linear PE. The polypropylene(PP) is even worse than branched PE, since PP has a tertiary carbon atom in every repeating unit[148]. Polystyrene is perhaps an exception. The stability of this polymer results either from steric protection of the labile hydrogen by the bulky aromatic rings or from the loss of resonance energy caused by unfavorable orientation of phenyl groups in the structure(149,150). In addition, morphological factors affect degradation. For example, semicrystalline materials usually show higher resistance to degradation since the oxygen cannot easily penetrate into the crystallites. Polymers whose crystalline structure is relatively permeable to oxygen do not exhibit significant differences in stability at temperatures either above or below the melting point[151].

II.3.3. Stabilization of Polymers

The two approaches to stabilize polymers are to either by modify molecular structure or by compounding with additives. One method or a combination of techniques may be employed, depending upon the mode of degradation. In the case of pyrolysis at elevated temperatures, the initiation rate is so high that additives would be overwhelmed by the large number of macro radicals formed. Hence, small amounts of additives may be less effective in preventing high temperature pyrolytic degradation than for oxidative degradation[142].

Stabilization by structure modification is based upon differences in dissociation energies of the chemical bonds in the polymer structure. Eliminating weak bonds can be expected to increase thermal stability, regardless of the degradation mechanism and has been applied in a number of cases with success. For example, polytetrafluoroethylene is significantly more stable than polyethylene because the C-H

bonds are substituted with much stronger C-F bonds. However, such a modification must be accomplished such that the original polymer maintains specified properties[152]. There are some polymers in which thermal stability has been improved by copolymerization. For instance, the relatively low thermal stability of poly(methyl methacrylate) is improved by random copolymerization with methyl acrylate monomer, which may be due to the fact that the copolymerization reduces the number of thermally unstable tertiary carbons in the polymer chain[153]. Such an approach may subtly modify the nature of the chain structure.

Thermosetting materials generally have excellent heat resistance relative to thermoplastics. Hence, crosslinking may be considered as a special type of structure modification. For example, surface crosslinking of poly(vinyl chloride) by radiation forms a product with outstanding thermal stability. Polymers in crosslinked networks tolerate a number of broken bonds before extensive degradation takes place. For this reason, many specialized polymers for high temperature applications have a highly crosslinked or ladder structure[154].

II.3.3.1. Stabilization against thermal oxidation

Semon[155] showed that phenolic compounds retard the autoxidation of rubber, and Ostwald[156] reported that aromatic amines also inhibit oxidative thermal degradation. The theoretical mechanism of antioxidation, initially referred to as the "negative catalyst theory", was proposed by Moureu and Dufraise[157,158].

In short term stabilization, antioxidants provide protection by migrating freely throughout the polymer mass to reach a number of initiation sites that are generated at elevated temperatures. Thermally sensitive polymers can oxidize to produce hydroperoxides at a significant rate. A variety of antioxidants have been used to inhibit degradation at this critical stage in the life cycle of polymers[159]. Low molecular weight

phenolic derivatives are effective for short term antioxidation behavior[144]. In general, short term antioxidants are not intended to give protection during extended use. For long term protection, different types of stabilizers must be employed, which are usually high molecular weight compounds with limited mobilities. The antioxidants are also classified by their mechanisms of stabilization i.e., preventative antioxidant and chain breaking type. The two different mechanisms of stabilization may be contrasted as follows[142]:

Preventative type : This type of antioxidants cause hydroperoxide to decompose by an alternate mechanism, which does not yield radicals capable of propagating degrading species in the initial stage of degradation.

Chain breaking type : This type of stabilizer are effective during the radical propagation step. They either serve as a trap or react with radicals which propagate oxidation, thus reducing the length of the oxidative chain. The following reaction represents the function of stabilization by labile hydrogen donating species.

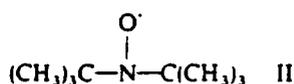
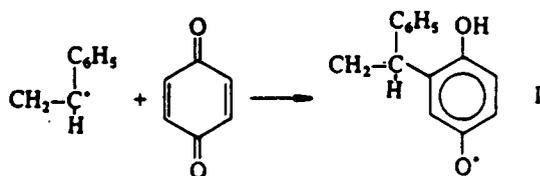


The A· radical is usually an unreactive and will be trapped and deactivated by coupling or disproportionation. There are two types of chain breaking antioxidant functioning by different mechanisms.

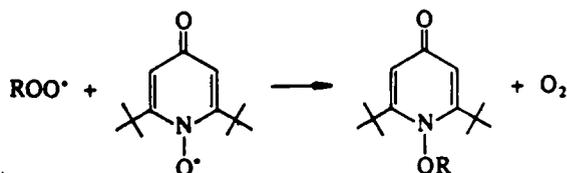
(a) Chain breaking antioxidants

1. Free radical traps

It was found that spontaneous polymerization of styrene is inhibited by the addition of small amounts of quinone compound[160]. This inhibition is attributed to the transfer of radicals to aromatic rings, as shown below.



and 2,2',6,6'-tetramethyl-4-pyridone nitroxide (III).



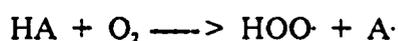
New radicals formed by transfer are relatively stable and hence unlikely to propagate. Free radical traps type stabilizers scavenge or trap the reactive radicals where they convert into stable species, however, these compounds must be unreactive toward the host polymer. There are a few examples of stabilizers in this category, such as di-tert-butyl nitroxide and 2,2',6,6'-tetramethyl 4-pyridone nitroxide[161].

2. Labile hydrogen donors

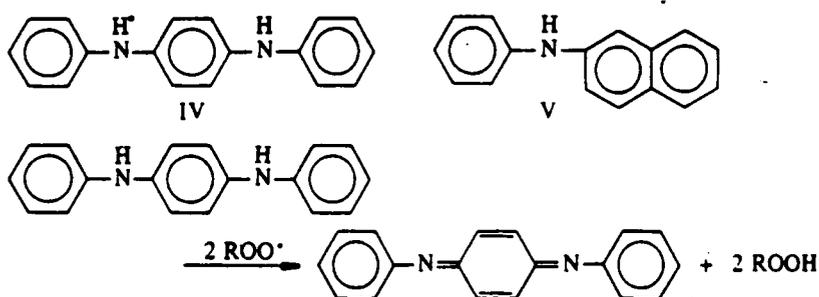
These are the most frequently used stabilizers for protecting polymers from oxidative degradation. This type of antioxidant provides an alternate reaction to the rate controlling step during propagation. The function of the hydrogen donating antioxidant was previously described. The key feature is the ease of hydrogen removal from these species in comparison to the abstraction of hydrogen from the polymer backbone[162]. This competition of hydrogen abstraction was proved by many investigators[163,164] via

isotropic studies. Polymer with C-D bonds, which have lower association energies than the C-H bond were speculated to degrade faster.

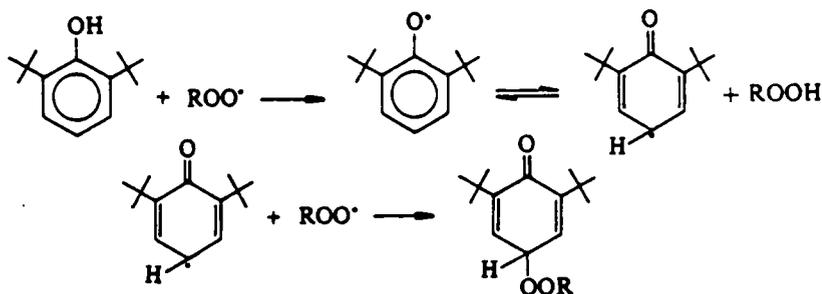
However, the loss of the hydrogen is minimized by direct reaction with oxygen. Shelton and coworkers[165] recognized that direct oxidation yields a radical which is capable of propagation.



Hindered phenols and secondary amines are the most frequently used labile hydrogen donors protecting elastomers and hydrocarbon polymers against thermal oxidation. In case of secondary amine antioxidants, the bond dissociation energy is 93 kcal/mole compared to 95 kcal/mole of C-H bonds of methylene group chains. Thus these compounds are effective in intercepting radicals from propagating species. N,N'-diphenyl-p-phenylene diamine and phenylnaphthyl amine are typical examples[145]. Unfortunately, they are also carcinogenic.



High molecular weight phenolic antioxidants are the favored stabilizers due to long retention times and efficient stabilization behavior. The hindered structure is designed to minimize the direct oxidation of the phenolic hydroxyl group. The following example shows the mechanism involved in the radical scavenging reaction of the antioxidant[165].



(c) Preventative antioxidants

Preventative antioxidants stabilize by retarding the rate of initiation, while chain-breaking antioxidants inhibits degradation at the propagation stage of thermal oxidation. The reaction involved in thermal oxidation with sulfur compounds has been extensively investigated[166-168]. It was found that alkyl sulfides and aryl disulfides are both effective preventative inhibitors for the oxidation of polymers. Hawkins and coworkers[169,170] studied the effect of aryl disulfides on the hydroperoxide decomposition of polyethylene. Concentration of naphthyl disulfide was varied from 0.1 to 0.3%. At 0.3% concentration, the inhibited polymer oxidized slowly with no indication of an autocatalytic reaction. The naphthyl disulfides reacts with hydroperoxide formed in the polymer yielding a corresponding thiosulfinate.



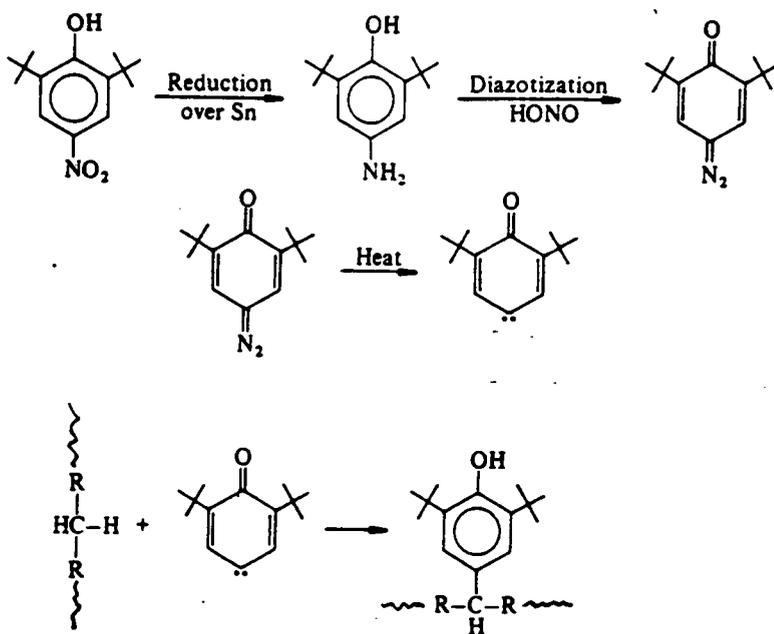
(d) Combination

Combination of different types of antioxidants may provide a very efficient protection against thermal oxidation. However, the result may be drastically varied for different cases. Simple additive effects are observed when two or more antioxidants of the

chain breaking type are used in combination. Components of such a combination are selected for their efficiency over the service temperature range.

Sometimes, antagonistic effects are expected if interactions occur which destroy the effectiveness of either component. Hawkins[171] observed that antagonism takes place when carbon black is used in combination with secondary amines or certain hindered phenols. Adsorption of amine or phenols onto the carbon surface may reduce the efficiency of the antioxidant activity of either compound. When the combination of antioxidants provides more protection than would be expected from the sum of that provided by the individual components, the phenomenon is referred to as synergism. Synergism has been observed with combinations of two hindered phenols, acting as chain breaking antioxidants. The more effective phenol is the primary deactivator of propagating radicals, while the less active phenol functions as a reservoir for hydrogen to regenerate the primary antioxidant.

Retention of antioxidants is essential when polymers need to be exposed to oxidative degradation for long periods. Even the high molecular weight antioxidants migrate to the surface due to high vapor pressure sufficient to cause evaporation. Antioxidants will not migrate if they exist as a part of polymer, i.e., if they are chemically bound to the polymer chain. Thus, the loss of antioxidant may be prevented. Kaplan and coworkers[172] have bound various phenols to polyethylene and poly(oxyethylene) by the following sequence of reactions.



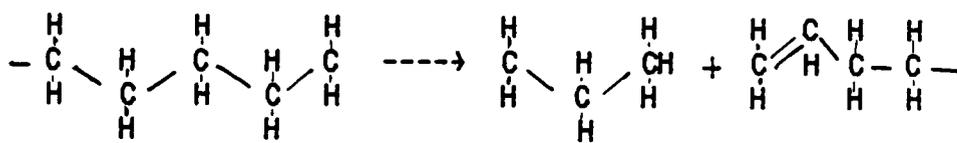
Bonding of the stabilizer moiety to the polymer could occur in several ways. One possibility is that diazooxide could decompose thermally into a carbene carbon which could be then inserted into C-H bond in the polymer.

An investigation of thermal stability of poly(ethylene oxide) and poly(propylene oxide) was undertaken by Madorsky and Straus[173] to compare these polymers with polyethylene and polypropylene. The pyrolysis of both polyethers was conducted in a vacuum chamber so that oxidative thermal degradation was eliminated. The volatile fraction due to pyrolysis was collected by a dry ice-acetone cold trap and analyzed by mass-spectrometer. The volatile fraction thus collected was ca. 12.8 and 20.0 wt% for atactic and isotactic polymers, respectively. The conclusion was that the isotactic polymer was more stable than the atactic analogue. The mass spectrometer results indicated that the most abundant yield was not the monomer, propylene oxide, but acetaldehyde, propene and acetone. However, acetone is isomeric with propylene oxide. The average molecular weight of the pyrolyzed product of isotactic poly(propylene oxide) determined by freezing point lowering of benzene was 606 ± 20 g/mole.

In comparison with polypropylene, poly(propylene oxide) showed lower thermal stability, which was attributed to the presence of the C-O bonds. Crystalline isotactic poly(propylene oxide) was more stable than the amorphous version. The yield of monomer fragments was larger than that of polypropylene, indicating that pyrolysis of poly(propylene oxide) may take place by both random scission as well as by depolymerization. On the other hand, the major mechanism of pyrolysis of polypropylene is regarded as random scission by intramolecular transfer of hydrogen. Scission results in one end becoming saturated and the other unsaturated. In scission where an intramolecular transfer of hydrogen does not take place, the end becomes a free radical which can produce monomer or monomer sized fragments by an unzipping reaction. Figure(6) illustrates two types of scission reactions. whether a Type I or Type II scission depends upon the supply of hydrogen in the immediate vicinity of the scission. Only Type I scission take place in polyethylene, whereas, in PMMA, only Type II scission may occur. In the case of poly(ethylene oxide) or poly(propylene oxide), in which the supply of hydrogen on the backbone of the chain in the neighborhood of the scission is somewhat limited, both types of scission can be expected to occur.

The kinetics of volatilization in thermal degradation of poly(propylene oxide) under nitrogen atmosphere were investigated by Van and coworkers[174]. Both thermogravimetry(TGA) and differential scanning calorimetry(DSC) were employed in the study. The thermal degradation behavior of poly(propylene oxide) yielded zeroth order kinetics, while the data obtained from thermogravimetric analysis fitted first order kinetics. According to the DSC study, the activation energy of thermal degradation under a nitrogen atmosphere increased with the molecular weight of polymer as given in Table(7). However, dynamic thermograms showed insignificant differences in the thermal degradation temperature among different molecular weights of polymer.

Type I



Type II

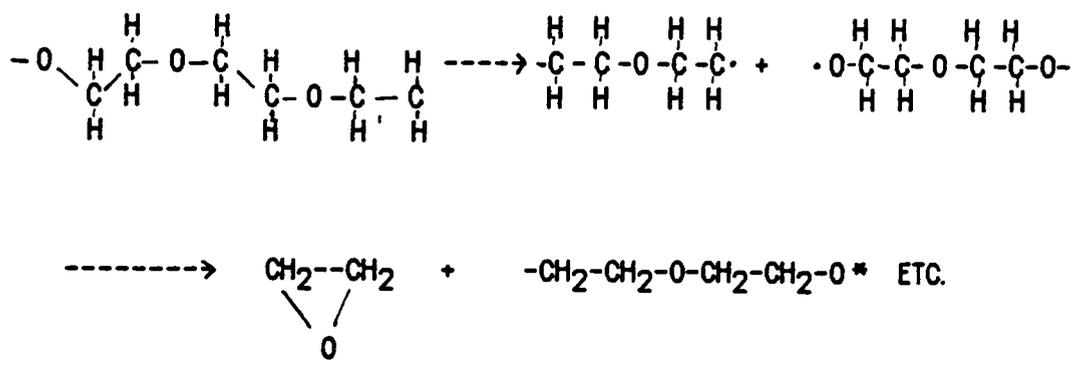


Figure 6. Thermal degradation mechanisms of poly(ethylene oxide) and polyethylene [173]

Table 7. Influence of molecular weight on overall energy of activation and on heat of decomposition [174]

Mol wt	E , kcal/g-mole	ΔH , kcal/g-mole
4025	9.8 ± 0.6	4140
2025	8.6 ± 0.8	2400
1025	7.9 ± 0.6	1040
425	6.7 ± 1.0	300

The kinetics of thermal degradation of high molecular weight poly(propylene oxide) were studied under vacuum by TGA. The result was reported by Madorsky and Strauss[173]. The activation energy was estimated to be 20 kcal/mole for high molecular weight polymers(PPO, $[M_n]=215,000$ and $16,000$ g/mole) respectively.

The kinetics of thermal degradation of poly(oxypropylene) glycol(POPG) under an oxidative environment was reported by Kilic and McGrath[175]. Both isothermal and dynamic thermograms were obtained by TGA and analyzed by Arrhenius type relations. Volatilization from 10 to 90 wt% was considered in calculating the activation energy of degradation of 17.8 kcal/mole. The degradation of POPG was again found to be zeroth order. The activation energy of POPG under dynamic heating conditions was calculated as ca. 24.0 kcal/mole by method of Reich and Ozawa[176] and 28.5 kcal/mole by using that of Coats and Redfern[177]. The governing equations for the calculation of activation energies are summarized in Table(8).

Table 8. List of some differential and integral methods [175-177]

Method	Basic Equations
Friedman	$\ln B(d\alpha/dt) = \ln A + \ln f(\alpha) - E/RT$ $f(\alpha) = (1-\alpha)^n$
Coats and Redfern	$\log(\alpha/T^2) = \log(A.R/B.E)(1-2RT/E) - E/2.3RT$ <p>$n = 0$ is assumed</p>
Reich	$E = \frac{4.6 \log(B_2/B_1)(T_1/T_2)^2}{(1/T_1 - 1/T_2)}$
Ozawa	$E = \frac{R \log(B_2/B_1)}{0.457 (1/T_1 - 1/T_2)}$

II.4. POLYMER HYBRIDS

Sophisticated applications of polymers are being developed that demand combinations of properties not attainable with simple homopolymers. As a result of this need, techniques for producing polymer "hybrids" have arisen. In general, there are two approaches to forming polymer hybrids. One is that of physical blending two polymers, and the other is via chemical bonding i.e., formation of copolymers. The latter includes block, graft, statistical copolymers and crosslinked systems[178-180]. These polymer hybrids not only combine the properties of their components but also display unique and interesting behavior. This section will briefly discuss typical copolymer hybrid systems.

II.4.1. Block Copolymers

Block copolymers are comprised of chemically dissimilar, terminally connected segments. Their sequential arrangement may vary from A-B structures containing only two segments to A-B-A block copolymers with three segments, to multiblock systems, (A-B)_n, possessing many segments[178].

The multiblock copolymers include segmented copolymers such as the polyurethanes, which are composed of "soft" polyether or polyester segments and hard polyurethane sequences. These systems behaved as a "virtually crosslinked" rubber, although they were soluble in organic solvents[178,181]. The development of well controlled living anionic polymerization techniques enabled the synthesis of architecturally well-defined block copolymers[182].

II.4.1.1. Architecture

The three basic architectural forms of block copolymers are shown schematically in Figure(7). The simplest arrangement is referred to as a diblock(A-B) copolymer, whereas the second form is the triblock copolymer. The important difference between a triblock and a diblock structure in determining polymer properties was recognized from the discovery by Milkovich. Triblock structures with soft segments in the middle behave as virtually crosslinked system, while diblock copolymers do not[184].

The third basic type is the (A-B)_n multiblock copolymer, which contains many alternating A and B blocks. Another variation is the radial or star-block copolymer. The structure takes the form of a star shaped macromolecule where three or more diblock sequences radiate from a central hub.

II.4.1.2. Properties of block copolymers

Architecture exerts a major influence on some of the properties of block copolymers, while other properties are independent of sequential arrangement. The architecture-dependent properties include thermoplastic elastomeric behavior, melt rheology and toughness, etc. The development of thermoplastic elastomers has been derived from the unique elastomeric behavior of A-B-A and (A-B)_n block copolymers. Such systems are composed of a two-phase physical network (i.e., a minor fraction of a hard block combined with a major fraction of a soft block), where the hard blocks associate to form small morphological domains that serve as physical cross-linking and reinforcement sites. Moreover, the sites are thermally reversible so that one may possibly process the material in the melt state at temperatures above the glass transition temperature or melting point of hard block.

The modulus temperature behavior of block copolymers is basically different from that of random copolymers. The difference in modulus-temperature behavior between

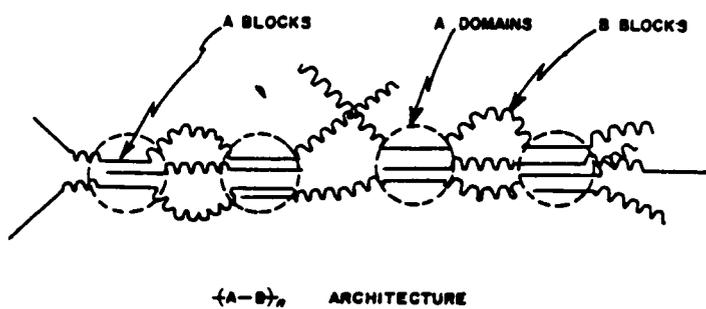
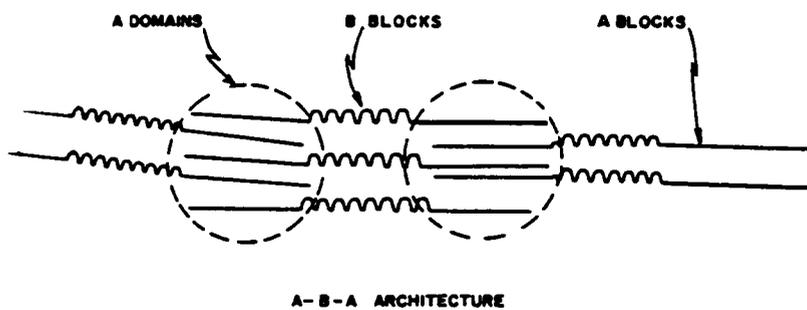
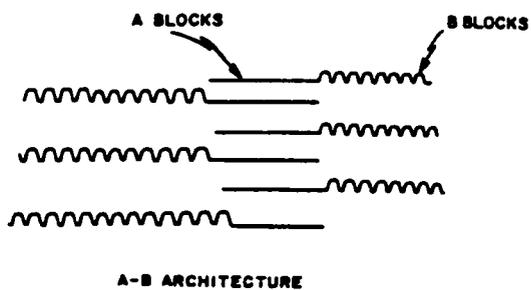


Figure 7. Schematic representation of block copolymer architectures [178]

homogeneous and microphase separated system is schematically illustrated in Figure(8). One should note the presence of the modulus plateau between the T_g 's of the components in the latter case. The level of the plateau modulus is determined by the composition of the copolymer, while its slope is governed by the degree of phase separation. The ability to undergo phase separation is dependent on both molecular weight and chemical structure of the block components. In amorphous block copolymers, phase separation is dependent on segment molecular weight and the differential solubility parameters[185].

Block copolymers that contain crystalline segments display phase separation at relatively short crystalline block lengths. This is due to the fact that crystallization requires phase separation and crystallization can occur at shorter block lengths than would be necessary to obtain two phases in a totally amorphous system. Block copolymerization of difunctional soft and hard segment homopolymers defines the thermoplastic nature. Moreover, rigid block copolymers composed of two hard segments may offer great advantages in mechanical properties such as creep or stress relaxation resistance. The toughness of an inherently brittle rigid polymer can be greatly improved via block copolymerization with a minor fraction of a soft segment. Two phase block copolymers may have the unique ability to show partial compatibility with their corresponding homopolymers. This phenomenon allows homopolymer block copolymer blends to be prepared that display a high degree of mechanical compatibility as a result of good interphase adhesion and phase separation. Perfect mutual solubility is not possible in such blends due to the dissimilar nature of the second segment of the block copolymer.

II.4.1.3. Synthesis of copolymers

A variety of approaches have been reported to synthesize block copolymers[186-189]. Among those techniques, there are some that give rise to predict-

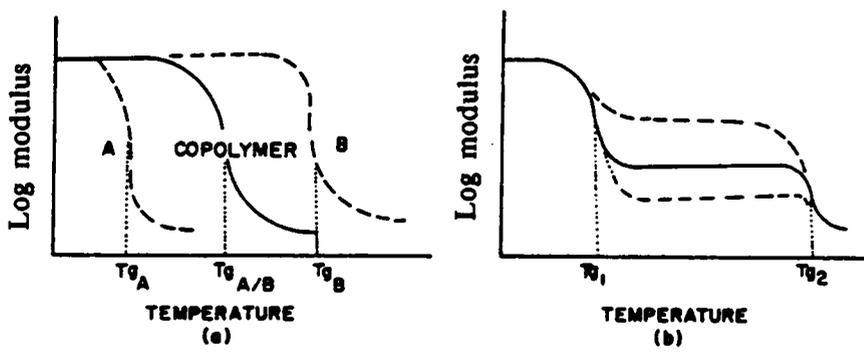


Figure 8. Thermomechanical behavior of copolymers: Log modulus-temperature behavior of a typical amorphous random copolymer(a), Two phase block copolymers(b)

able structures with a high degree of block integrity. Examples include living addition polymerization or step growth polymerization.

Living polymerization with sequential addition process can be utilized to synthesize a wide spectrum of systems. Since living polymerizations are devoid of terminating reactions, structural control is a valuable asset in the preparation of block copolymers. Both olefin and ring opening polymerization can be carried out via living polymerization. One of the best examples of a well-defined block copolymer synthesized by anionic living techniques is the alkyl lithium-initiated polymerization of styrene followed by the sequential addition of butadiene[190]. The polymerization of olefins such as ethylene and propylene initiated by Ziegler-Natta transition metal catalysts is considered to proceed via a coordination but not necessarily living polymerization mechanism. Many catalyst systems have been reported to produce block copolymers by sequential addition of two monomers[191], but the claim is controversial.

The interaction of functionally terminated oligomers may be an alternative way to generate block copolymers, since the intersegment linkage may be formed during the copolymerization. Generally, difunctional oligomers may lead to an (A-B)_n block copolymer structure. The end groups of the polymers are derived from the end group of the monomer used in excess during the step growth polymerization. However, in the case of ring opening or addition polymerization, the end group can be predetermined via initiator or by end capping[179]. Another approach is via polymer growth from oligomer end groups[192]. This technique essentially combines the features of the first two methods. All three block copolymers architectural types can be synthesized by this oligomer/monomer approach: the architecture is dependent upon monomer type and oligomer functionality. The reaction of addition or ring opening monomers with mono- or difunctional oligomer generates A-B and A-B-A structures, respectively.

II.4.1.4. Poly(alkylene oxide) containing block copolymers

A typical example of this kind is the block copolymer of poly(propylene oxide) and poly(ethylene oxide). Since poly(propylene oxide) is relatively hydrophobic while poly(ethylene oxide) is hydrophilic, these block copolymers have useful non-ionic surfactant properties. They are normally synthesized by the sodium alkoxide initiated polymerization of sequentially added propylene oxide and ethylene oxide at 140°C [193]. These low molecular weight (< 3000 g/mole) liquid block copolymers are used as non-ionic detergents and dispersing agents.

A poly(acetaldehyde)-poly(propylene oxide) block copolymer has been prepared by means of a triethyl aluminum-water co-catalyst system [194]. Propylene oxide was first polymerized at room temperature, after which the temperature was reduced to -78 °C to inhibit further polymerization of unreacted propylene oxide. Acetaldehyde was then added and polymerized for a period of 45 hours. The block structure of this copolymer was only rather indirectly determined on the basis of the copolymer solubility and hydrolysis behavior.

Block copolymers of poly(ethylene oxide) and polystyrene typically occurs by a two-step process[195]. In the first step, styrene is polymerized by a butyl-lithium initiator at 0-80°C for an hour. Then, ethylene oxide is added to the living polystyrene at -80°C to convert the carbanions to alkoxide end groups. The relatively slow process of ethylene oxide polymerization is continued for 1-2 days at 25°C-75°C. The properties of ethylene oxide-styrene block copolymers are very interesting because they contain a crystalline block, poly(ethylene oxide), and an amorphous block, polystyrene. Differential scanning calorimetry indicated a crystalline melting point of 53-56°C due to the poly(ethylene oxide) segment and a glass transition temperature(T_g) of 96-98°C for the polystyrene blocks[196].

Block copolymers of ethylene oxide and ethylene were reportedly prepared from hydroxyl-terminated polyethylene telomers made by peroxide initiation of ethylene in the presence of oxygen- containing telogens. They were converted to the sodium alkoxide form and used to initiate the polymerization of ethylene oxide[197]. The products were utilized in aqueous emulsion coating applications. The efficiency of this process was probably quite low.

II.4.1.5. Poly(caprolactone) containing block copolymers.

(a) Polymerization of caprolactone

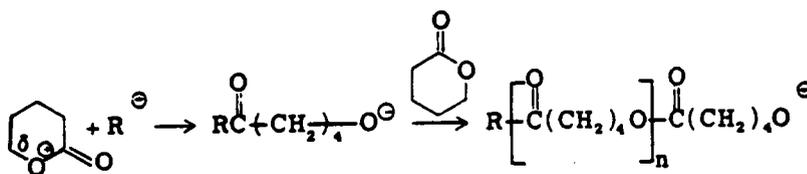
Most lactone monomers can be polymerized by one of three types of systems given in Table(9). In general, uncatalyzed lactone polymerization with conventional active hydrogen initiators such as alcohols, amines, and carboxylic acids are relatively slow, hence the cases are restricted to the synthesis of low molecular weight polyesters and even these are usually catalyzed by tin compounds[198]. High molecular weight polyesters may be synthesized by using anionic or cationic catalysts, or initiators, which belong to Type 2 as specified in Table(9). A typical example of this system is the dibutyl-zinc initiated polymerization of ϵ -caprolactone, wherein the polymer molecular weight was found to be inversely proportional to the dibutyl zinc concentration[199]. Organometallic catalysts such as stannous octanoate have been able to polymerize ϵ -caprolactone in the apparent absence of hydrogen initiators. However, one needs to be certain that water is completely absent before making this conclusion.

Molecular weight and end group control can be obtained by the use of an active hydrogen initiator in conjunction with a catalyst.(Type 3, Table(9)). Polyols, polyamines, carboxylic acids, etc., have been used with catalysts such as stannous esters[200] and stannic esters[201] to control molecular weight and the polymer end groups. The anionic

Table 9. Types of caprolactone polymerization [198]

Type	System	Examples
1	Active hydrogen initiator, no catalyst	ROH, RNH ₂ , etc.
2	Nonactive hydrogen initiator, or catalyst only	R ₂ Zn, Sn(OR) _{2, 4} , etc.
3	Active hydrogen initiator plus catalyst	ROH + Ti(OR) ₄ , etc.

polymerization of lactone involves acyl-oxygen fission with propagation through an alkoxide anion[202], as described in this equation:



(b) Properties and application of polycaprolactone

Polycaprolactone is a partially crystalline polymer and has been reported to have a crystalline structure similar to that of polyethylene, with the a and b dimensions of the unit cell of two polymers being almost identical. In addition, Bittager and coworkers[203] found that it has an extended planar zigzag chain conformation with a orthorhombic unit cell. Polycaprolactone has a greater degree of rotational freedom than polyethylene, which leads to a significantly higher entropy of fusion and therefore a relatively low melting point. Polycaprolactone crystallizes very readily and can not be quenched to a glass[204]. In general, high molecular weight polycaprolactone may be classified as a ductile crystalline polymer of moderate melting point.

Polycaprolactone is blendable with a variety of other polymers over wide composition ranges. The materials that results after blending often demonstrate very useful properties. There are three types of blending mechanisms which may be observed when the polycaprolactone is added to another polymer: blending by crystalline interaction, true miscibility and "mechanically" compatible blending[205-210].

A crystalline interaction was reported to exist when polycaprolactone was blended with a polyolefins such as polyethylene. The blend of the two polymers only affects the alpha transition of polyethylene, which is related to the vibrational or reorientational motion in the crystals of the polymer[211].

It is difficult to obtain true compatibility in the blending of two polymers. The change in Gibb's free energy should be negative to favor the mixing. However, mixing is usually an endothermic process and the enthalpic change is usually positive. The entropy change is again positive but rather small due to the small number of molecules involved. Surprisingly, polycaprolactone is miscible with a number of different polymers[205]. For example, amorphous polycaprolactone has been found to be miscible with poly(vinyl chloride). These blends have glass transition temperatures that extrapolate to value of -71°C for the glass transition temperature of amorphous polycaprolactone[207,208] and hence, the polycaprolactone in the blend acts as a polymeric plasticizer. As the polycaprolactone content in the blend is increased, the modulus decreases and elongation increases. With time, the polyester actually partially crystallizes from the blend.

(c) Block copolymers of polycaprolactone

Block copolymers of caprolactone and another composition such as a polyether, or vinyl polymer have been prepared. The preparation of a polycaprolactone-b-poly(propylene oxide) and polycaprolactone-b-poly(ethylene oxide) block copolymers have been reported[212]. Propylene oxide was polymerized in the presence of dibutyl zinc, after which caprolactone was added and the reaction continued at the same temperature. Some block copolymers containing a segment of caprolactone and a segment of polybutadiene, polyisoprene, poly(methyl methacrylate), or polystyrene are synthesized by initiating polymerization of the lactone with the living anionically polymerized vinyl polymer, then followed by initiation of the lactone polymerization[213]. Characterization of these materials was unfortunately quite limited.

CHAPTER III. EXPERIMENTAL

III.1. GENERAL CONSIDERATION

Coordinate anionic polymerization of cyclic ethers is characterized by two sequential steps. Firstly, monomer coordinates on the metallic catalyst site and forms a complex which is then attacked by the growing anionic species. This feature allows the initiation and propagation of polymerization at moderate reaction conditions. Since the propagation proceeds through the insertion of monomer into an alkoxide associated with catalyst site, the control of active hydrogen impurities is the most crucial aspect in the synthesis. The primary goal of this study is concerned with the synthesis of molecularly designed polymeric materials such that any side reaction caused by unknown impurities is largely avoided. Impurities may be responsible for premature termination and chain transfer and hence a low yield of polymer. Therefore, the importance of monomer and solvent purity can never be overemphasized in ionic or coordination polymerizations.

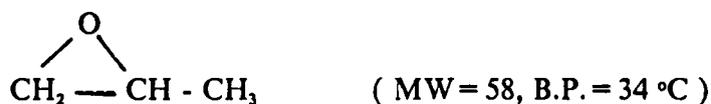
This chapter of the dissertation is composed of three sections. In the first part, purification of chemical reagents employed in the study has been discussed and is followed

by the detailed description of experimental procedures for polymer synthesis and subsequent post reactions. Finally, the techniques used for characterization of each polymeric species are presented along with instrumentation and sample preparations.

III.2. PURIFICATION

III.2.1. Monomers and Catalyst

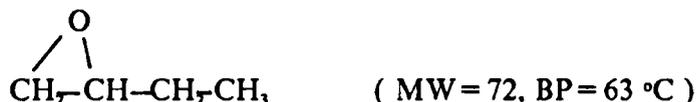
III.2.1.1. Propylene oxide (PO)



Propylene oxide was obtained from Aldrich Chemical, Dow Chemical or Arco Chemical Company and was purified by fractional distillation from calcium hydride. Typically, 500 ml of propylene oxide was charged into a 1000 ml round bottom flask. Then, 2-3 grams of ground calcium hydride powder was added and capped with a drying tube. The mixture was stirred at least 3 days at room temperature. The flask was connected to a fractional distillation unit and PO was distilled under nitrogen atmosphere. Mild heating was provided by a heating mantle and the middle fraction (ca. 300 ml) was collected. To the middle fraction collected by this first distillation, added 1-2 ml of triethyl aluminum in hexane solution (1 mole/liter) and stirred 24 hours to remove residual moisture in the monomer. The solution was again fractionally distilled under dry nitrogen atmosphere and the middle fraction was collected. Moisture content of the

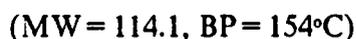
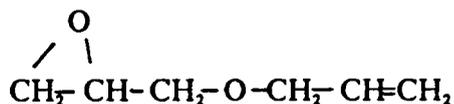
distillate was analyzed by using a Karl-Fisher water titrator. If the water content was below 50ppm, it was used for polymerization.

III.2.1.2. Butylene oxide (BO)



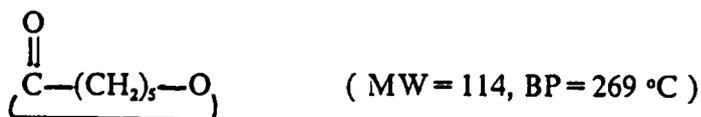
Butylene oxide was obtained from Dow Chemical. Once received, it was kept over 3A molecular sieve until purified. Butylene oxide was purified by the same procedure as propylene oxide.

III.2.1.3. Allyl glycidyl ether(AGE)



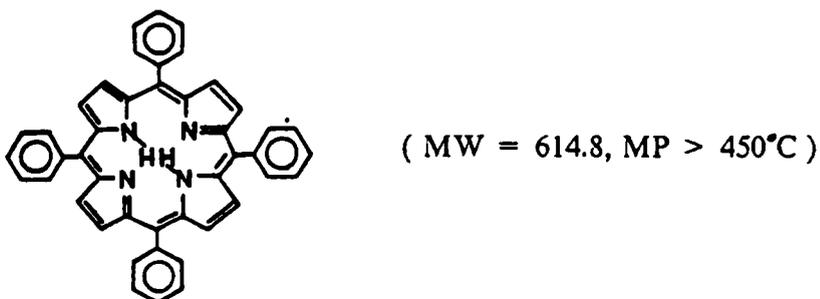
Allyl glycidyl ether(AGE) was obtained from Aldrich Chemical Company and purified by vacuum distillation. The AGE was charged into a round bottom flask and stirred over calcium hydride at least 24 hours with mild heating by either a heating mantle or an oil bath, then vacuum distilled from calcium hydride by collecting the middle fraction boiled over a 3°C range.

III.2.1.4. Epsilon - caprolactone



Epsilon-caprolactone was provided by Union Carbide Corporation or Aldrich Chemical Company. The purification was achieved by vacuum distillation from calcium hydride. Typically, 300ml of Epsilon-caprolactone was charged into a 500ml round bottom flask containing 1-2g of calcium hydride. The mixture was stirred at least for 24 hours, followed by vacuum distillation. Water content was measured with a Karl-Fischer water titrator and usually found to be less than 30 ppm. The distillate was stored in a round bottom flask containing 3Å molecular sieves and subsequently was purged with dry nitrogen.

III.2.1.5. Tetraphenyl porphyrin (TPPH₂).



Tetraphenyl porphyrin was purchased from Aldrich Chemical Company. The raw material contains 1-3 wt% of impurities, which were substantially eliminated by recrystallization from co-solvent of HPLC grade chloroform and methanol. After a homogeneous solution was obtained by refluxing the chloroform, 20 ml of methanol was

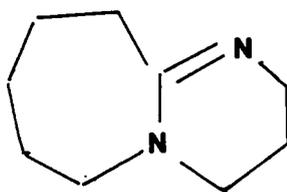
gradually added to the solution. The mixture was cooled slowly to room temperature, then kept in a refrigerator. After 3-4 days, shiny purple crystals were obtained on the bottom of the container, which were then recovered by filtration with a yield of 70-80%. The purple crystals were analyzed by HPLC and $^1\text{H-NMR}$ to insure the purity of the material.

III.2.1.6. Triethyl aluminum and diethyl aluminum chloride.



Triethyl aluminum and diethyl aluminum chloride were provided by Ethyl Corporation. Triethyl aluminum was supplied in a solution of hexane(1 mole/liter) and diethyl aluminum chloride was in heptane(0.82 Mole/liter). These compounds were used without further purification.

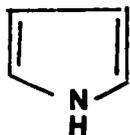
III.2.1.7. Diazobicyclo-un-decene(DBU).



(MW = 152.24, BP = 80-83°C/0.6 mmHg)

Diazobicyclo-un-decene was supplied by Aldrich Chemical Company. This catalyst was used for the modification of hydroxyl terminal end group to amine or caboxylic acid without further purification.

III.2.1.8. Imidazole.



(MW = 68.1, MP = 89-91°C)

Imidazole was obtained from Aldrich Chemical Company and purified by recrystallization from ethanol. The white crystal was isolated and dried at 40°C under vacuum. This compound was used for the same purpose as DBU.

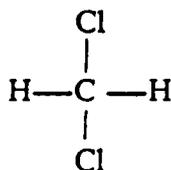
III.2.1.9. Stannous octanoate.



Stannous octanoate was provided by Pfaltz & Bauer Incorporated. This catalyst was used in the polymerization of caprolactone in the presence of hydroxyl end group as received.

III.2.2. Solvents

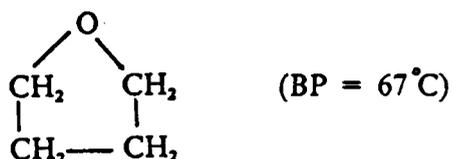
III.2.2.1. Dichloromethane



(BP = 39 °C sp.gr. = 1.32)

The reagent grade dichloromethane was obtained from Fischer Scientific Company. The purification was accomplished by fractional distillation from calcium hydride. About 500 ml of the solvent was charged into 1000 ml round bottom flask with 2-3 g of calcium hydride powder. The mixture was stirred for a minimum of 72 hours and fractionally distilled under nitrogen atmosphere. The middle fraction was collected and stored under slight positive pressurized of nitrogen. Typically, the purified solvent contains 30-40 ppm of water content.

III.2.2.2. Tetrahydrofuran(THF)



Tetrahydrofuran was obtained from Fisher Scientific Company. This was purified by fractional distillation either from calcium hydride or phosphorus pentoxide(P_2O_5). The slurry mixture was stirred about 2-3 days and refluxed 30 minutes before distillation. After refluxing, the solvent was fractionally distilled.

III.2.2.3. Toluene



Toluene was supplied by Fischer Scientific Chemical Company. Typically, 500 ml of toluene was stirred over 2-3 g of calcium hydride with a minimum of 48 hours of

stirring, the solvent was refluxed and vacuum distilled with collection of the middle fraction. The solvent was purified right before use.

III.2.2.4. Ethyl alcohol.



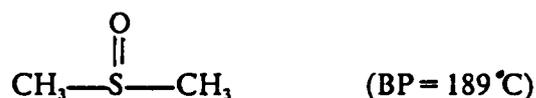
Anhydrous ethyl alcohol was obtained from Pharmco Incorporation. The compound typically contains 0.2 wt% of moisture. Most of the moisture was eliminated by stirring over calcium hydride for 72 hours. Then the ethanol was fractionally distilled and first half portion was collected.

III.2.2.5. Dimethyl formamide (DMF).



The DMF(Fischer Certified grade) was stirred over calcium hydride for a minimum of 24 hours to remove any dissolved water. The DMF was then vacuum distilled from the calcium hydride with collection of the middle fraction.

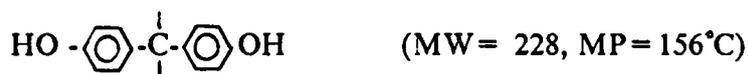
III.2.2.6. Dimethyl sulfoxide (DMSO)



Fisher certified grade DMSO was dried and distilled as per DMF.

III.2.3. Initiators and Other Reagents

III.2.3.1. Bisphenol A (2,2 Bis (4-hydroxy phenol) propane).



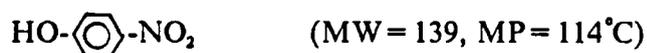
Reagent grade bisphenol A was supplied by Dow Chemical Company. Typically, 25 % by weight of bis.A was dissolved in toluene. The mixture was stirred while heating until complete dissolution occurred. Approximately, 1 g of activated charcoal was added per 500 ml of this solution to eliminate conjugated impurities. The solution was further diluted to 20 wt% by additional toluene and treated with Celite(R). The clear colorless bis.A solution thus obtained was cooled to room temperature. White crystalline bis.A was formed and isolated by suction filtration. Yield was ca. 75-80 %.

III.2.3.2. Hydroquinone



Hydroquinone was obtained from Tennessee Eastman Company and purified by recrystallization from acetone. Oxygen free acetone was prepared by boiling and bubbling argon through the solvent. Generally 15 g of hydroquinone was dissolved in 100 ml of hot acetone, which was then filtered through a fluted filter paper. By boiling and bubbling the filtrate, the volume of solution was reduced to half and allowed to cool to room temperature with stirring. Hydroquinone was recrystallized from the acetone solution in a few days when kept in refrigerator. The white crystals were isolated by suction filtration. Purified hydroquinone was stored in a nitrogen purged desiccator.

III.2.3.3. p-Nitrophenol



The p-nitrophenol obtained from Aldrich Chemical Company was purified by recrystallization from ethanol. The slightly yellowish crystalline material was isolated from the solution.

III.2.3.4. Benzyl alcohol



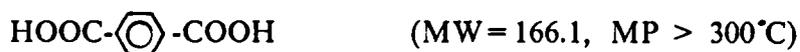
Benzyl alcohol(Fisher Scientific) was purified by very careful fractional distillation at reduced pressure with collection of middle fraction.

III.2.3.5. Terethaloyl chloride (TC)



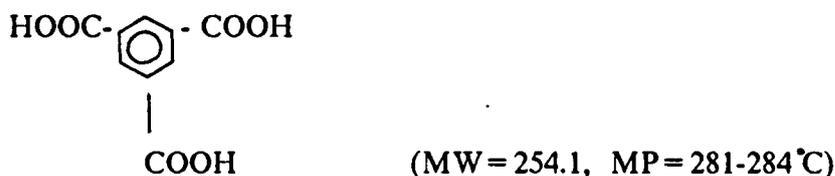
Reagent grade terethaloyl chloride(Aldrich Chemical) was once again purified by recrystallization from hexanes. Typically, 150 grams of TC was dissolved in 1000 ml of hot hexanes. The solution was hazy white due to hydrolyzed acidic impurities. The solution was filtered through filter paper and a clear, colorless filtrate was obtained. The volume of solution was reduced to 600- 650 ml by distilling off the excess hexanes, cooled to room temperature slowly and kept in the refrigerator. Finally, white crystals were isolated from the solvent and dried in the vacuum oven without heating for a minimum of 24 hours.

III.2.3.5. Terephthalic acid



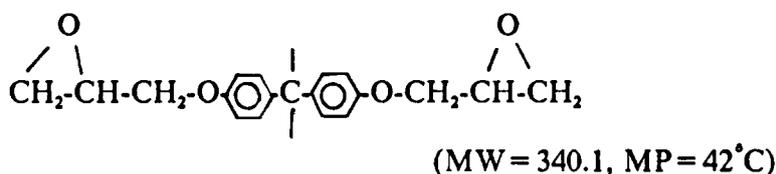
Terephthalic acid(Aldrich Chemical Company) was neutralized by aqueous sodium hydroxide and dissolved in distilled water. The solution was filtered in order to remove any insoluble residue. The filtrate was acidified with HCl to regenerate the terephthalic acid. The white crystals were precipitated from the aqueous solution and isolated by suction filtration. The crystals were washed with water to remove any residual acid and salt. The product was kept under vacuum at 90°C for at least 24 hours before use.

III.2.3.6. 1,3,5-Benzene tricarboxylic acid



The purification of benzene tricarboxylic acid(Aldrich Chemical Company) was identical to the process of terephthalic acid.

III.2.3.7. Diglycidyl Ether of BIS A (DGEBA)



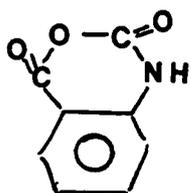
Crude DGEBA supplied by Dow Chemical Company under the trade name of DER 332 was dissolved in co-solvent of methyl isobutyl ketone and 2-ethoxyethyl ether (60:40 by volume). The solution was filtered to remove insoluble impurities and stored in a refrigerator for 3 days. The white crystals obtained were recovered by suction filtration. The high boiling solvent(MIBK) was washed out with hexanes. The DGEBA was dried under vacuum with no heat until it was used.

III.2.3.8. Diphenyl methane diisocyanate (MDI)



The MDI was obtained from Tokyo Kasei Chemical Company. Purification of MDI was accomplished by vacuum distillation with collection of the middle fraction. Liquid MDI was distilled at 135- 140°C under high vacuum. The distillation unit was wrapped with a heating tape to prevent premature solidification. White crystals were obtained after cooling and stored in the refrigerator.

III.1.3.9. Isatoic anhydride



(MW = 163.1 MP = 233°C)

Isatoic anhydride(Tennessee Eastman Co.) was purified by recrystallization from tetrahydrofuran(THF). Typically, 50 g of raw material was dissolved in 1 liter of boiling THF and the solution was allowed to cool down to room temperature slowly. After 5 days in a refrigerator, a white crystalline material was isolated and washed with THF.

Phthalic anhydride was purified by recrystallization from chloroform. The purification of other chemicals generally followed standard procedures described in the literature[214].

III.3. SYNTHESIS OF MOLECULARLY DESIGNED POLY(PROPYLENE OXIDE)

III.3.1. Synthesis of Aluminum Porphyrin Catalysts

Aluminum porphyrin(TPPAlCl, TPPAlEt) catalyst was synthesized by aluminum chloride or triethyl aluminum in a round bottom flask equipped with a magnetic stirrer and a three way stop cock. A sketch of the experimental apparatus is shown in Figure(9). The materials needed for the synthesis of PPO([Mn]= 10,000 g/mole) are as follows;

Tetraphenyl porphyrin (TPPH₂) : 1.57 g (5 mmole)

Triethyl aluminum(1 mole/l in hexane) : 2.5 ml (5 mmole) or

Diethyl aluminum Chloride(0.82 mole/l in heptane) : 3.05 ml (5 mmole)

Methylene chloride : 50 ml

Propylene oxide : 30 ml

Typically, the TPPH₂ was charged into a 250 ml round bottom flask which was capped with a three-way stopcock and purged with dry nitrogen. In order to eliminate moisture in the container, vacuum was applied to the flask followed by a nitrogen purge. This procedure was repeated 5-6 times by manipulating a three way stopcock valve. The solvent was then added through a transfer needle to dissolve TPPH₂. Upon obtaining a

homogeneous mixture by agitation, diethyl aluminum chloride was added to this solution by hypodermic syringe. The pressure build-up due to generated ethane was periodically released through an escape needle. As the reaction proceeded, the dark purple color of the solution gradually changed to reddish purple. The reaction was allowed to proceed for 5-6 hours in order to obtain a quantitative conversion[119].

III.3.2. Monofunctional Hydroxyl Terminated Polymer

III.3.2.1. Bulk polymerization.

After the catalyst has been synthesized and all the volatile materials were removed by reduced pressure (for a bulk polymerization), the reactor was flushed with dry nitrogen, followed by addition of propylene oxide. Care must be taken in the initial stage of polymerization. Because of vigorous exothermic initiation, considerable heat was generated, which is enough to cause boiling of the monomer. Therefore, the reactor was normally kept in ice-water bath for a minimum of 15 minutes after the monomer is added. In the case of solution polymerization, the heat of reaction was dissipated via the solvent so that the extreme caution taken in bulk process was not necessary. Usually propylene oxide was directly added to the reactor via either hypodermic syringe or transfer needle. Alternatively, pressure reactors sketched in Figures(10) and (11) were used for the polymerization at the elevated temperature, above the boiling point of propylene oxide.

III.3.2.2. Termination and isolation of poly(propylene oxide).

After appropriate period of time (100-120 hours for solution process at room temperature, 24 hours, for bulk process), a large amount of wet acetone was added to the

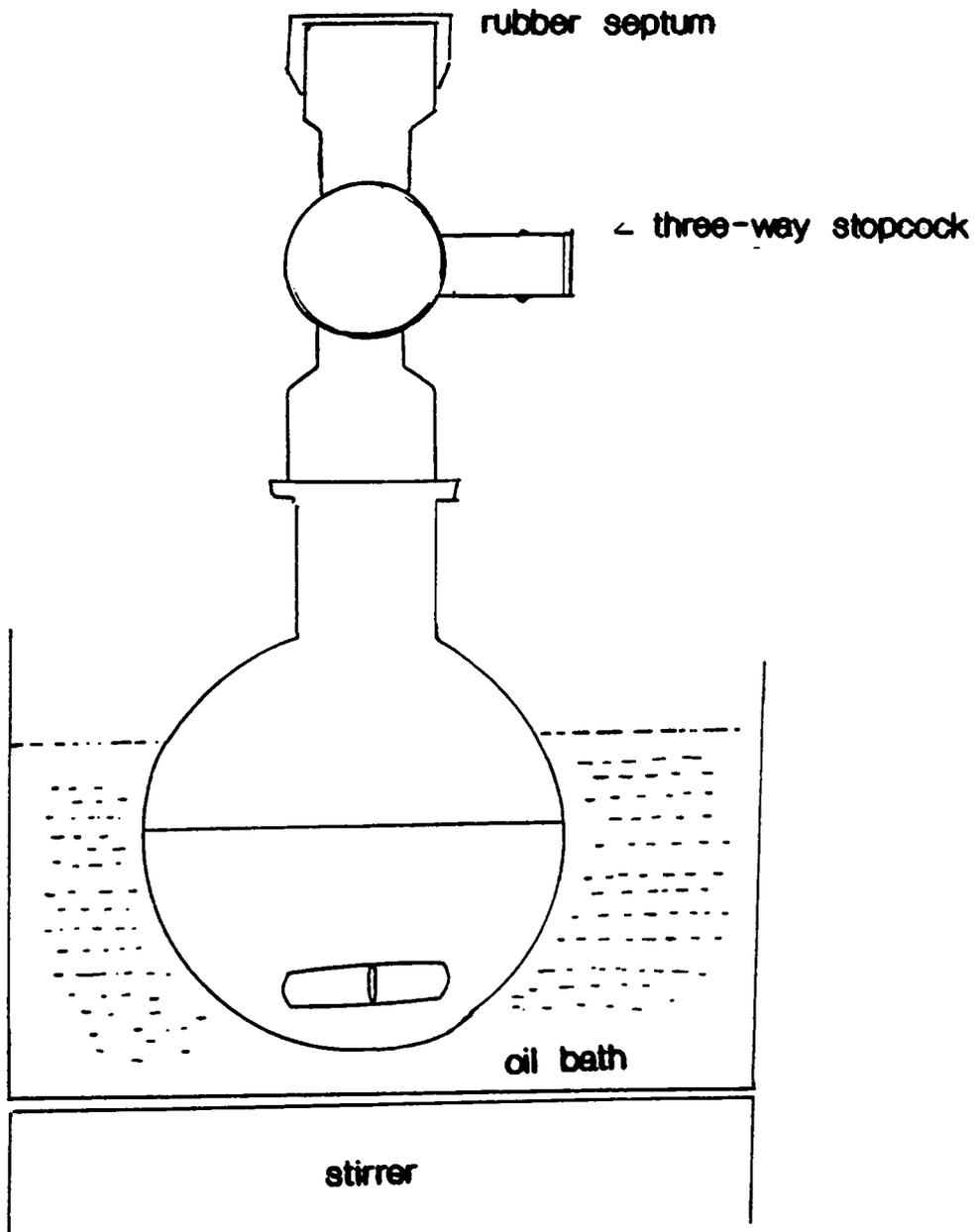


Figure 9. Reaction apparatus for polymerization

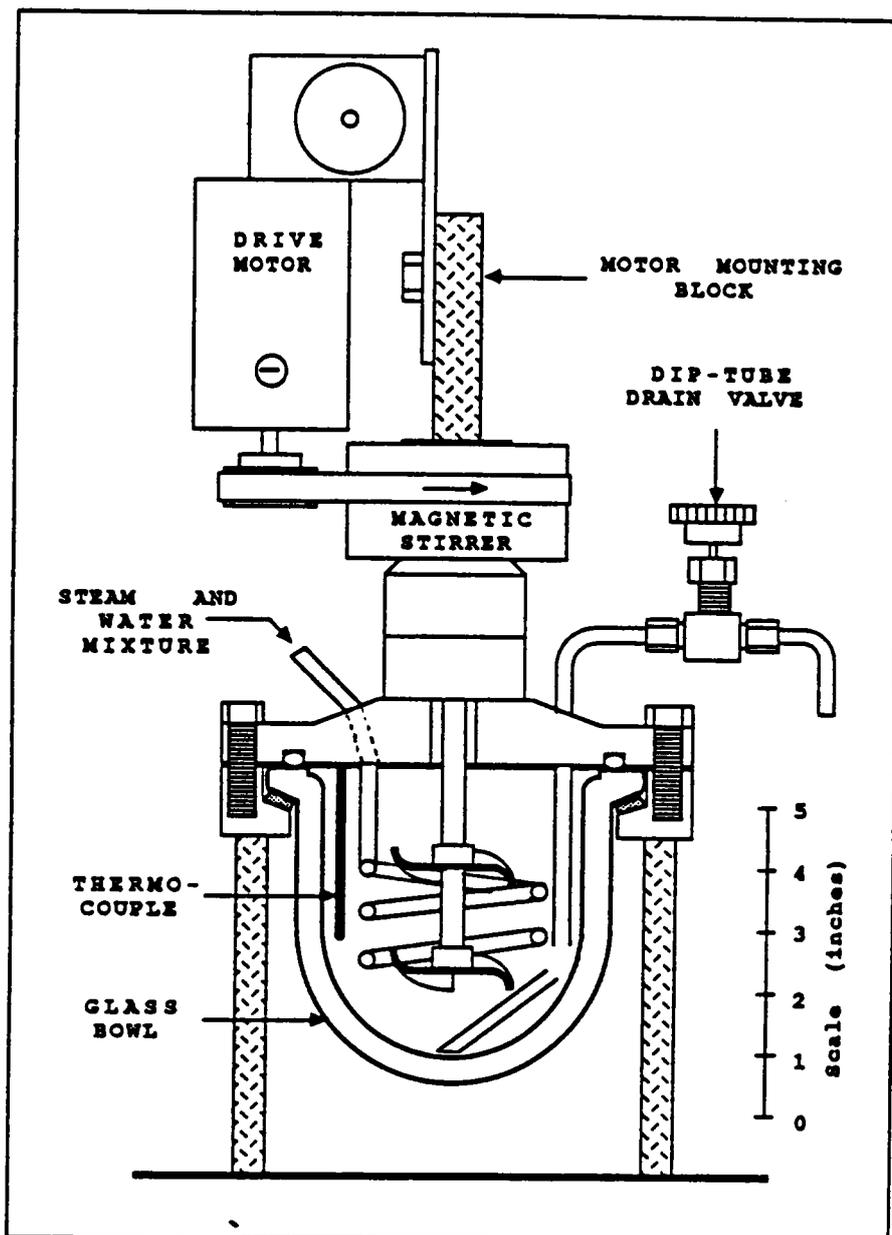


Figure 10. High pressure reactor apparatus[99]

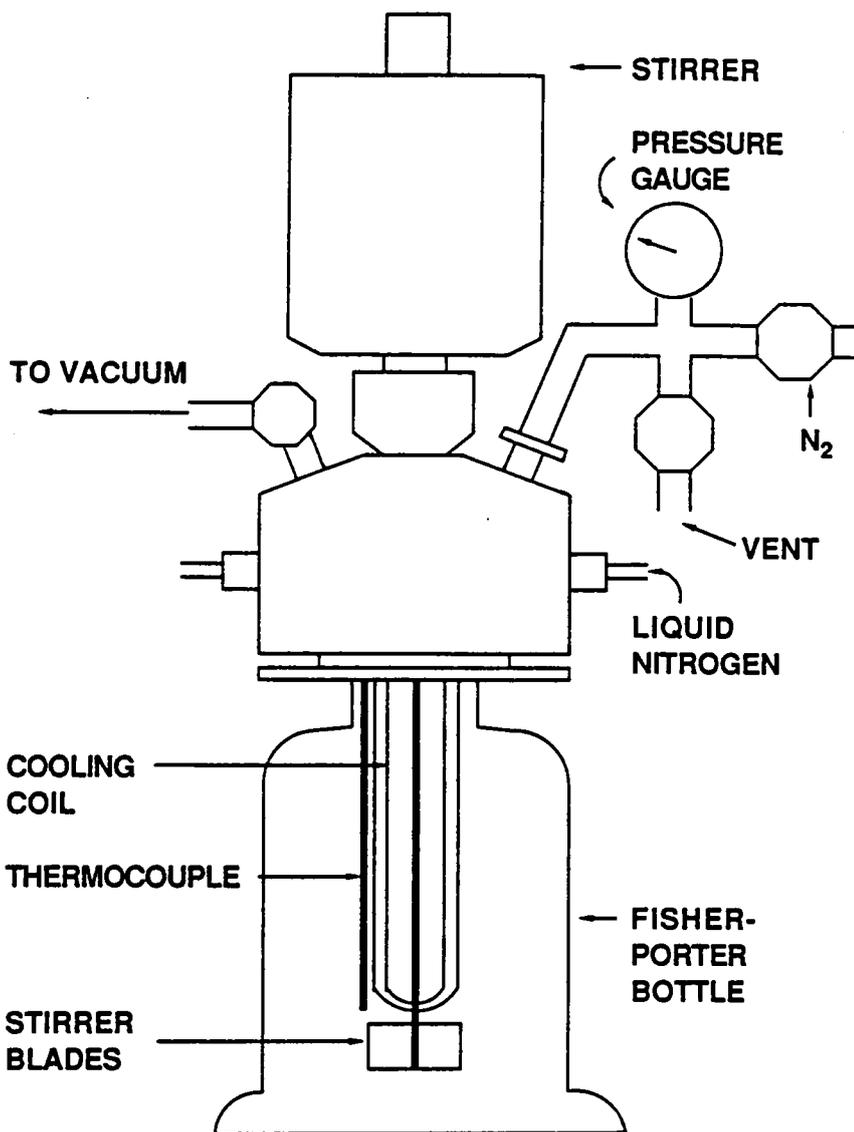


Figure 11. Pressure reactor

reactor. The mixture was again stirred for one hour and followed by removal of solvents and unreacted monomer by reduced pressure. Next, the polymeric material was dissolved in hexanes, typically making ca. 5 wt/vol% solution. Catalyst residue was precipitated from the solution. The hexane soluble polymer was recovered by filtering the catalyst from the solution. The purple color of the polymer/hexane solution, which was due to trace amount of catalyst, was essentially eliminated by activated charcoal. Finally, hexane was distilled off to afford a colorless polymer. The polymer was kept in a vacuum oven at 60°C for 24 hours to remove residual solvent.

III.3.3. Synthesis of End Reactive Poly(propylene oxide)

III.3.3.1. Secondary hydroxyl terminated polymers.

The catalyst was synthesized by an equimolar reaction of tetraphenyl porphyrin and triethyl aluminum in methylene chloride as described. Modification of the catalyst was achieved with difunctional hydroxyl initiators such as bisphenol A or hydroquinone. Typically, bisphenol A was weighed into a 20 ml vial with a rubber septum and the vial was purged with dry nitrogen. The amount of bisphenol A was varied from one half to twenty five times of catalyst concentration. After THF was added by hypodermic syringe into a vial, the predissolved solution was transferred to the reactor. The portion of THF was kept low enough to prevent excessive dilution of catalyst concentration, yet high enough such that the bisphenol A did not precipitate out from the co-solvent. Generally, the volume ratio between methylene chloride and THF was 5 to 1. The modification of catalyst by bisphenol A also generated ethane as a by-product, which was relieved periodically by an escape needle. This modification step was allowed to proceed for 5-6 hours. A wide variety of difunctional initiators were utilized including hydroquinone, hexane diol, 5-nitro xylene diol, p-hydroxy nitro benzoic acid, etc.

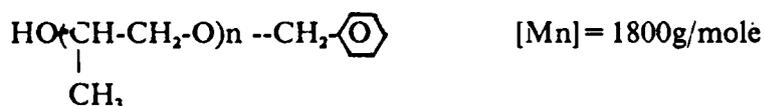
III.3.3.2. Primary hydroxyl terminated PPO.

(a) Synthesis of benzyl ether terminated PPO.

Primary hydroxyl terminated poly(propylene oxide) was synthesized by using a benzyl alcohol modified catalyst. The procedure was similar to that of the difunctional hydroxyl terminated polymer which used the bisphenol A modified catalyst. However, benzyl alcohol was injected directly to the catalyst solution since it is a liquid reagent and miscible with methylene chloride. Generally, a three to five fold excess of benzyl alcohol was added to the catalyst solution. The excess benzyl alcohol served as chain transfer agent in the polymerization. A typical polymerization for 2,000 g/mole PPO was conducted with following materials:

Tetraphenyl porphyrin	: 0.615 g (1 mmole)
Triethyl aluminum	: 1 ml (1 mole/liter, 1 mmole)
Methylene chloride	: 20 ml
Benzyl alcohol	: 0.324 g (3 mmole)
Propylene oxide	: 7 ml (0.1 mole)

Upon completion of polymerization, a large excess of methanol was added to the mixture to terminate any growing species. It was demonstrated that benzyl ether terminated poly(propylene oxide) was obtained with the following chemical structure;



(b) Coupling reactions.

One secondary hydroxyl end group of a benzyl ether terminated poly(propylene oxide) may be utilized for coupling reactions using terephthaloyl acid chloride or MDI to result in a difunctional benzyl ether terminated polymer. The material needed for the coupling reaction was as follows:

Poly(propylene oxide) (1,800 g/mole)	: 9 g (0.005 gmole)
Terephthaloyl chloride	: 0.483 g (0.0025 gmole)
Triethyl amine	: 1 ml (0.008 gmole)
Hexane	: 50 ml

For a trifunctional version, trimellitic acid chloride was employed as a coupling agent. First, poly(propylene oxide) was weighed into a 100 ml pressure bottle reactor with an overhead mechanical stirrer and subsequently purged with nitrogen. Next, purified hexane was introduced to the reactor by a transfer needle from a 50 ml round bottom flask which was capped with a rubber septum. At this point, 10 ml of hexane was saved and 40 ml was injected out of 50 ml. Then, terephthaloyl chloride was dissolved in the remainder of hexane. Triethyl amine was added to the pressure reactor by syringe. Finally, terephthaloyl/hexane solution was introduced to the reactor by three divided steps via hypodermic syringe. First, 80 % of solution was charged. The reaction was allowed to proceed for 30 minutes. Finally, the remaining hexane/acid chloride solution was added dropwise over a period of 15 minutes and allowed to continue for another 2 hours. Upon cooling the reaction mixture to room temperature, the mixture was filtered to remove triethyl amine salt. Excess triethyl amine and hexane was distilled off and a difunctional benzyl ether terminated poly(propylene oxide) was obtained. It should be noted that extreme care must be taken to remove all moisture from the poly(propylene oxide) and hexane prior to the reaction.

(c) Hydrogenolysis.

Primary hydroxyl functionality of the polymer was achieved through hydrogenolysis of the benzyl ether end group. The procedure can be outlined as follows: Poly(propylene oxide) (5 g, [Mn]=2000) was weighed into a 250 ml round bottom flask or pressure bottle reactor. Next, 60 ml of anhydrous isopropanol was added to the reactor. Finally, 10%Pd/C catalyst (0.5 g) was charged into the reactor with an extreme caution as a suspension in the same solvent (0.5 g/20 ml isopropanol). When a round bottom flask was used as a reaction vessel, hydrogen was bubbled through the solution at 60°C for 24-48 hours. When the pressure vessel was employed for hydrogenolysis, usually 45-50 psig of pressure was applied by hydrogen to promote the solubility of the gas and vigorous agitation was provided by an overhead mechanical stirrer. The hydrogenation was allowed to continue for 24 hours and then the Pd/C catalyst was isolated by filtration. Solvent and volatile materials were distilled off from the polymer. Since hydrogenation is a dangerous process, caution must be taken for a safe operation. This is particularly true, since the Pd/C catalyst is an extremely pyrophoric compound (complete drying of this catalyst was avoided during suction filtration).

III.3.3.3. Amine terminated poly(propylene oxide).

(a) Catalyst modification and polymerization.

By using nitrophenol instead of benzyl alcohol as a co- initiator, an amine terminated polymer was obtained. The catalyst(TPPAl- Et) was prepared in a 250 ml round bottom flask as previously described. Nitrophenol was dissolved in THF in a vial capped with a

rubber septum and transferred to catalyst solution for modification. From one to ten fold excess of nitrophenol to catalyst was normally used. The mixture was stirred for 5-6 hours and an appropriate amount of propylene oxide was injected. The following materials are required for 2000 [Mn] nitrophenyl terminated poly(propylene oxide);

TPPH ₂	: 0.307 g (0.5 mmole)
Al(Et) ₃	: 0.5 ml (1 mole/l, 0.5 mmole)
CH ₂ Cl ₂	: 10 ml
THF	: 2.5 ml
Nitrophenol	: 0.343 g (2.5 mmole)
Propylene oxide	: 5.6 ml (80 mmole)

After the polymerization was over, the polymer was isolated by the procedures previously outlined. The poly(propylene oxide) obtained using the nitrophenol co-initiator has secondary hydroxyl group at the other end. The terminal hydroxyl group was further utilized for coupling reactions. Alternately, nitrophenyl isocyanate was stoichiometrically added to the polymer to obtain difunctional nitro-terminated polymer. This end capping reaction was completed in 5 hours at the reflux temperature of THF. In addition, p-nitro fluorobenzene could be used to achieve difunctionality. The procedure will be outlined in the modification of hydroxyl terminated poly(propylene oxide).

(b) Reduction of nitro group by hydrogenation.

The hydrogenation of the aromatic nitro groups were carried out in a pressure reactor. The nitro terminated polymer(5 g) was dissolved in absolute ethanol(100 ml). Then 0.5 g of 10%Pd/C catalyst was carefully added. The hydrogenation was conducted at room

temperature under 45 psig of hydrogen pressure. Periodically, samples of solution were taken out to measure conversion by titration. Generally, the reaction was completed within 24 hours. Alternately, the conversion of reaction could be monitored by variations in the pressure gauge. For a first 24 hours of period the pressure reactor was connected to hydrogen cylinder supplying hydrogen at 45 psig of pressure. Next, the hydrogen line was closed and the pressure decrease in the reactor was monitored. If there was no further change in the pressure gauge for a period of 24 hours, then the reaction was judged to be completed. The color of the poly(propylene oxide) due to the residual porphyrin was also substantially eliminated by the hydrogenation.

III.3.3.4. Acrylate terminated poly(propylene oxide).

Acrylate or methacrylate terminated PPO has prepared by subjecting PPO to reactions. For mono-functional acrylate terminated PPO, the polymerization was carried out as described in mono-functional hydroxyl terminated PPO. After appropriate time was allowed for quantitative polymerization of propylene oxide, residual unreacted monomer was removed by reduced pressure. To this reactor, a calculated excess amount of acryloyl chloride or methacryloyl chloride was charged. It was necessary to add solvent to insure efficient stirring of the mixture. An elevated temperature(60°C) was employed in an attempt to accelerate the reaction. Typically, a two-fold excess of the stoichiometric amount of methacryloyl chloride was used.

III.3.3.5. Multifunctionality by DGEBA.

Multifunctional hydroxyl terminated PPO was synthesized by diglycidyl ether of bisphenol A(DGEBA) modified catalyst. The catalyst, tetraphenyl porphyrin aluminum chloride, was prepared in methylene chloride solution. Predissolved DGEBA solution in methylene chloride was charged to the catalyst solution by hypodermic syringe. Various

ratios of DGEBA to the catalyst were employed for to control the functionalities of polymers. Some statistical functionality to the ratios are listed below:

<u>Functionality</u>	<u>[DGEBA] / [TPPAI-Cl]</u>
2	0.50
3	0.67
4	0.75
5	0.80

Multifunctional amine or primary hydroxyl terminated poly(propylene oxide) could be prepared by post-coupling of growing polymer chains with DGEBA. After the polymerization was quantitatively proceeded with modified catalysts, the residual monomer was stripped off by reduced pressure. Then, the calculated amount of DGEBA was added in the solution of methylene chloride. The coupling reaction continued for 24-48 hours. The same statistical functionality to [DGEBA]/[TPPAI-OR] ratios may be applied to this post coupling reaction.

III.4. MODIFICATION OF HYDROXYL TERMINATED POLY(PROPYLENE OXIDE)

III.4.1. Conversion of Hydroxyl to Carboxylic Acid

Hydroxyl end group of poly(propylene oxide) was modified to carboxylic by phthalic anhydride or nitro phthalic anhydride. In general, a standard procedure also used for titration of the hydroxyl content was followed. It was necessary to remove all volatile residual solvent and moisture for a minimum of 2 hours. Then, a slight excess of imidazole was introduced and stirred about 15 minutes for complexion. Finally, a stoichiometric amount of phthalic anhydride was charged into the reactor and in a DMF solution. A Typical example of material used for this reaction was as follows:

PPO (difunctional hydroxyl terminated 2,000 g/mole)	
	: 20 g (0.01 mole)
Imidazole	: 1.6 g(20% excess, 0.024 mole)
Phthalic anhydride	: 5.92 g (0.02 mole)
Dimethyl formamide(DMF)	: 30 ml
Hexane	: 300 ml

The reaction was continued for 24 hours and the progress was monitored by FT-IR. If remaining hydroxyl groups were observed, the reaction was allowed to proceed an additional 12 hours for completion. After the reaction was completed, the solvent was removed by reduced pressure and the carboxylic acid terminated polymer was extracted by hexane.

III.4.2. Conversion of Hydroxyl to Amine Group

Converting hydroxyl functionality to amine group was carried out in several ways. The modifying reagents include isatoic anhydride, p-fluoro nitrobenzene, nitrophenyl isocyanate. The detailed procedures are discussed below.

III.3.2.1. By isatoic anhydride.

(a) Model reaction.

A difunctional hydroxyl compound such as butane diol was converted to the corresponding diamine compound by isatoic anhydride. The butane diol was dissolved in dimethyl formamide and a stoichiometric amount of imidazole was charged into a 100 ml round bottom flask. Isatoic anhydride was charged to the reactor. The mixture was rapidly stirred for 3 hours under nitrogen stream. Upon addition of isatoic anhydride, gas bubbling was observed due to evolution of carbon dioxide as a byproduct. At the end of a 3 hours period, CO₂ bubbling was no longer observed indicating that the reaction was essentially completed. Typical ingredients for this reaction were as follows;

Reactor : 100 ml two neck round bottom flask with nitrogen inlet and outlet

Materials :

1,4 Butane diol:	:5 g (0.0625 gmole)
Imidazole	:8.51 g (0.1251 gmole)
Dimethyl formamide(DMF)	:50 ml
Isatoic anhydride	:20.391 g (0.125 gmole)

At the end of the reaction, approximately half of DMF in the flask was distilled off by reduced pressure and the remainder was quenched into a large amount of methanol

(ca. 500 ml). A fine white powder was precipitated from the methanol solution and subsequently recovered easily by filtration. The compound was repeatedly rinsed with additional methanol and dried in a vacuum oven at 60°C for 24 hours. Yield of the reaction was quantitative and melting point was 101-103 °C.

(b) Poly(tetramethylene oxide) and poly(propylene oxide).

The modification of hydroxyl terminated polymer was attempted in the same manner as the model reaction. The following materials were used for the reaction;

PTMO or PPO ([Mn]= 2000)	: 40 g (0.02 gmole)
Diazobicyclo un-decene(DBU)	: 0.8 g
DMF(for a solution reaction)	: 100 ml
Isatoic anhydride	: 6.46 g (0.04 gmole)

Due to a relatively low concentration of hydroxyl end groups in the polymer, a longer reaction time was allowed. Typically, 5 hours was given for complete conversion of the hydroxyl group to an aromatic amine. After the reaction was complete, the solvent was removed by vacuum distillation. Polymer was extracted by a hexane/toluene (1:1) co-solvent and volatile materials were removed resulting in the final product. In the case of poly(propylene oxide), an even longer reaction time was allowed because of the lower reactivity of the secondary hydroxyl end group. A minimum of 24 hours was allowed for the reaction time.

III.4.2.2. By p-fluoro nitrobenzene.

Moisture free hydroxyl terminated poly(propylene oxide) was dissolved in purified toluene. A stoichiometric amount of n-butyl lithium(to hydroxyl groups) was added to this solution. The mixture was heated to 80°C to form a alkoxide species. However,

vigorous agitation was required to obtain a homogeneous mixture. Generated butane gas was released from the reactor in a nitrogen stream. After 1-2 hours of stirring, a homogeneous solution was achieved, then, dimethyl formamide(DMAC) was added to the vessel by transfer needle. The reaction was allowed to continue 5-8 hours at 140°C. At the end of the reaction, the DMAC and unreacted fluoro nitrobenzene were removed by reduced pressure. Final polymer was extracted by hexanes. The hexane/polymer solution was treated with 1-2 wt% of activated charcoal and the nitro terminated PPO was obtained after distilling off the hexane. The following materials were needed for this reaction.

Reactor : Two neck flask with nitrogen inlet and outlet

Materials : Hydroxyl terminated PPO

([Mn] = 2000, difunctional)	: 20 g
N-butyl lithium(1.3mole/l)	: 15.4 ml
Toluene	: 60 ml
DMAC	: 60 ml
Fluoro nitrobenzene	: 2-3 fold excess to hydroxyl group

The aromatic nitro terminated polymer was subjected to hydrogenation to generate amine functionality as discussed earlier.

III.5. SYNTHESIS OF COPOLYMERS

III.5.1. Block Copolymers of Propylene Oxide and Caprolactone

Triblock copolymers of propylene oxide and caprolactone were prepared by a two step process. The first step was the synthesis of difunctional hydroxyl terminated poly(propylene oxide) prepolymer with controlled molecular weight via bisphenol A chain transfer, which has been previously described. The second step was the initiation and propagation of the poly(caprolactone) block from the hydroxyl end group of poly(propylene oxide) in the presence of stannous octanoate catalyst. The molecular weight of poly(propylene oxide) first block was 36,000 g/mole from the GPC analysis. The calculated amounts of caprolactone monomer were charged to synthesize the block copolymers with various compositions. The materials required in the process are listed below;

PPO(36K) :	4.14g	Toluene: 10cc	caprolactone: 2g
	4.18g	10cc	4g
	2.90g	20cc	12g
	3.63g	20cc	7.5g

stannous octanoate : 0.1 - 0.2 wt% of product

First, poly(propylene oxide) was charged into a round bottom flask(100 ml) with a magnetic stirrer. Then the reactor was flushed with dry nitrogen. Toluene and catalyst(stannous octanoate) were added by a hypodermic syringe. The mixture was agitated for 15 minutes until a homogeneous solution was obtained. Finally,

caprolactone was injected into the vessel by a syringe. After the reaction was continued for 24-40 hours at 100-110°C, the mixture was cooled to room temperature and precipitated in large amount of methanol (ca. 10 times of polymer solution in toluene). If the composition of poly(propylene oxide) in the block copolymer was more than 50 wt%, then, the solution was quenched in methanol/water (50:50 by volume) co-solvent. The product was recovered by suction filter and dried in a vacuum oven to constant weight.

III.5.2. Synthesis of Statistical Copolymers

III.5.2.1. Statistical copolymers of propylene oxide and allyl glycidyl ether.

Statistical copolymers of propylene oxide and allyl glycidyl ether were prepared on toluene by using aluminum porphyrin catalyst. Experimental procedures are similar to that of homo- polymer of propylene oxide except using co-monomers. These copolymers contained less than 10 mole% of allyl glycidyl ether unit in the main chain, therefore they could be worked up by the same procedure as applied to poly(propylene oxide).

III.6. CHARACTERIZATION

III.6.1. Gel Permeation Chromatography (GPC)

Gel permeation chromatography in connection with UV (218,254 nm) and differential refractive index detectors was used to determine number average and weight average molecular weights of poly(propylene oxide) and its copolymers. A Waters 244 model equipped with styragel column of 105-500 angstrom pore size was used. Polystyrenes or poly(methyl methacrylate)s were employed as standards. Typically, polymer was dissolved in tetrahydrofuran by 0.1-0.15 wt% and eluted with a flow rate of 1.0 ml/min.

III.6.2. Fourier Transfer Infrared Spectroscopy (FT-IR)

Fourier transfer infrared spectra(500-4000 cm^{-1}) were obtained for the oligomers and polymers by using a Nicolet MX-1 spectrometer. The FT-IR spectra provided a qualitative information on the functionalities and compositions of polymers. The spectra were obtained in different ways depending on the state of samples. Liquid poly(propylene oxide) was directly coated on sodium chloride crystal window. However, thermoplastic material was solvent cast on the salt plate and dried in the vacuum to remove all the volatile components. Powder-like compound was prepared as potassium bromide pellet by 5-10 wt%.

III.6.3. Intrinsic Viscosity

A Cannon-Ubbelohde viscometer was used to measure the intrinsic viscosity of polymer. Typically, four concentrations of the polymer in chloroform were used to estimate the time. All the measurements were conducted in a thermostated water bath at 25 °C . Generally, a pure solvent time was determined followed by three measurements of time for a solution of 0.1 g in 25 ml of solvent. This solution was further diluted by the same solvent three times and flow times were determined. Typically, the dilution was made as follows. 10 ml of original polymer solution was taken out and 5 ml of fresh solvent was added. And additional 5 ml of solvent was added in every dilution step. The intrinsic viscosity value was determined by the intercept of specific viscosity of each concentration of solution. The specific viscosity is approximately equal to the ratio of flow times for the solvent and solution.

III.6.4. Nuclear Magnetic Resonance Spectroscopy (NMR)

Proton and carbon NMR spectra were obtained for polymers and oligomers using a JEOL 270 MHz spectrometer. Fluorine NMR spectra were obtained from 200 MHz IBM FT-NMR multinuclear probe. Spectra were run in 10 and 25 wt% solution in deuterated chloroform for proton and carbon NMR spectra, respectively. Tetramethylene silane was used as an internal standard for proton spectra. The ¹⁹F NMR spectra were run to determine the primary and secondary hydroxyl functionality of oligomers. In this case, each hydroxyl end group was derivatized by trifluoroacetic anhydride, ca. 2 hours of agitation followed by stripping off the residual volatile mate-

rials. Again deuterated chloroform was used as solvent and ca. 2 wt% of fluorobenzene was added to the solution as an internal standard.

III.6.5. Titration

The number average molecular weight and functionality was determined by potentiometric titration. These titrations were performed by Fisher Scientific Titrimeter II. A standard calomel electrode was used with a double junction reference. Titration of the amine group was carried out in chlorobenzene by hydrochloric acid in isopropanol (N/10 standard solution). Typically, 0.05-0.1 g of oligomer ([Mn]= 1000-5000 g/mole) was weighed into 100 ml beaker followed by addition of solvent and stirring by magnetic stirring bar. The titration started when the electrometer is stabilized and continued until a peak is observed on the derivative curve. Usually the titration was repeated three times and number average molecular weight was calculated based upon the following equation.

$$[\text{Mn}] = \frac{(\text{sample weight}) \times (\text{number of functionality})}{(\text{equivalent of titrant at end point})}$$

III.6.6. Differential Scanning Calorimetry (DSC)

Thermal properties such as glass transition temperatures, melting transition of polymer were determined by differential scanning calorimetry on a Perkin-Elmer Model DSC-2. Temperature and heat of fusion was periodically calibrated by Indium standards.

The heating rate was normally 5-20 K/min. and the sample tested was prepared as liquid prepolymer or solvent cast film or compression molded film. Usually, both first and second heats were recorded to provide a consistent thermal history.

III.6.7. Thermomechanical Analysis (TMA)

Thermomechanical analysis on polymer film was carried out by Perkin-Elmer Thermal Mechanical Analyzer over the temperature of 173 K-373 K on PPO-PCL block copolymers. Typically, heating rate of 5 K/min. under constant load of 5 grams was employed throughout the measurement.

III.6.8. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis(TGA) was performed in order to study thermal degradation behavior of poly(propylene oxide) and increased to where the polymers degrade completely. Both isothermal and dynamic thermogram were measured. Typically, dynamic thermogram were obtained by heating rate of 10 K/min. under air or nitrogen environment. Isothermal Thermograms of the aromatic amine terminated poly(propylene oxide) was obtained at 225°C for an hour in air.

III.6.9. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical behavior was observed by means of Perkin Elmer DMTA at a frequency of 1 Hz. The sample was rapidly quenched to -100°C and the measurement

was made at the heating rate of 5°C/min. up to 80°C for poly (propylene oxide)-poly (caprolactone) block copolymers.

III.6.10. Tensile Test

Uniaxial stress-strain behavior was determined via an Instron tester at room temperature. Dog-bone specimens were prepared from compression molded films. The test was conducted at a strain rate of 100% per minute based on the initial sample gauge length.

III.6.11. Sample Preparation

Oligomers and polymers synthesized by the procedure described previously were properly prepared to be characterized by various instrumentation. For spectroscopic analysis, liquid state oligomers were directly utilized, however in many case film type specimen was required, which were obtained by solvent casting or compression molding.

III.6.11.1. Compression molding.

Solid state polymers at room temperature were made into film form by compression molding of the sample. Typically, a 7"x7" teflon sheet was placed on the ferrotype plate, then 2-3 g of vacuum dried polymer was placed on the center. Sometimes spacer was placed to control the thickness of film. Then, another teflon sheet and ferroplate was used to cover the sample. The ferroplate was sandwiched by heavy metal iron plates and placed between the platens of the compression molder. The platens were heated above the melting point of the sample. No pressure was applied until the platen reached the

preset temperature. Once the temperature was reached, the pressure was increased up to 10,000 psig and followed by release of the pressure to remove entrapped gas within the sample. This process was repeated three times. Finally, the pressure was increased to 10,000-20,000 psig to obtain desired thickness of film. After maintaining the pressure five minutes, the film was quenched by cooling water.

III.6.11.2. Solvent casting.

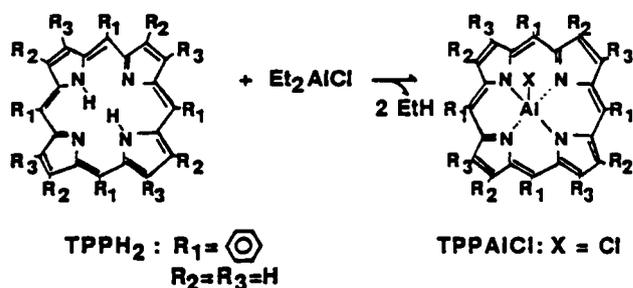
Polymers are dissolved in a proper solvent, which should have intermediate boiling point. Generally, 1 g of polymer was dissolved in 15 ml of solvent most likely chloroform or tetrahydrofuran, and cast on a glass plate. The glass plate was covered by perforated aluminum foil to prevent the rapid evaporation of solvent. After 12 hours of drying, the polymer film was removed from the plate and kept under vacuum for a minimum of 24 hours.

CHAPTER IV. RESULTS AND DISCUSSION

IV.1. SYNTHESIS OF POLY(PROPYLENE OXIDE)

IV.2.1. Synthesis of Aluminum-Porphyrin Catalyst

The catalyst for the synthesis of poly(propylene oxide) was prepared according to the procedure of Inoue and Aida[122]. Tetraphenyl porphyrin was dissolved in purified methylene chloride and reacted with an equimolar amount of diethyl aluminum chloride under an inert atmosphere for 5 hours. The reaction proceeds, evolving ethane as described in the following scheme:



A yield of the reaction was carefully measured by gravimetric analysis. After 5 hours of reaction, all the volatile materials were removed by reduced pressure and the final product was weighed. Since the tetraphenyl porphyrin has a molecular weight of 641.75 g/mole, the final product, (tetraphenyl porphyrinato aluminum chloride), is expected to have a molecular weight of 675.25 g/mole after complete reaction with diethyl aluminum chloride. By comparing the weight of the product obtained from the reaction with the theoretical value, the conversion of the reaction was estimated to be as high as 99.4%.

In the ^1H -NMR spectrum of tetraphenyl porphyrin given in Figure(12), the peak at 8.87ppm is assigned as the pyrrole proton of the tetraphenyl porphyrin compound and the other peaks centered at 8.25 and 7.8ppm are indicative of the phenyl protons of the product. The integrated ratio of these peaks corresponds to the number of protons of the particular moiety of porphyrin compound.

The ^1H -NMR spectrum of the aluminum porphyrin obtained from the reaction displayed that the pyrrole proton peak originally located at 8.87ppm shifted downfield to approximately 9.07ppm. This shift is attributed to coordination of aluminum in the center of porphyrin structure. The electron density of the pyrrole hydrogen may be reduced by the electron withdrawing effect of the aluminum atom in the center, therefore the peak moved ca. 0.20ppm downfield. On the other hand, the peaks from the phenyl moiety were not affected by association with aluminum. Judging from both gravimetric and spectroscopic analysis, a quantitative conversion of the catalyst synthesis reaction was verified.

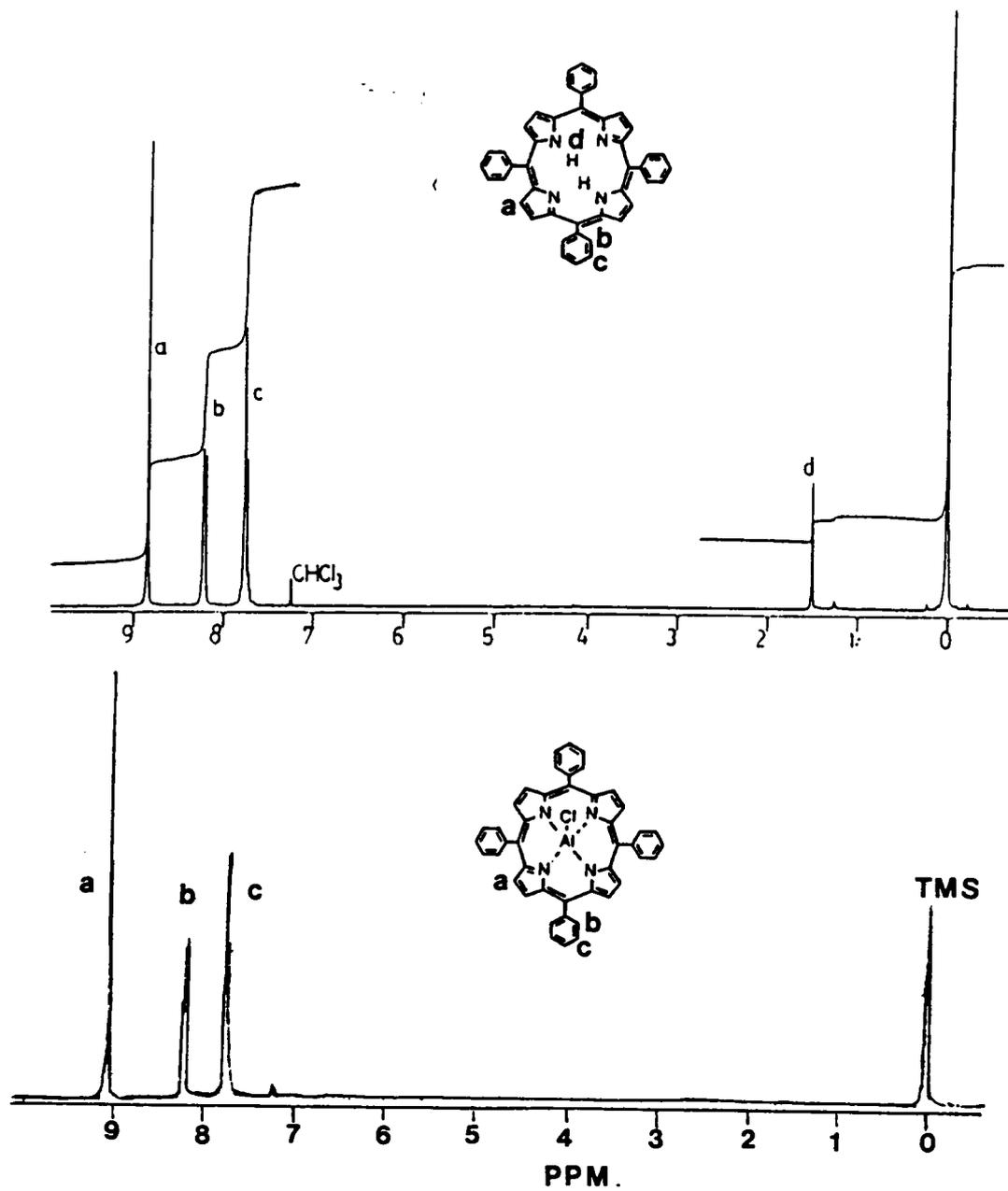
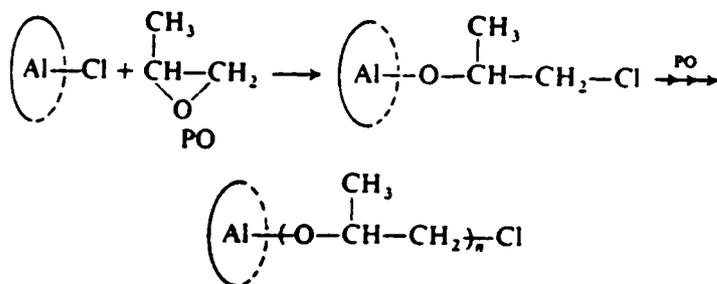


Figure 12. Proton-NMR spectra of tetraphenyl porphyrin and its aluminum coordinated derivative

IV.1.2. Synthesis of Poly(propylene oxide)

One of the most important concerns about this aluminum porphyrin catalyst system is whether it could possibly synthesize poly(propylene oxide) over wide range of controlled molecular weights([Mn]) from a few hundred to a hundred thousand grams per mole or higher. The base catalyzed anionic route affords the preparation of poly(propylene oxide) up to only 5,000-6,000 g/mole molecular weights, if one allows a considerable amount of unsaturated allyl or propenyl end groups, as discussed in Chapter II. The control of molecular weight in the aluminum porphyrin catalyst was investigated by employing various charge ratios of monomer to catalyst. It was based on the assumption that if one catalyst molecule serves as an initiator for a single polymer chain, the molecular weight of the polymer can be predicted by the initial charge ratio of monomer to catalyst as well as by the conversion of monomer to polymer.



$$[\text{Mn}] = \{[\text{monomer}]_0 / [\text{catalyst}]\} \times \text{conversion} \times 58$$

,where 58 is the molecular weight of each repeating unit in the polymer and [Mn] is the number average molecular weight.

The observed molecular weights of poly(propylene oxide) by gel permeation chromatography(GPC) using polystyrene standards are compared with the estimated values in Table (10). The GPC molecular weights correspond to the predicted values within a ca. $\pm 10\%$ deviation. The successful synthesis of high molecular weight polymer

Table 10. Results of mono-hydroxyl terminated poly(propylene oxide) synthesis by aluminum porphyrin catalysts

[Mo.]/[Cat.]	Conv.(%)	[Mn] ^{calc}	[Mn] ^{GPC}	MWD	Time(hr)	Remarks
100	95	5500	5800	1.10	140	Sol'n
150	90	8100	7600	1.12	120	Sol'n
200	96	10500	8800	1.25	24	Bulk
300	98	17100	18000	1.06	120	Sol'n
400	99	23000	22000	1.16	140	Sol'n
600	98	34000	35000	1.12	140	Sol'n
4000	50	116000	86000	1.37	96	Bulk
5000	35	100,000	89000	1.23	120	Bulk

- * Polymerizations were carried out either in methylene chloride solution or bulk reaction at room temperature..
- * Number average molecular weights and molecular weight distributions are obtained from GPC by polystyrene standards.

demonstrated that the polymerization proceeds without serious side reactions at the given conditions. The molecular weight distributions of the poly(propylene oxide)s were reasonably narrow, ca. 1.10, over the wide range of molecular weight. Some broadening of the molecular weight distribution was noticed in case of bulk polymerization (MWD = 1.3). However, these observations clearly indicate that all of the aluminum porphyrin catalyst participates in the polymerization maintaining the homogeneous reactivities unlike previous coordination catalysts.

A quantitative yield is reached after an appropriate reaction time. Moreover, the molecular weights show a linear relationship with the conversion of monomer to polymer, while the molecular weight distribution remains narrow throughout the reaction. This again verifies that one catalyst molecule affords the generation of one polymer chain, unless it is deactivated by impurities such as moisture in the system. Thus, the polymerization is essentially of living nature as well as an irreversible process. These observations are presented in Figures(13,14). Note that these apparently slow reactions were conducted at room temperature.

Spectroscopic analysis of the poly(propylene oxide) was performed by FT-IR in a transmittance or absorbance mode. Typical FT-IR spectra of poly(propylene oxide) are presented in Figure(15). The peak at 1101cm^{-1} is characteristic of the ether linkage(C-O-C) in poly(propylene oxide) and the absorbance peak over $3100\text{-}2700\text{ cm}^{-1}$ is an indication of the C-H stretching. The peak at 3547cm^{-1} is attributed to the O-H stretching of hydroxyl end group.

Figure(16) shows a representative $^1\text{H-NMR}$ spectrum of poly(propylene oxide) prepared by the aluminum porphyrin catalysts. A 270 MHz-NMR enabled the resolution of the structure. The methyl groups of poly(propylene oxide) appear at 1.15ppm as a doublet due to the coupling with methine the hydrogen. Also, peaks centered at 3.55 and 3.42ppm were assigned as methylene and methine hydrogens, respectively.

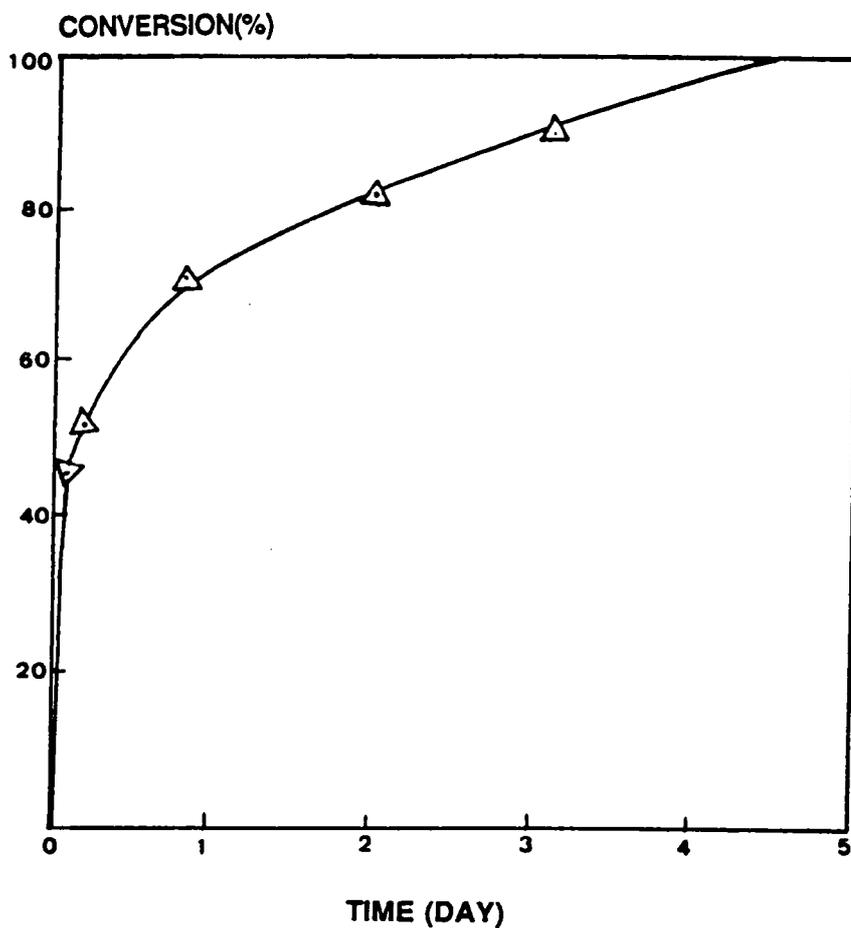


Figure 13. Typical time vs conversion plot for the polymerization of propylene oxide by aluminum porphyrin catalysts: reaction temperature = 27 °C, $[M]_0 = 7$ mole/liter, $[\text{catalyst}] = 23$ mmole/liter, solvent; methylene chloride

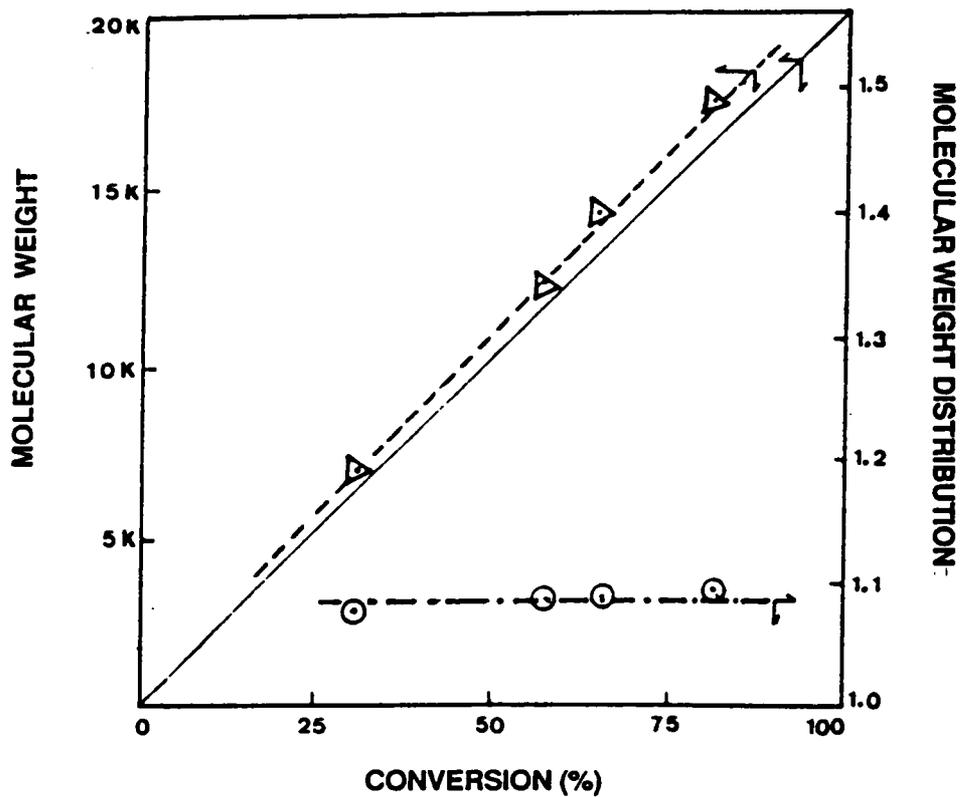
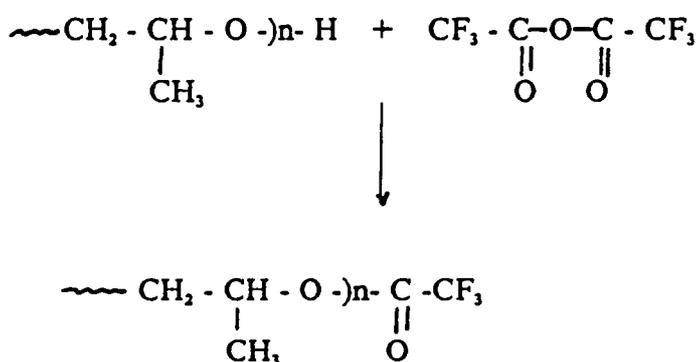


Figure 14. Molecular weights and molecular weight distributions vs conversion: solid line = theoretical [Mn], dotted line = observed [Mn] and MWD from GPC by using polystyrene standards

The mode of cleavage of a three-membered epoxide monomer is an important criteria to judge the propagation mechanism. As briefly discussed in Chapter II, methylene-oxygen bonds are exclusively cleaved in anionic polymerization, whereas methylene-oxygen and methine-oxygen bonds are equally broken in cationic polymerizations. The latter mechanism results in a significant amount of head to head or tail to tail chain configuration, since ring opening occurs spontaneously due to the increased polarization effect upon coordination to the catalyst sites.

If methylene-oxygen bonds are cleaved by the attack of growing alkoxide species, the end groups of poly(propylene oxide) will be secondary hydroxyls. However, after terminating the growing polymer chain, the poly(propylene oxide) prepared through the cationic route will possess a mixture of statistically determined secondary and primary hydroxyl end groups.

The hydroxyl terminal of poly(propylene oxide) prepared by the aluminum porphyrin catalyst were derivatized with trifluoroacetic anhydride and characterized by ^{19}F -NMR. One percent monofluoro-benzene was added as an internal standard in the deuterated chloroform solution.



Due to the long range coupling of the trifluoromethyl with the methine or methylene protons, ^{19}F -NMR spectroscopy allows one to differentiate the primary and secondary

hydroxyl groups. In the ^{19}F -NMR spectra, two peaks are detected in addition to the peak from the internal standard. A peak located at 36.7ppm downfield from the standard is due to trifluoro acetic acid, which is the byproduct of the derivatization reaction. The second peak is located at 37.6ppm, which is believed to be trifluoro acetates derived from the reaction. As a reference, 2-propanol was analyzed by ^{19}F -NMR in the same manner. The peak from the trifluoro acetate derivative of the secondary hydroxyl end group was detected at exactly the same location as that of the poly(propylene oxide). The corresponding derivatives of the primary hydroxyl groups are detected at approximately 0.3-0.4ppm downfield from the secondary hydroxyl derivative. The ^{19}F -NMR spectra are presented in Figure(17). Consequently, it may be concluded from ^{19}F -NMR experiments that the propagation is taking place through the cleavage of the methylene-oxygen bonds of propylene oxide by the nucleophilic attack of the alkoxide growing species. This in turn suggests that the apparent ring opening of propylene oxide via the aluminum-porphyrin catalyst system is analogous to an anionic polymerization.

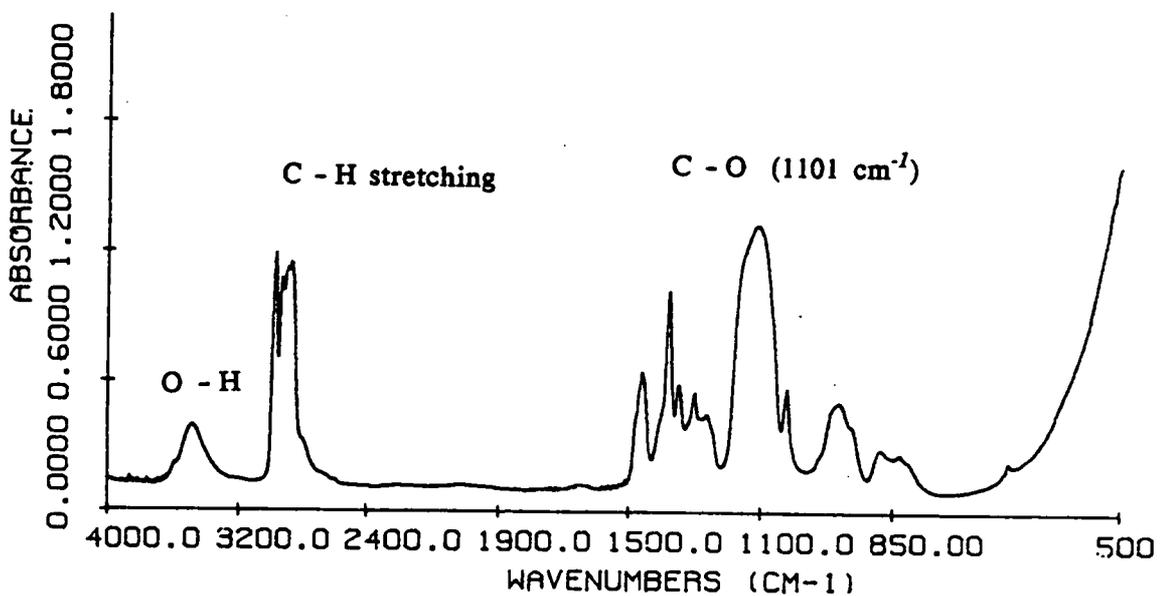


Figure 15. FT-IR spectrum of poly(propylene oxide) in absorbance mode

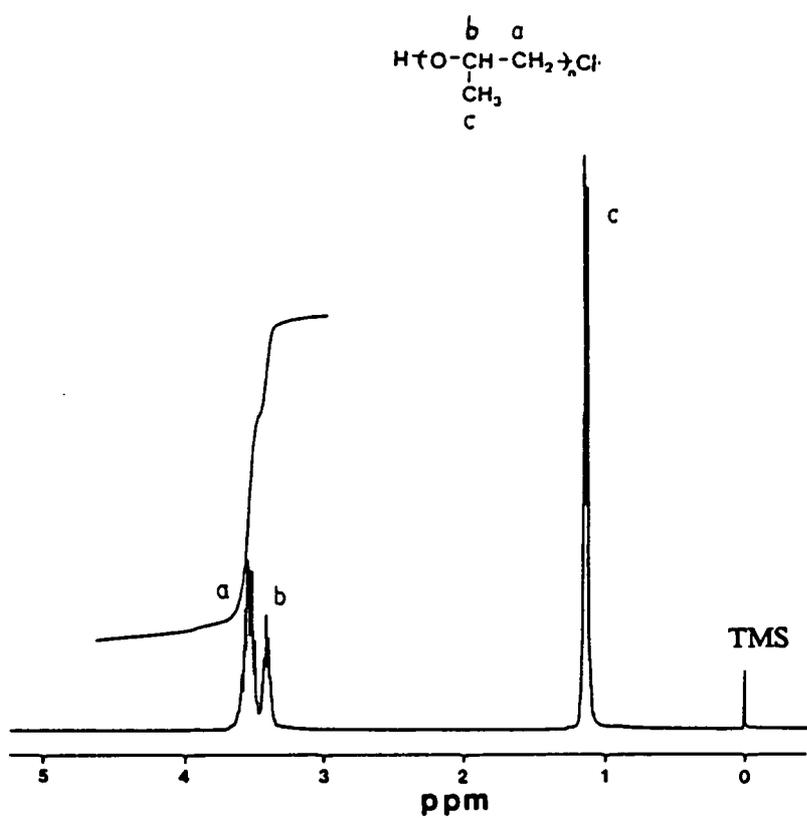


Figure 16. A typical proton-NMR spectrum of poly(propylene oxide)

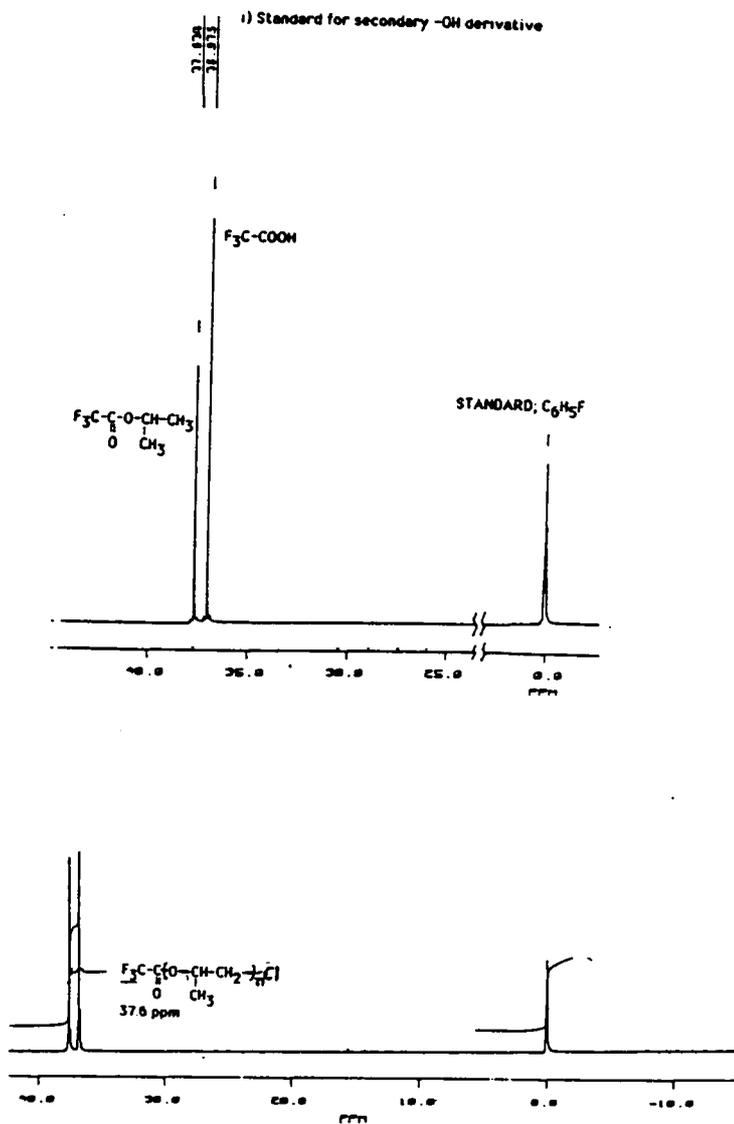


Figure 17. Fluorine-NMR spectra of derivatized end group of isopropanol and poly(propylene oxide) by trifluoroacetic anhydride

IV.1.3. Kinetic Studies

Poly(alkylene oxide) may be synthesized via ionic polymerization which include anionic, cationic and coordination mechanisms. Kinetic studies of anionic polymerizations have been reported by a number of investigators[47-50]. Typically, the rate of polymerization shows first order dependency on the concentrations of both monomer and catalyst in the anionic polymerization.

Thus, $d[M]/dt = k[M][C]$, where $[M]$ is concentration of monomer in the reaction mixture and $[C]$ is the initial concentration of catalysts.

Since the reaction involves the nucleophilic attack of monomer by the growing anionic species, the rate constants would be expected to be significantly dependent upon the degree of association with a gegenion. Dissociated anionic growing species, which are favored in polar solvents may demonstrate high reactivities relative to tightly associated ion pairs in non-polar solvents.

The recent development of aluminum porphyrin catalysts are recognized as a major breakthrough in coordination polymerization in many respects. First of all, this catalyst displays the excellent capability to control the molecular weights of poly(alkylene oxide)s with remarkably narrow molecular distributions, which had never been achieved by any previous organometallic type catalysts. Generally, only small fractions of organometallic type coordination catalysts (ca. 0.1-0.01%) actually participate in the polymerization. In addition, the usual active catalyst sites differ in their reactivities, resulting in broad molecular weight distributions. This fact may be attributed to the heterogeneous and highly aggregated structure of the catalysts (It is believed that in some systems, more than ten metal atoms are combined in one catalyst unit). On the other hand, one aluminum-porphyrin catalyst molecule initiates one polymer chain in the absence of cointiators. Moreover, all of the active sites are considered to be of equal re-

activity toward the monomer due to their uniform structures. Therefore, the aluminum porphyrin system allows the study of the kinetics on the coordination polymerization of alkylene oxides without many of the usual complications.

IV.1.3.1. Experimental observations.

(a) Effect of monomer concentration

A series of polymerizations were conducted under carefully controlled experimental conditions. The catalyst with an alkoxide growing species ((TPP(O-CH(CH₃)CH₂)_x-Cl), x = 1-2) was prepared in a pressure reactor in methylene chloride solution. A calculated amount of monomer was added by a transfer needle. In all experiments, catalyst concentrations were maintained at 17.2 mmole/liter and the temperature was kept constant at 47 ± 1°C throughout the reaction.

Samples were taken from the reactor periodically and the polymerization was immediately terminated with a water/acetone mixture. Conversions were determined by gravimetric analysis after removing solvent and unreacted monomers by reduced pressure. Conversion vs. time was plotted for three different initial monomer concentrations, as shown in Figure(18). The conversion versus time curves for each experiments are similar for three monomer concentrations of 10.3 mole/liter, 8.5 mole/liter and 7.1 mole/liter (± 2% deviation). Thus, the fact clearly indicates that this system basically follows either first or zeroth order kinetics with respect to the monomer concentrations within tested range. The following equations elucidate the relationship between conversion at a given time and initial monomer concentration. The initial monomer concentration affects the conversion only in overall second order kinetics. The classical equations for each case are provided below;

$$\text{zeroth order} \quad r_p \propto [M]^0, \quad x = k t$$

first order $r_p \propto [M]^1, \quad -\ln(1-x) = k t$

second order $r_p \propto [M]^2, \quad x/(x-1) = -k [M]_0 t$

,where x is conversion, t is time, $[M]_0$ is initial monomer concentration and k is apparent or global rate constant.

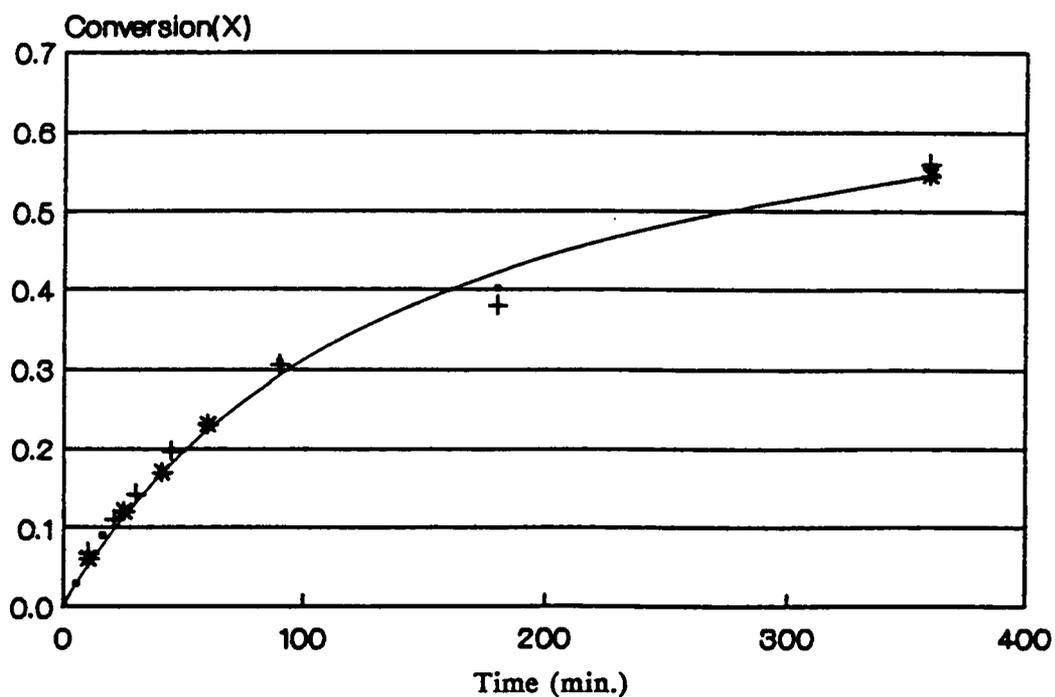
The zeroth and first order dependency on the monomer concentration were examined at low conversions of less than 20%. As illustrated in Figure(19) and (20), this system may be more properly represented by first order kinetics than zeroth order with respect to the monomer concentration. However, propagation rate decreased, resulting in a deviation from the first order kinetics at higher conversions of 20-25%.

This retardation of propagation rate is not rare and may be attributed to several reasons. First, as the polymer chain grows, the coordination sites of the catalyst molecules may be occupied by linear ether group of the polymers and the access of monomer to the growing chain end becomes thereby limited. Moreover, the saturation of catalyst may inhibit the attack of growing species onto the coordinated monomer.

(b) Effect of catalyst concentration

The effect of catalyst concentration was investigated in a similar manner. Three different catalyst concentrations (17, 32, 43 mmole/liter) were employed, while maintaining the other reaction variables constant. Initial monomer concentrations of all experiments were 7.1 mole/liter and the reaction temperature was controlled at 25°C. Conversion versus time for these three experiments are recorded in Figure(21). Obviously, higher conversions were obtained at higher catalyst concentrations, in almost a linear fashion. The $-\ln(1-x)$ versus time curves are plotted in Figure(22), assuming that the polymerization follows first order kinetics with respect to the monomer concentration.

As shown in the Figure(23), the slope of each plot, which is a product of catalyst concentration and rate constant, has a linear dependency on the catalyst concentration. Since temperature was maintained constant at 25°C for the experiments, only the cata-



. [M]₀=10.3 mole/liter + [M]₀=7.1 mole/liter * [M]₀=8.5 mole/liter

Figure 18. Conversion vs time at various initial monomer concentrations: catalyst conc = 17.2 mmole/liter, 47 °C

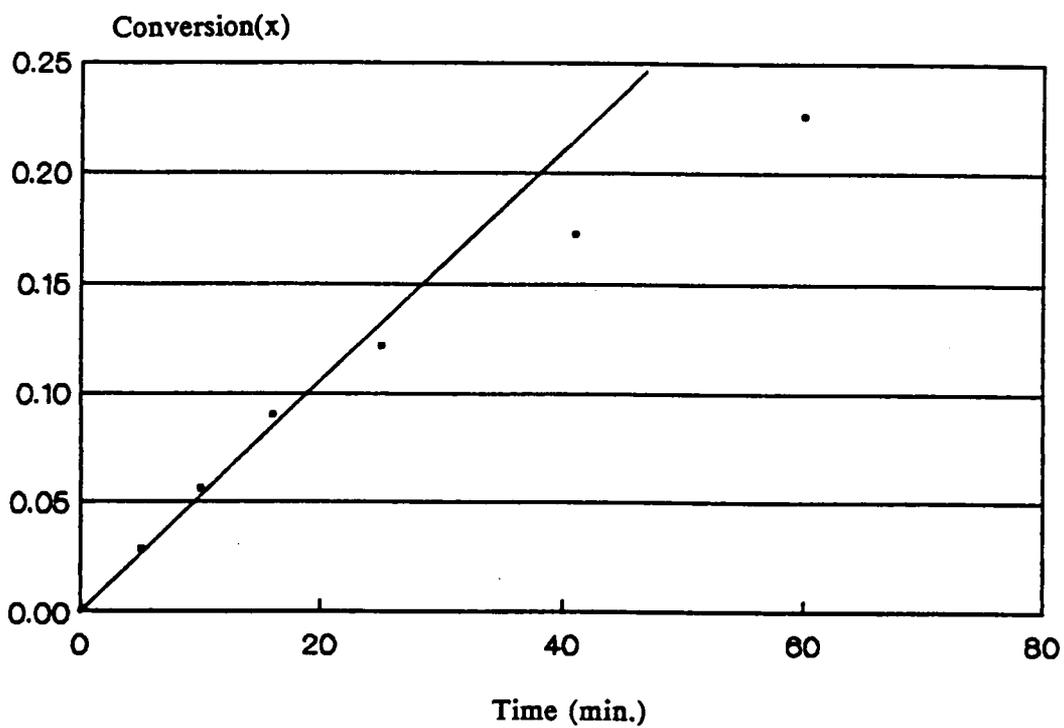


Figure 19. Zeroth order plot on monomer concentration: $[\text{cat}] = 17.2 \text{ mmole/liter}$, $[\text{M}]_0 = 10.3 \text{ mole/liter}$, 47°C

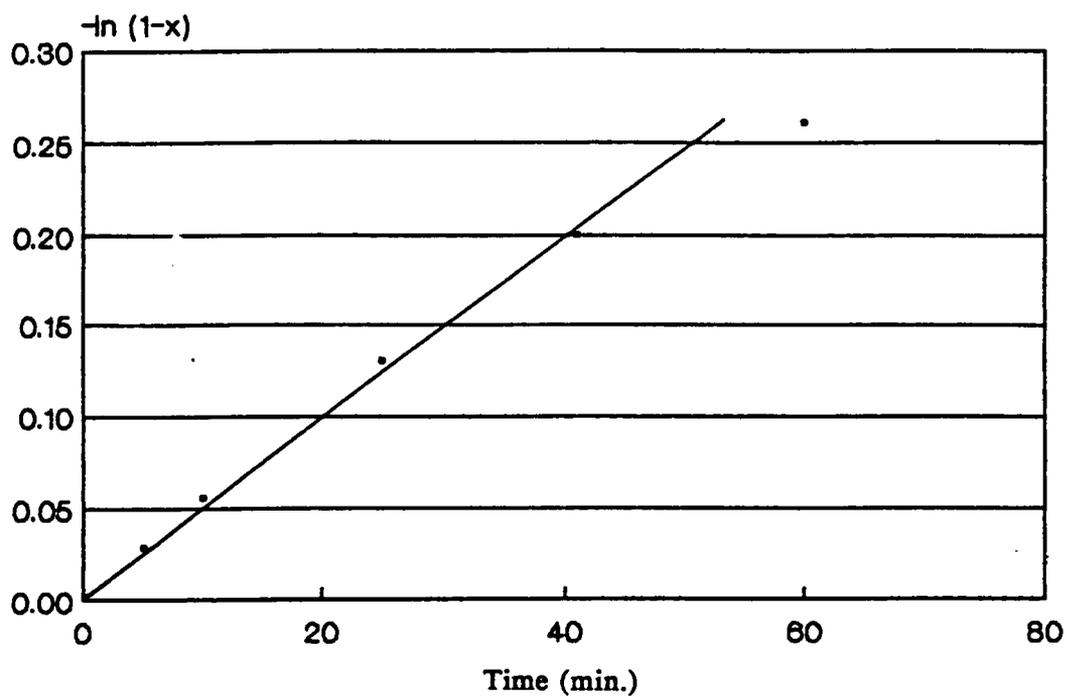


Figure 20. First order plot of monomer concentration: $[\text{cat}] = 17.2 \text{ mmole/liter}$, $[\text{M}]_0 = 10.3 \text{ mole/liter}$, 47°C

lyst concentration should contribute to the difference in slopes. As a result, the rate of polymerization appears to be proportional to the first order of the catalyst concentration (i.e., the concentration of the active centers in the propagation).

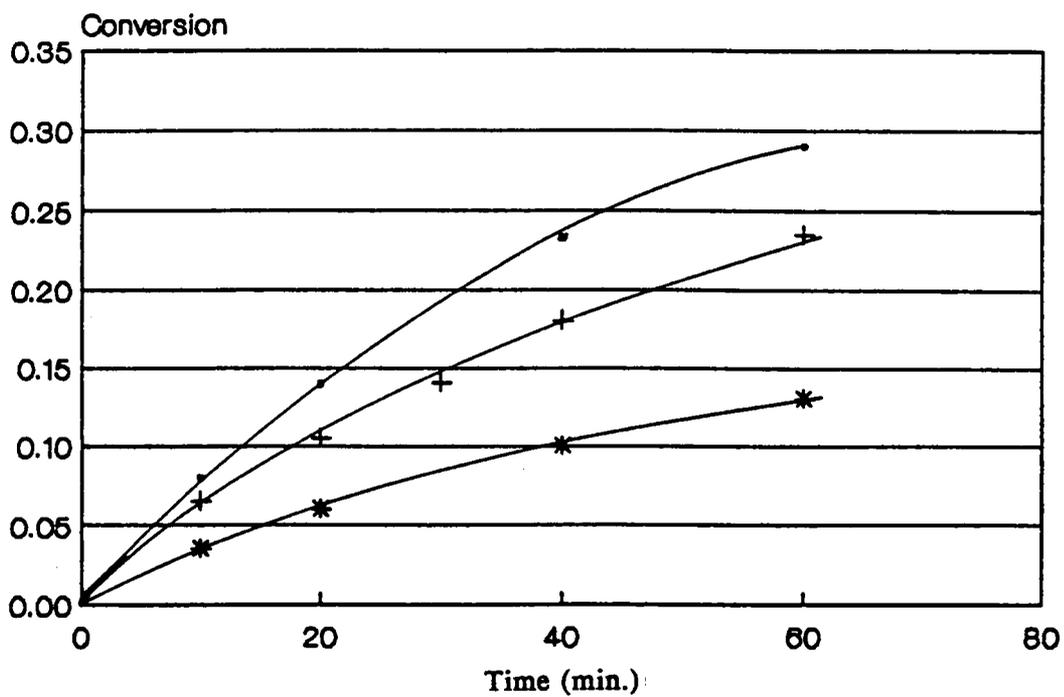
(c) Effect of polymerization temperature

An accelerated propagation rate is observed at elevated temperatures for both bulk and solution polymerizations as expected. In order to determine the activation energy of the propagation, the polymerizations were carried out at various temperatures (30°C, 47°C, 56°C), in methylene chloride, at the same monomer and catalyst concentrations. Conversion versus time curves at three different temperatures are plotted in Figure(24). A differential analysis, where the rates of reactions are directly compared at same monomer and catalyst concentration, was employed to calculate the activation energy of polymerization. However, the integral method which was employed for the catalyst concentration effect was also used and results from both methods are compared. In general, the rate of polymerization can be expressed as a function of temperature, monomer concentration and catalyst concentration.

$$R_p = [M]_0 \frac{dx}{dt} = k_0 \text{Exp}(-E/RT) F([M], [\text{Cat}])$$

$$M = [M]_0 (1 - x),$$

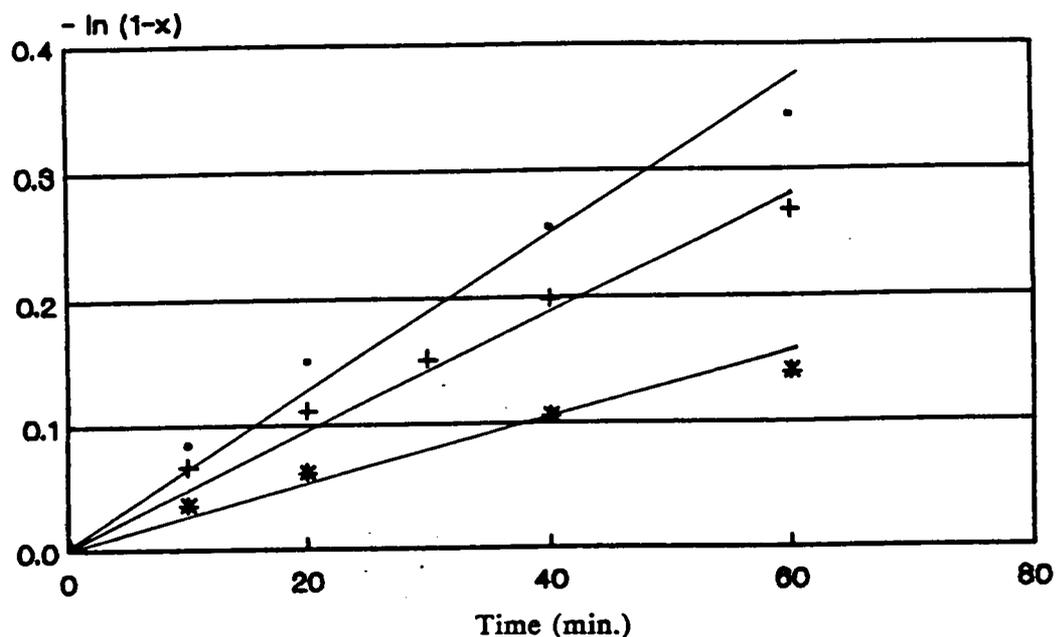
where $[M]$ and $[M]_0$ are present and initial monomer concentration respectively. $[\text{Cat}]$ is the catalyst concentration and x is conversion of monomer to polymer. The rate of polymerization was ratioed at the same conversion of polymerization among reactions at various temperatures as depicted in Figure (25). These comparisons were made at least three conversions and average value was taken. In order to obtain an accurate slope, a conversion vs time plot was fitted with a polynomial equation by linear re-



. [Cat]=43 mmole/liter + [Cat]=32 mmole/liter * [Cat]=17 mmole/liter

[M]₀ = 7.1 mole/liter, 25°C

Figure 21. Conversion vs time at various catalyst concentrations



• [Cat]=43 mmole/liter + [Cat]=32 mmole/liter * [Cat]=17 mmole/liter

[M]₀=7.1 mole/liter, 25 °C
 Slope : k [cat]=0.0082 (•),
 0.0047 (+), 0.0026 (*) min⁻¹

Figure 22. Time vs $-\ln(1-x)$ at various catalyst concentrations: $[M]_0 = 7.1$ mole/liter, polymerization temperature = 25°C

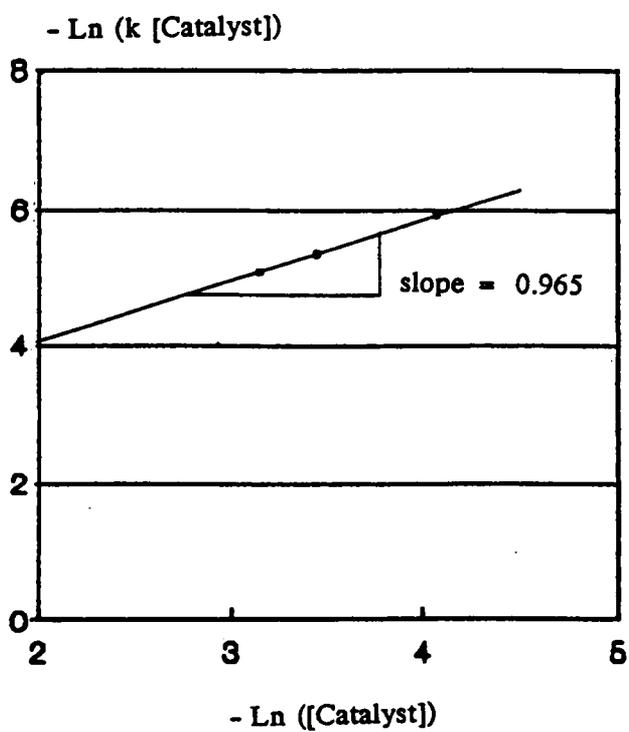


Figure 23. Log-log plot of polymerization rate vs catalyst concentration: $[M]_0 = 7.1$ mole/liter, temperature = 25°C

gression analysis, from which the rate of conversion was expressed as a function of conversion for each experiment. The activation energy of the polymerization is estimated from the tangent of $-\ln(dx/dt)$ vs. $(1/T) \times 1,000$, yielding 11.1 ± 0.5 kcal/mole (45.8 ± 2.1 kJ/mole) in the differential analysis.

In the integral method, $-\ln(1-x)$ vs. reaction time was plotted for each experiment and the slopes of the plots i.e., $k[\text{Cat}]$, were obtained as shown in Figure(26). The rate constants were obtained after division by catalyst concentration. By plotting logarithm of rate constant versus reciprocal temperature, the activation energy was estimated as 9.7 ± 0.4 kcal/mole (40.0 ± 1.6 kJ/mole) from the slope of the Arrhenius plot given in Figure(27).

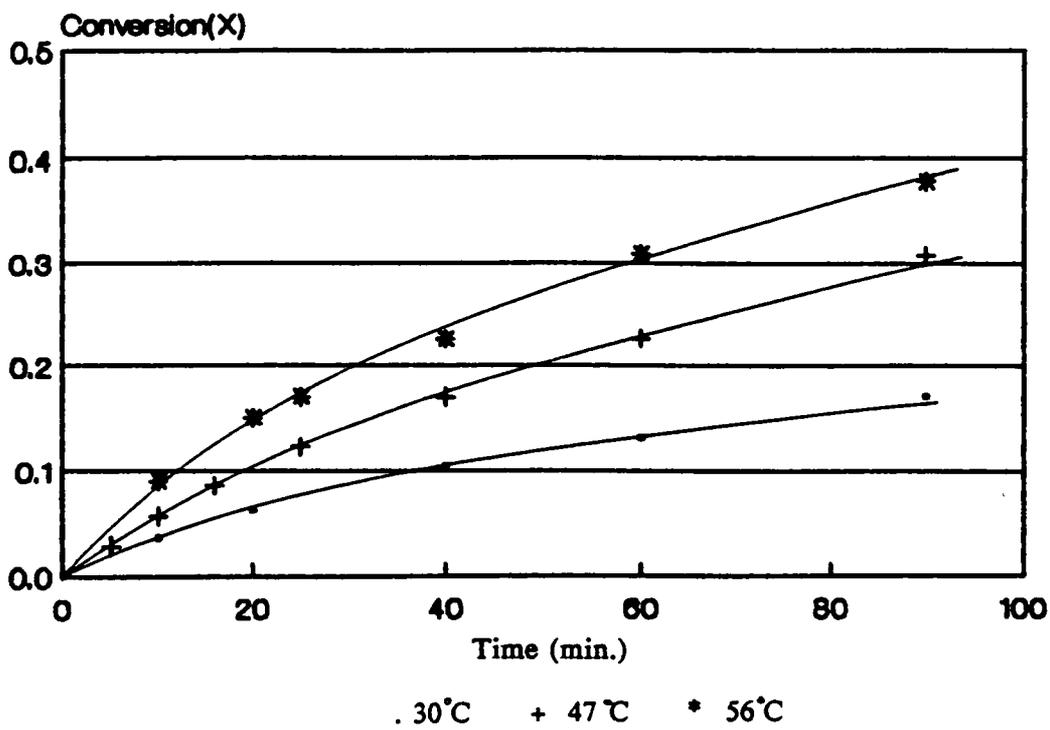


Figure 24. Conversion vs time at various reaction temperatures: [Cat] = 17.2 mmole/liter, [M]₀ = 10.3 mole/liter

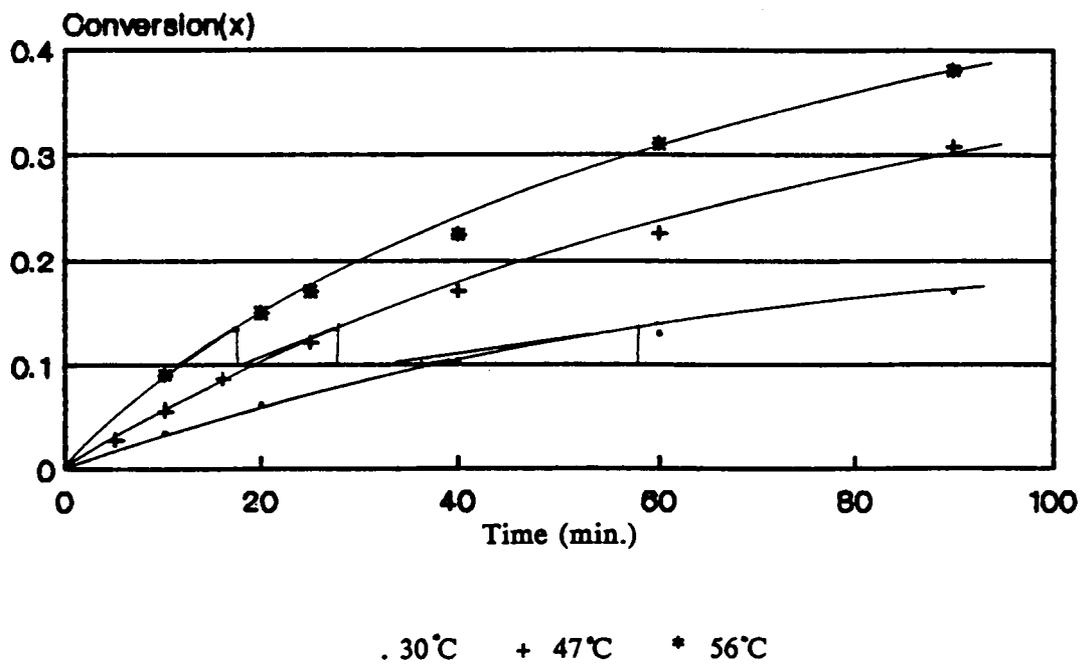


Figure 25. Differential method in evaluation of activation energy: $[\text{Cat}] = 17.2 \text{ mmole/liter}$, $[\text{M}]_0 = 10.3 \text{ mole/liter}$

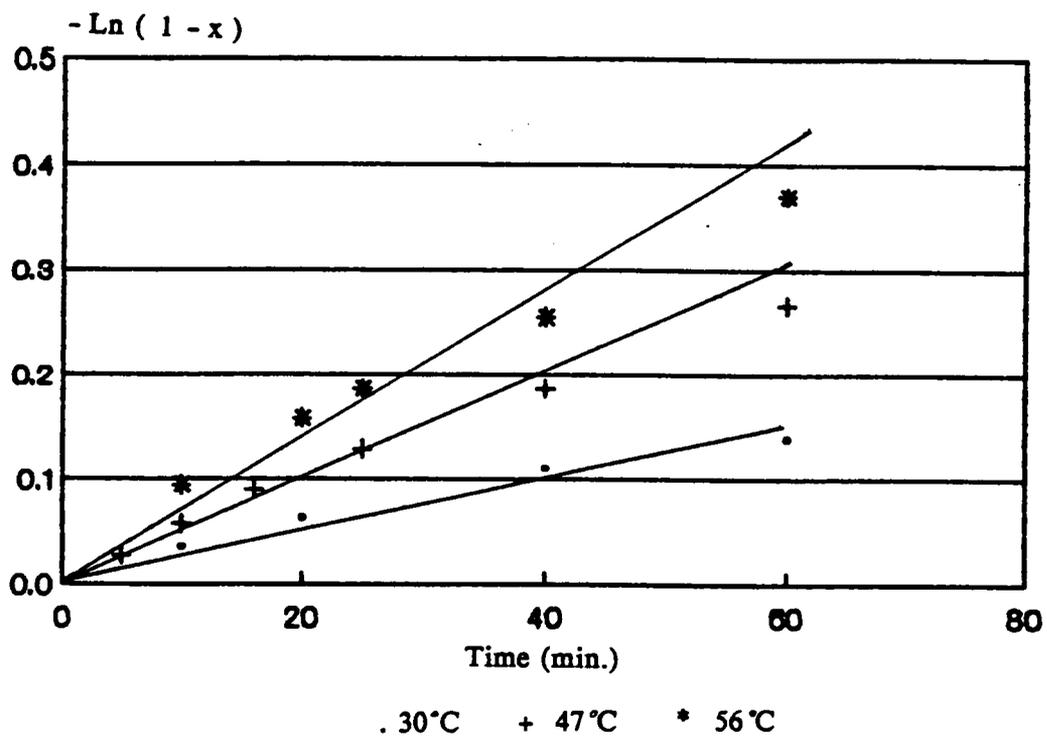


Figure 26. $-\text{Ln}(1-x)$ vs time at various reaction temperatures: $[\text{Cat}] = 17.2$ mmole/liter, $[\text{M}]_0 = 10.3$ mole/liter

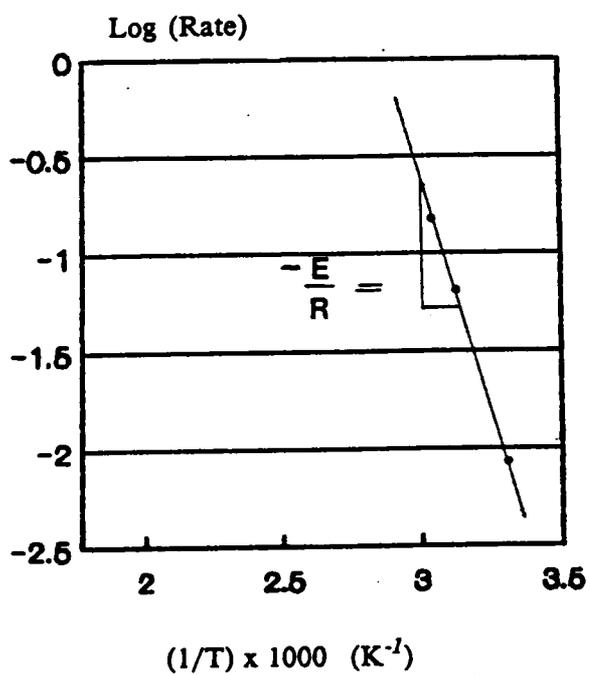
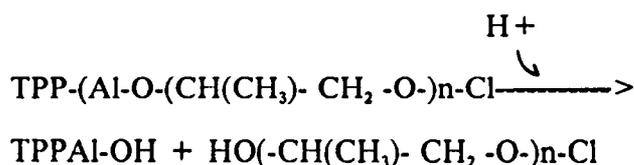


Figure 27. Arrhenius plot for the calculation of activation energy

IV.1.4. Isolation of Polymer and Regeneration of Porphyrin

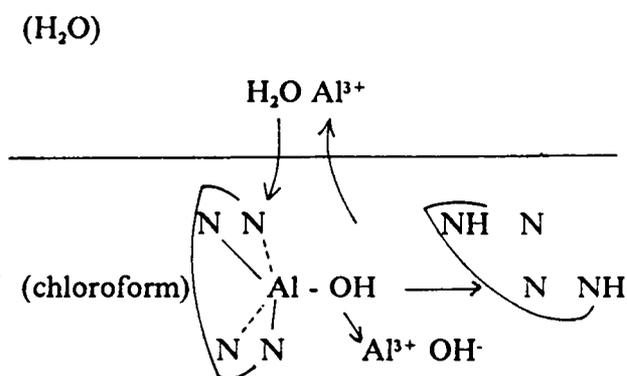
The disadvantage of high cost and the dark purple color of the porphyrin compounds have been major limitations of this catalyst system. After polymerization was terminated, all the volatiles were removed by reduced pressure. Then, the reaction mixture was dissolved in a large amount of hexane. The poly(propylene oxide) was isolated from the reaction mixture according to the procedure outlined in Chapter III. At the same time, catalyst residue was separated quantitatively via precipitation from hexane and subsequent filtration, since hexane is a non solvent for the porphyrins. However, the purple color is still present to some extent due to the slight solubility of the porphyrin compound in the polymeric solution. The solution was further treated with 1-2 wt/vol% of activated charcoal in order to eliminate trace amounts of porphyrin. As the catalyst residue has a considerable solubility in poly(propylene oxide), a dilute polymer solution (ca. 5 wt/vol% in hexane) was preferred for an effective isolation of metalloporphyrin by either precipitation or charcoal adsorption. Alternatively, hydrogenation with Pd/C catalyst was a very effective method to remove residual porphyrin from the solution. It is worthwhile to note that the conjugation in a porphyrin molecule ceases to exist as soon as at least one double bond in the macro-ring(pyrrole) is hydrogenated[102].

Upon terminating the growing polymer chain with an acetone/water mixture, the catalyst residue is believed to be instantaneously converted to tetraphenyl porphyrin aluminum hydroxide, which does not demonstrate any catalytic activity in the polymerization.



To improve the economic feasibility of this system, the regeneration of tetraphenyl porphyrin was attempted. In general, the dissociation of metal from the metalloporphyrin compound is believed to be a reversible process[102]. Moreover, since aluminum form a stable bonding with the nitrogen of porphyrin, concentrated strong acid may be employed for this type of dissociation reaction, often leading to rapid equilibration. However, a quantitative yield is seldom achieved. The proton-NMR spectrum of aluminum porphyrin treated with concentrated hydrochloric acid showed that the pyrrole protons located at both 9.07 and 8.87ppm, indicating that only a part of metalloporphyrin has been dissociated.

Considering this is an equilibration process between associated and dissociated metallic species, a two phase reaction (organic phase:chloroform, aqueous phase:water) was designed to shift the equilibrium to a favorable direction by the elimination of the dissociated metallic species to the aqueous phase. The schematic diagram of a pseudo interfacial reaction is depicted in the following:



The aqueous phase is a proton source for the hydrolysis of nitrogen-aluminum bonds in the aluminum porphyrin. Dissociated aluminum species could be transferred to the

aqueous phase so that the reaction proceeds in the forward direction, resulting in quantitative yields.

The use of an acid was avoided to prevent the formation of acid salts with secondary and tertiary amines of porphyrin. The regenerated porphyrin product was subjected to ¹H-NMR analysis. The pyrrole protons of tetra phenyl porphyrin are initially located at 8.87ppm. When aluminum coordinates inside the porphyrin ring, the pyrrole peak shifted downfield by 0.2ppm due to the electronic attraction by the aluminum atom. Pyrrole proton peak of the regenerated porphyrin was found at the identical location as the original compound(8.87, 8.3, 7.8, 2.5ppm). In addition, the integrated ratios of each peak verify the structure of tetraphenyl porphyrin(8.9:8.3:7.8:2.5ppm = 8/8/12/2) as illustrated in Figure(28). Furthermore, the recovered porphyrin was reused in the synthesis of catalyst for the polymerization of propylene oxide and continues to exhibit good catalyst/initiator activity, yielding polymer with controlled molecular weight and narrow molecular distribution as well.

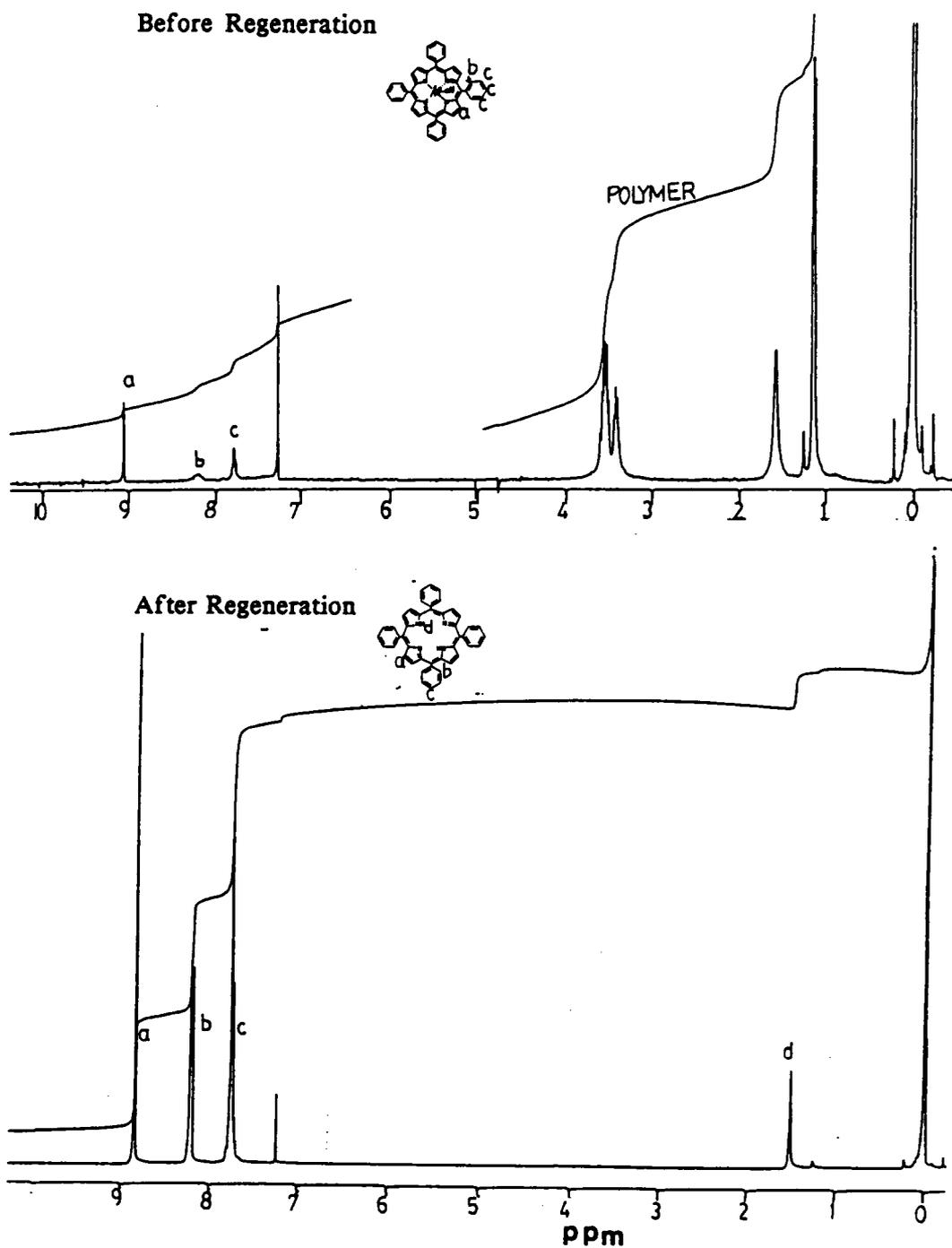


Figure 28. Proton-NMR spectrum of regenerated tetraphenyl porphyrin by pseudo two phase reaction

IV.1.5. Control of Functionality

IV.1.5.1. Modification of catalyst and coupling.

The nature of the original Inoue's aluminum porphyrin catalyst only affords the preparation of monofunctional hydroxyl terminated alkylene oxide polymers[64]. In the synthesis of molecularly designed poly(propylene oxide), the control of the functional end groups may be the most critical aspect of all. Present anionic synthetic routes produce hydroxyl terminated poly(propylene glycol) with di-, tri- or tetra-functionality. However, due to side reactions, perfect functionality is hard to obtain[34b]. Titration of unsaturation by the well known mercury acetate method shows that the oligomer from the anionic technique contains ca.3.5 meq/g polymer of the unsaturated end group. Consequently, only 93% of the polymer chains have difunctional hydroxyl end groups in the case of 2,000 molecular weight product.

The control of functional end groups in poly(propylene oxide) has been attempted through the modification of the original aluminum porphyrin catalyst system. The original system had been prepared via an equimolar reaction of tetraphenyl porphyrin with diethyl aluminum chloride as previously described. In the modification, triethyl aluminum was employed instead of diethyl aluminum chloride to yield a product with third ethyl group, which will readily react with the functional groups carrying labile proton such as hydroxyls or carboxylic acids. The aluminum alkoxide shielded with a huge macrocyclic ring of porphyrin could be generated from the two step route depicted in Figure(29).

The polymerization was initiated by nucleophilic attack of aluminum alkoxide on the methylene groups of propylene oxide. In the course of the polymerization, the target functional group, denoted by 'X' in the figure, may remain at the end of polymer chain unless it interacts with monomers.

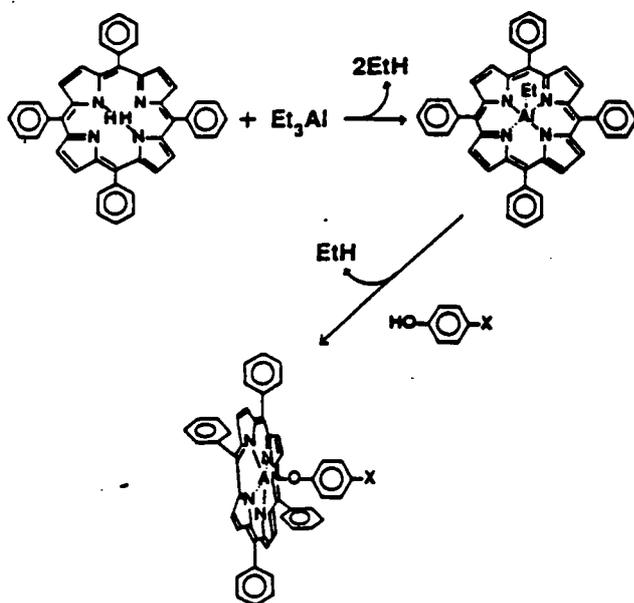
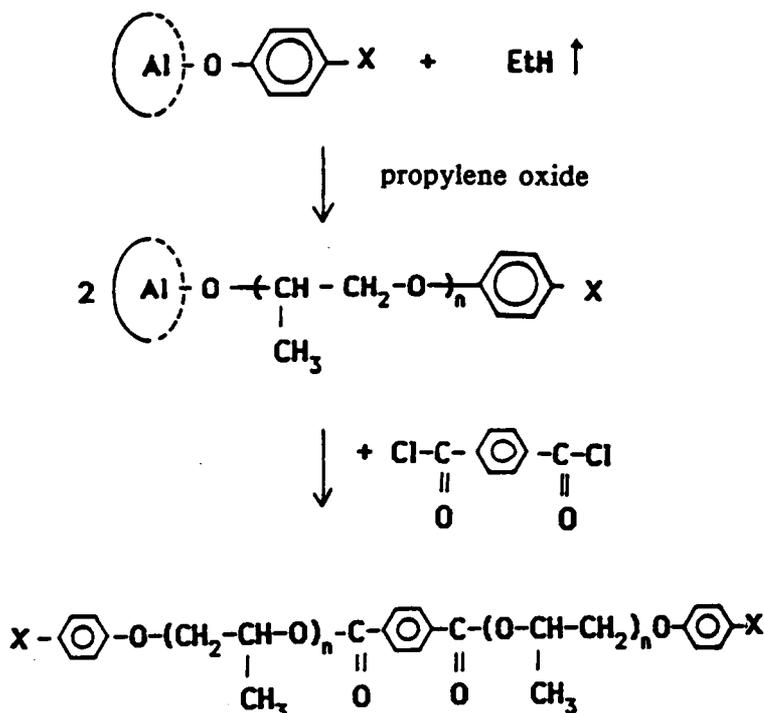


Figure 29. Modification of aluminum porphyrin catalyst system: Reaction conditions; room temperature, nitrogen atmosphere, methylene chloride/THF cosolvent, 4-6 hours for each step

Functionality may be controlled by following approaches; After polymerization is completed, the growing polymer chain may be terminated with multifunctional acid chloride such as terephthaloyl chloride or trimellitic chloride, which serves as a coupling agent for di- or trifunctionality. The reaction between aluminum alkoxide and acid chloride is considered instantaneous and therefore leads to multifunctionality. The reaction scheme is described in the following:



IV.1.5.2. Limitations.

The approach proposed above can not be directly applied to most functional end groups with a labile hydrogen, because the desired functional group 'X' must be inert to the catalyst (TPPAI-Et) during the modification. In addition, no interaction with monomers should occur during the polymerization. In order to control functionality by the coupling reaction, the functional groups must be inert to acid chloride. Unfortu-

nately, the majority of valuable functional groups have been screened out by these limitations. The functional groups containing labile hydrogens such as primary hydroxyls, carboxylic acids or amine groups are all very reactive to the catalyst as well as the coupling agents.

These problems have been resolved by employing the following approaches; First, one may protect the reactive functional groups and then eliminate the protecting group after the coupling reaction. Thus, the desired end group of poly(propylene oxide) may be generated. The second approach involves a post reaction with a secondary hydroxyl terminated polymer which can be obtained by utilizing multifunctional initiators. This post reaction turned out to be a facile route to convert a secondary hydroxyl to a primary amine, primary hydroxyl or carboxylic acid. In this section, a study on the control of functional end groups of poly(propylene oxide) will be extensively discussed. The experimental procedure involved in each functional group has been outline in chapter III in detail. The functional groups of consideration include primary and secondary hydroxyls, primary amines(aromatic), carboxylic acids, methacrylates, etc..

IV.1.5.3. Secondary hydroxyl terminated poly(propylene oxide).

The poly(propylene oxide) prepared by the aluminum porphyrin catalyst in the absence of a co-initiator has monofunctional secondary hydroxyl end group. To be utilized as reactive oligomers for the synthesis of block copolymers via condensation routes and for toughening of crosslinked systems, functionality of two or higher is required. During this study, it was possible to synthesize well-defined poly(propylene oxide) with difunctional or even multifunctional secondary hydroxyl end groups through the modification of the aluminum porphyrin catalyst system. The reaction scheme for the synthesis of difunctional hydroxyl terminated poly(propylene oxide) using bisphenol A as co-initiator as well as chain transfer agent is illustrated in Figure(30). It was possible to

utilize an excess amount of co- initiator as an effective chain transfer agent, which essentially allows catalyst concentration to be reduced, which, in any practical system, could be quite significant. Under the experimental conditions as outlined in Table(11), it was demonstrated that it was possible to use a ten fold excess of chain transfer agent, which would allow one to reduce the catalyst concentration by an order of magnitude for a particular desired molecular weight.

The calculated and measured number average molecular weights of the synthesized polymers are tabulated in Table(12) together with molecular weight distributions. As can be seen from this table, the number average molecular weights that are determined by using GPC and ^1H -NMR are in good agreement with the calculated values from monomer/chain transfer agent ratios. The data in Table(12) basically indicates this fact. For example, in run No.4, the molecular weight can be controlled by the concentration of the chain transfer agent. If this had not been the case, the number average molecular weight would have been around 10,000 g/mole instead of the approximately 1,000 g/mole value observed. This is significant for the preparation of poly(propylene oxide) with controlled molecular weight and narrow molecular weight distribution at low levels of the aluminum catalyst concentration. Clearly, the propagation step must be slow relative to the transfer step to achieve such a narrow distribution.

However, at higher concentrations of chain transfer agent slower propagation rates were observed. In run No.4, where the $[\text{I}]/[\text{CAT}]$ ratio was 10, a quantitative conversion of polymerization was observed after 120 hours even though the polymerization was conducted at 40°C in bulk reaction. The reaction took about only 24 hours in the case of run No.2, where the ratio of chain transfer agent to catalyst was 3. The kinetic effect of chain transfer agent concentration was studied varying the $[\text{bisphenol A}]/[\text{TPPA}|\text{Cl}]$ ratio from 0 to 6. As shown in Figure(31), it was found that each equivalent of bis A.

to catalyst reduced the polymerization rate by ca. 7 ± 1 % at given experimental conditions.

Difunctional co-initiators employed in the polymerization include bisphenol A, ethylene glycol, hexane diol, propylene glycol, xylene diol and hydroxy benzoic acid. Difunctional hydroxyl terminated poly(propylene oxide) synthesized using bisphenol A was analyzed by GPC to determine the molecular weight and molecular weight distribution. The polymer solution (0.1 wt% in THF) was injected into styragel GPC column and the eluted polymer solution was detected by both refractive index(RI) and ultraviolet(UV) detector at 254nm or 218nm. The poly(propylene oxide) was detected by the UV detector yielding same trace as detected by alternative RI detector (Figure (32)). This again confirms that the co-initiator segment was incorporated into the polymer chain.

Figure(33) shows that the isopropylidene and the aromatic group of bisphenol A were detected in the FT-IR spectrum of the poly(propylene oxide) at 1640 cm^{-1} and 1511 cm^{-1} , respectively. ^1H -NMR was also utilized to analyze the structure of poly(propylene oxide) and the spectrum is given in Figure(34). All the peaks were properly assigned in accordance with the proposed structure. The peaks centered at 1.6ppm, 6.7ppm and 7.1ppm indicate the incorporation of bisphenol A in the polymer chain. The molecular weight of the polymer could be estimated by ratioing the aromatic peaks of bisphenol A to the aliphatic hydrogen peaks from poly(propylene oxide), which generated corresponding number average molecular weights to those obtained from GPC analysis. Table(13) summarizes the molecular structures of di- and trifunctional hydroxyl terminated poly(propylene oxide)s prepared by utilizing various co-initiators.

Synthesis of multifunctional hydroxyl terminated poly(propylene oxide) may be also achieved by coupling of the aluminum porphyrin catalyst with the diglycidyl ether of bisphenol A(DGEBA). The DGEBA has two terminal epoxide rings which may be

opened by the catalyst. Thus, if the $[TPPAICl]/[DGEBA]$ ratio is set to 2, difunctional hydroxyl terminated polymer can be obtained by subsequent addition of propylene oxide monomer after two catalyst molecules are coupled by one DGEBA molecule as depicted in Figure(35). Furthermore, if the ratio is 1.5, trifunctional hydroxyl terminated poly(propylene oxide) could be obtained. The topology, functionality and theoretical number average molecular weight of the polymer may be predicted by the number of catalyst molecules combined with DGEBA as illustrated in Table(14). As the ratio of $[TPPAICl]/[DGEBA]$ decreased, the molecular weight distribution broadened. However, the key feature is that one may obtain star shaped poly(propylene oxide) with multi-functional hydroxyl end groups.

Essentially an "inside-out" star-like macromolecule be synthesized. Clearly, there are some limits if one wishes to avoid gelation. The results of this experiment are presented in Table(15).

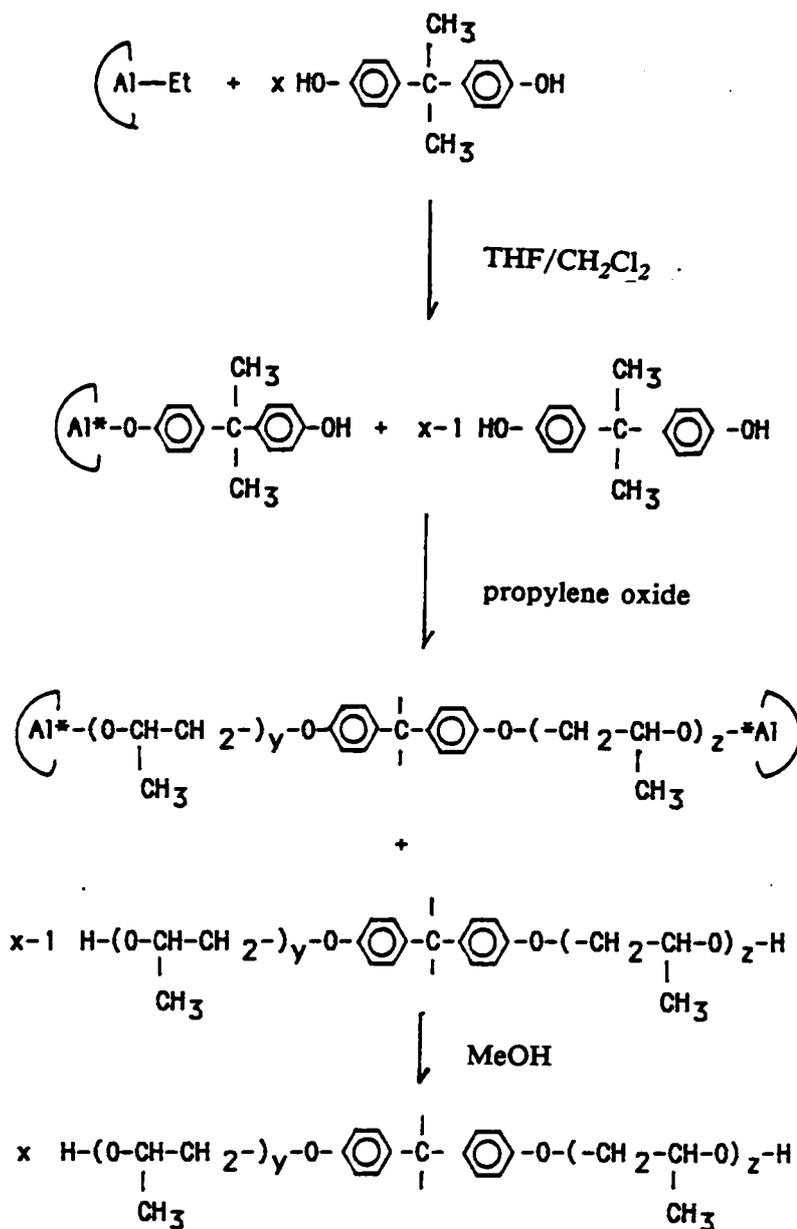


Figure 30. Reaction scheme for difunctional hydroxyl terminated poly(propylene oxide) with bisphenol A modified catalyst

Table 11. Experimental conditions for the synthesis of hydroxyl terminated poly(propylene oxide)

RUN	X(=[I]/[CAT.])	TEMP.(°C)	TIME(h)	CONV.
1	3	27	55	QUANT.
2	3	40	24	QUANT.
3	5	40	160	35 %
4	10	40	120	QUANT.
5	3	27	120	QUANT.
6	3	27	120	QUANT.
7	3	27	240	45 %

i) Initiators

- RUN 1,2 : [I] =[BIS. A]
- RUN 4 : [I] =[BIS A], BULK REACTION
- RUN 3 : [I] =[HYDROQUINONE], BULK REACTION
- RUN 5 : [I] =[5-NITRO ,m-XYLENE α,α' DIOL]
- RUN 6 : [I] =[P-HYDROXY, NITRO BENZOIC ACID]
- RUN 7 : [I] =[HEXANE DIOL]

ii) Solution polymerizations were run at 40-60 % monomer by volume.

Table 12. Calculated and observed molecular weights of difunctional hydroxyl terminated poly(propylene oxide)s

RUN	\bar{M}_n calc	\bar{M}_n GPC	\bar{M}_n NMR	MWD
1	2700	3500	-	1.21
2	2600	3000	2730	1.06
3	1000	900	980	1.06
4	1010	900	1030	1.07
5	4500	5400	-	1.06
6	4500	5000	-	1.05
7	1150	1000	-	1.14

- i) \bar{M}_n CALC was obtained by [Monomer]/[I] ratios.
- ii) \bar{M}_n GPC was obtained by polystyrene standards.
- iii) \bar{M}_n NMR was calculated by hydrogen ratio of methyl group to aromatic group.

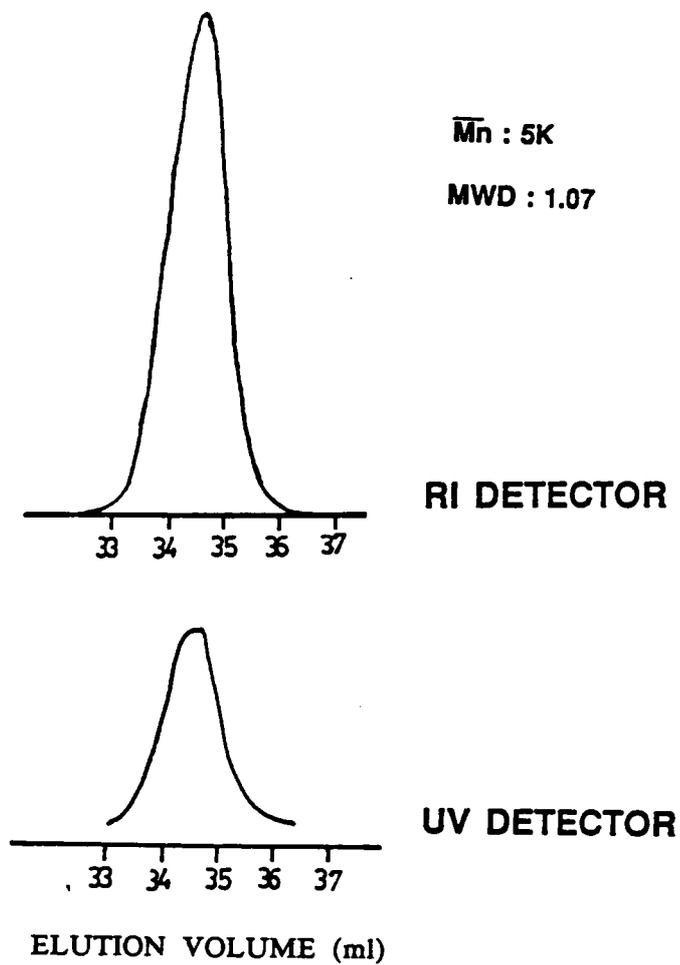


Figure 32. GPC trace of typical difunctional hydroxyl terminated poly(propylene oxide)

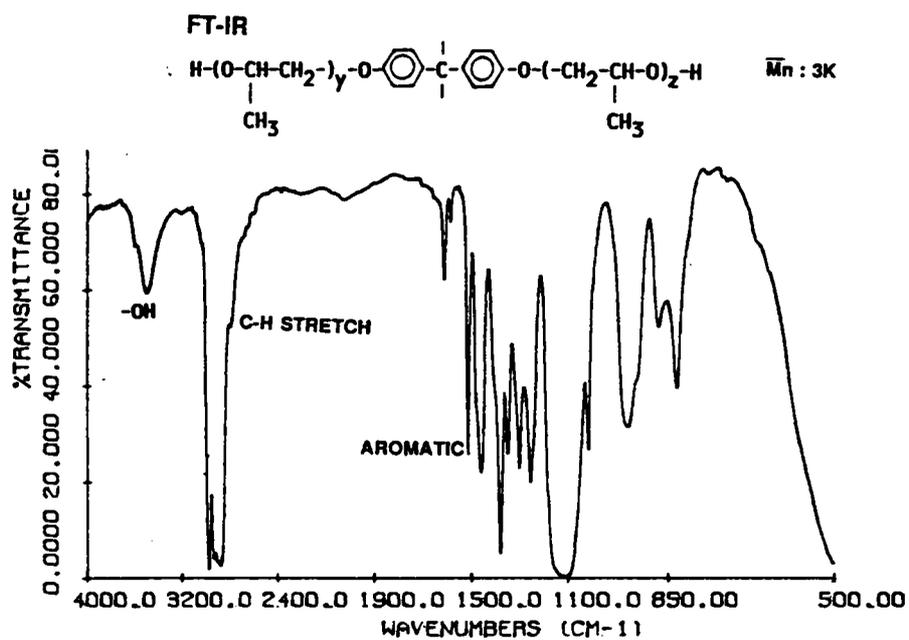


Figure 33. FT-IR spectrum of poly(propylene oxide) prepared from TPPAIEt/Bis A system

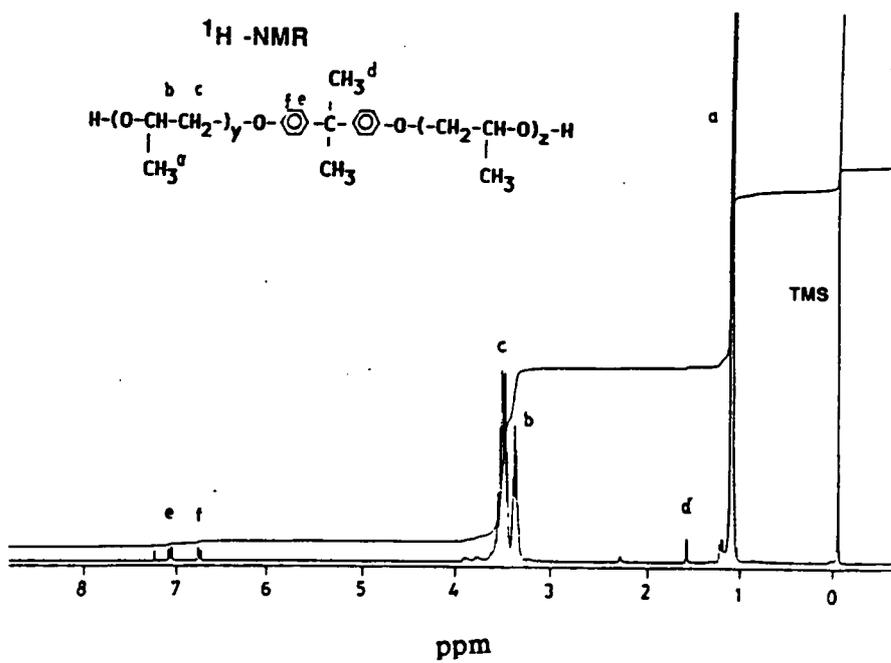


Figure 34. Proton-NMR spectrum of poly(propylene oxide) prepared from TPPAI Et/Bis A system

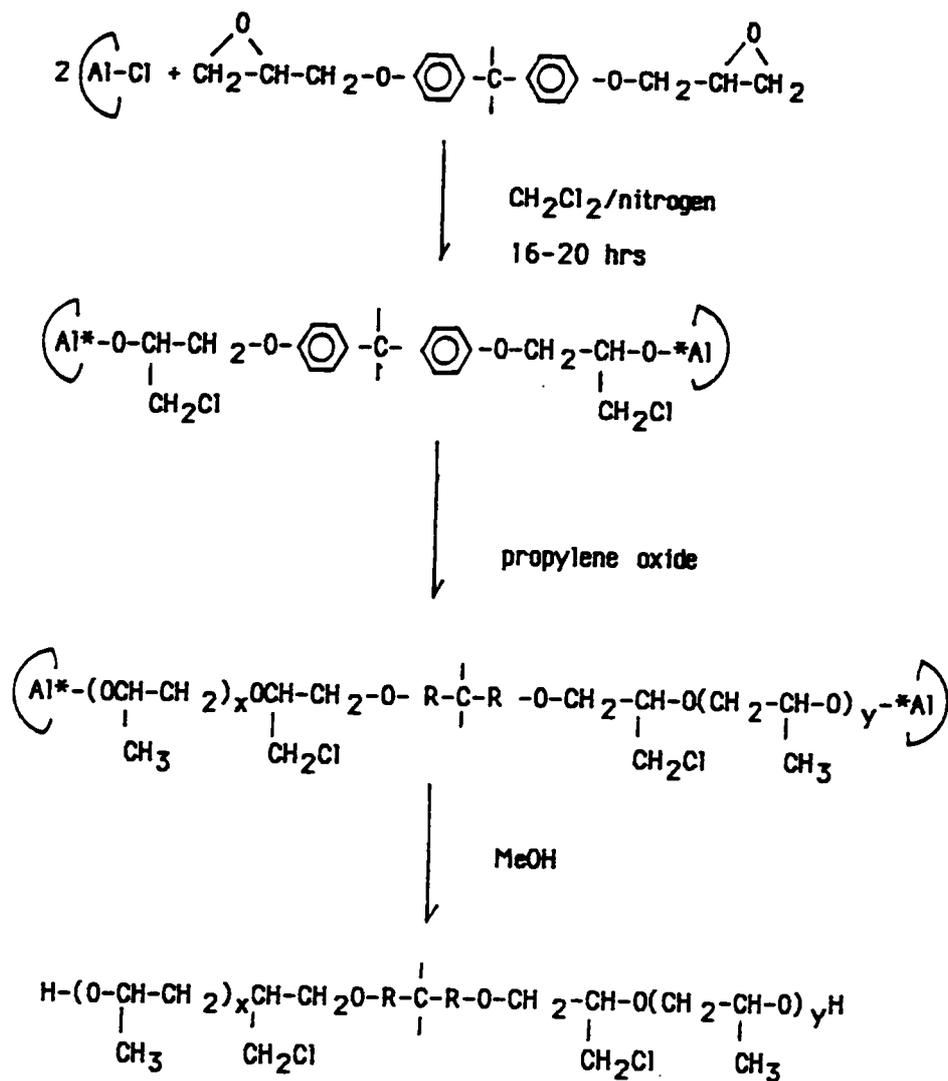
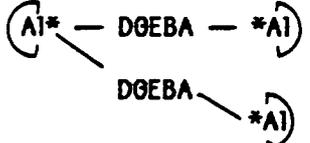
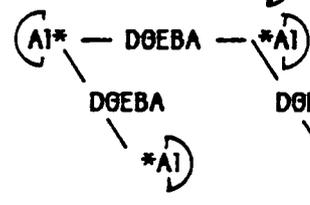


Figure 35. Polymerization of propylene oxide with DGEBA prereacted catalysts

Table 14. Reaction of aluminum porphyrin catalysts with DGEBA

[Catalyst]:[DGEBA]	Proposed Structure	FAVE.	$[\bar{M}_n]$
2 : 1		2	$[\bar{M}_n]^1 \times 2$
3 : 2		3	$[\bar{M}_n]^1 \times 3$
4 : 3		4	$[\bar{M}_n]^1 \times 4$

- i) $[\bar{M}_n]^1$ is the number average molecular weight calculated by $[\text{Monomer}]/[\text{Catalyst}] \times (\text{Mol. wt. of Monomer})$.
- ii) FAVE is the expected functionality of hydroxyl end group after polymerization and termination.
- iii) Symbol '*' represents active site for propagation.

Table 15. Experimental results of DGEBA prereacted catalyst system

RUN	[DGEBA]/[Cat.]	$[\overline{M}_n]^1$	$[\overline{M}_w]$	$\langle MWD \rangle$	f_{av}^*
1	0.5	3500	6900	1.31	1.9
2	0.5	3500	7000	1.31	-
3	0.6	6600	16400	-	2.3
4	1.0	5800	22800	1.7	4.9

i) $[\overline{M}_n]$ and $\langle MWD \rangle$ were obtained by GPC with polystyrene standards.

ii) The functionality, " f_{av} " was obtained semiquantitatively from the hydroxyl peak in the FT-IR spectra.

iii) $[\overline{M}_n]^1$ is number average molecular weight calculated by $[\text{Monomer}]/[\text{catalyst}] \times (\text{mol. wt. of Monomer})$.

IV.1.5.4. Primary hydroxyl terminated poly(propylene oxide).

The reactivity of secondary hydroxyl end groups is often not high enough to be utilized in certain rapid processes such as polyurethane reaction injection molding. Secondary hydroxyl terminated poly(propylene glycol) demonstrates lower reaction rates with isocyanates relative to primary hydroxyl terminated poly(tetramethylene oxide) of similar molecular weight by the factor of three or more[4,5].

In the conventional anionic route, ethylene oxide is added at the end of the polymerization of propylene oxide to achieve the primary hydroxyl terminated polymer[8], but inherent problems may arise from this approach. Typically, to accomplish a quantitative amount of primary hydroxyl end groups, one has to add a considerable amount of ethylene oxide monomer, since the ethylene oxide tends to propagate rapidly at the primary alkoxide growing species, once formed. It is well recognized that quantitative primary hydroxyl end group may be obtained if 25-40 % of total repeating unit is ethylene oxide. Consequently, the polymer with primary hydroxyl end groups is essentially a block copolymer of propylene oxide and ethylene oxide. But properties of poly(ethylene oxide) blocks such as crystallinity and water solubility, may not be desirable features for certain purposes. For elastomeric applications, crystallization makes a material stiffer upon stretching, yielding a low elongation point as well as high hysteresis. To avoid these problems in the primary hydroxyl terminated poly(propylene oxide) containing poly(ethylene oxide), the following approach has been attempted to prepare primary hydroxyl terminated poly(propylene oxide) without the ethylene oxide incorporation: Aluminum-porphyrin catalysts were prepared by an equimolar reaction of tetraphenyl porphyrin and triethyl aluminum. The catalyst was further modified with benzyl alcohol, the protective initiator, which resulted in the benzyloxy derivative of the catalyst. By subsequent addition of propylene oxide monomer, followed by propagation

and termination with methanol, benzyl ether terminated poly(propylene oxide) has been obtained(Figures(36,37)).

The molecular weights and molecular weight distributions of the polymers were obtained by GPC(10mg polymer /10ml THF). The number average molecular weight obtained from GPC shows fair agreement with the value estimated from the following equation as summarized in Table(16).

$$[Mn] = \{ [M]_0 / [\text{Benzyl alcohol}] \} \times 58 \times \text{Conversion.}$$

,where $[M]_0$ is the initial monomer concentration and 58 is the molecular weight of each repeating unit. The resulting polymer was also analyzed by Fourier Transformed Infrared Spectroscopy(FT-IR), which showed an absorbance at 700cm^{-1} indicative of carbon-oxygen bonds with aromatic substitution on the carbon atom. The product was also characterized by ^1H -NMR and ^{19}F -NMR. In the proton-NMR, peaks appeared at 7.25ppm and 4.55ppm, indicating that the aromatic and the methylene group of the benzyl moiety are present. The ^{19}F -NMR of derivatized hydroxyl end group by fluoroacetic anhydride showed peaks at 37.6 and 36.9ppm relative to an internal standard (mono fluorobenzene) at 0.0ppm. Peaks at 37.6 and 36.9ppm are indicatives of secondary hydroxyl groups and trifluoroacetic acid.

After hydrogenation of the benzyl ether terminated PPO, the polymer was analyzed by FT-IR. FT-IR does not show the characteristic absorbance of the carbon-oxygen with aromatic substitution on carbon atom (700cm^{-1}). This absence indicates the quantitative hydrogenolysis of the benzyl group. The ratio of the hydroxyl absorbance at $3200\text{-}3600\text{cm}^{-1}$ to the reference C-H stretch is almost doubled, from 8.9% before hydrogenation to 17.7% after hydrogenation. This change indicates an increase in hydroxyl groups due to hydrogenation, consistent with the removal of the benzyl group.

The polymer was also analyzed by proton and fluorine-NMR spectroscopy. Proton-NMR shows no peaks at 7.25 or 4.55ppm, again demonstrating the absence of

aromatic and methylene hydrogen atoms of the benzyl groups after hydrogenolysis. Fluorine-NMR of the polymer derivatized by trifluoroacetic anhydride shows peaks at 37.9, 37.6 and 36.9ppm relative to the standard of monofluorobenzene at 0.0ppm. The peak at 37.9ppm indicates that the primary hydroxyl groups have been generated through hydrogenation. A ratio of the integrations of the peaks corresponding to primary and secondary hydroxyl groups reveals a ratio of 15:17 after hydrogenolysis, which is consistent with about half primary and half secondary hydroxyl groups. These spectroscopic analysis of benzyl ether terminated poly(propylene oxide) and its hydrogenated adduct are presented in Figures(38-40). A gel permeation chromatography trace of the polymer retains the same shape before and after the hydrogenolysis with same MWD of 1.08. However, after the hydrogenation, the elution volume of the GPC trace(RI detector) is slightly shifted to higher retention time([Mn] changed from 1850 to 1750). No chromatogram was traced by the UV detector (254nm) due to the complete disappearance the benzyl group as shown in Figure(41).

This synthetic approach demonstrates the possibility of using benzyl alcohol as a single molecular protective initiator for the polymerization of propylene oxide using a porphyrin catalyst. Subsequent removal of the benzyl group yields a polyether polyol having primary hydroxyl groups on the termini from which the benzyl group is removed.

The hydroxyl number of poly(propylene oxide) oligomer having both a benzyl ether and a secondary hydroxyl group were determined via phthalic anhydride/KOH titration method and the oligomer was coupled with terephthaloyl chloride. After the reaction, refluxing THF for 5 hours in the presence of triethyl amine, the GPC trace shows that coupling has occurred by a decrease in the observed retention time, indicating an increase in molecular weight. Infrared spectroscopy in Figure(42) shows a peak corresponding to ester carbonyls (1737cm^{-1}), indicating that terephthaloyl esters are formed.

Subsequent removal of the benzyl groups yields poly(propylene oxide) having primary hydroxyl groups at both ends.

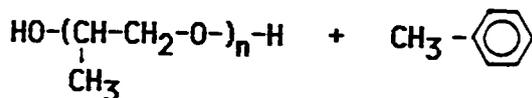
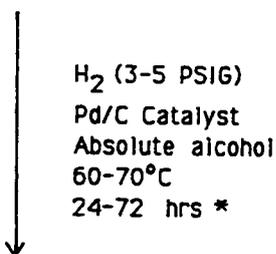
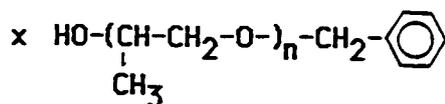
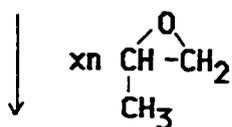
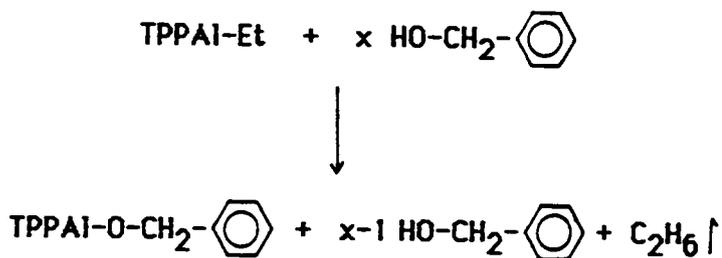
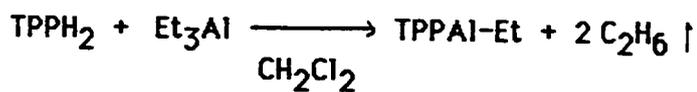


Figure 36. Synthesis of poly(propylene oxide) with primary hydroxyl end group(s)

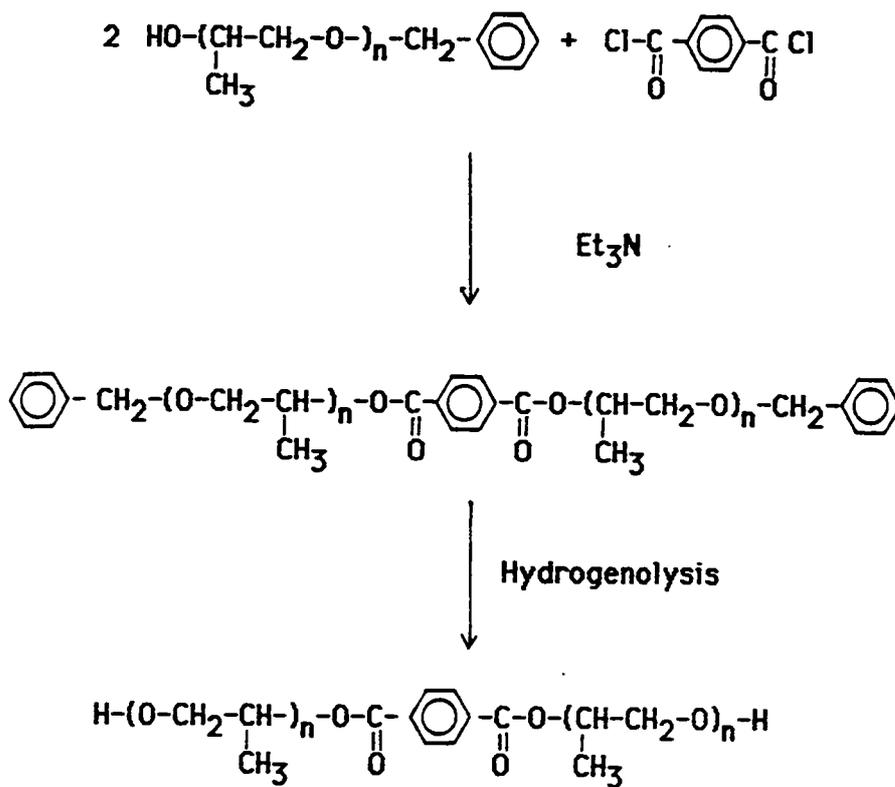


Figure 37. Difunctional primary hydroxyl terminated poly(propylene oxide) by coupling with terephthaloyl chloride

Table 16. Reaction conditions and results of benzyl ether terminated poly(propylene oxide) synthesis

Run	$[I]^0/[cat]$	$[Mn]_{th}$	time	temp.	conv.	$[Mn]_{gpc}$	$[Mn]_{nmr}$
1 ⁱⁱ	6	282	-	r.t.	100%	-	282
2 ⁱⁱⁱ	4	1700	70hrs	r.t.	96%	1800	1850
3 ⁱⁱⁱ	3	4200	72hrs	r.t.	95%	4500	4900

i) $I=[\text{benzyl alcohol}]$, $[cat]=[\text{TPPA1-Et}]$

ii) The run 1 is for a model compound which has only three repeating units.

iii) The polymerizations were carried out in methylene chloride solution with ca. 50 % solid contents.

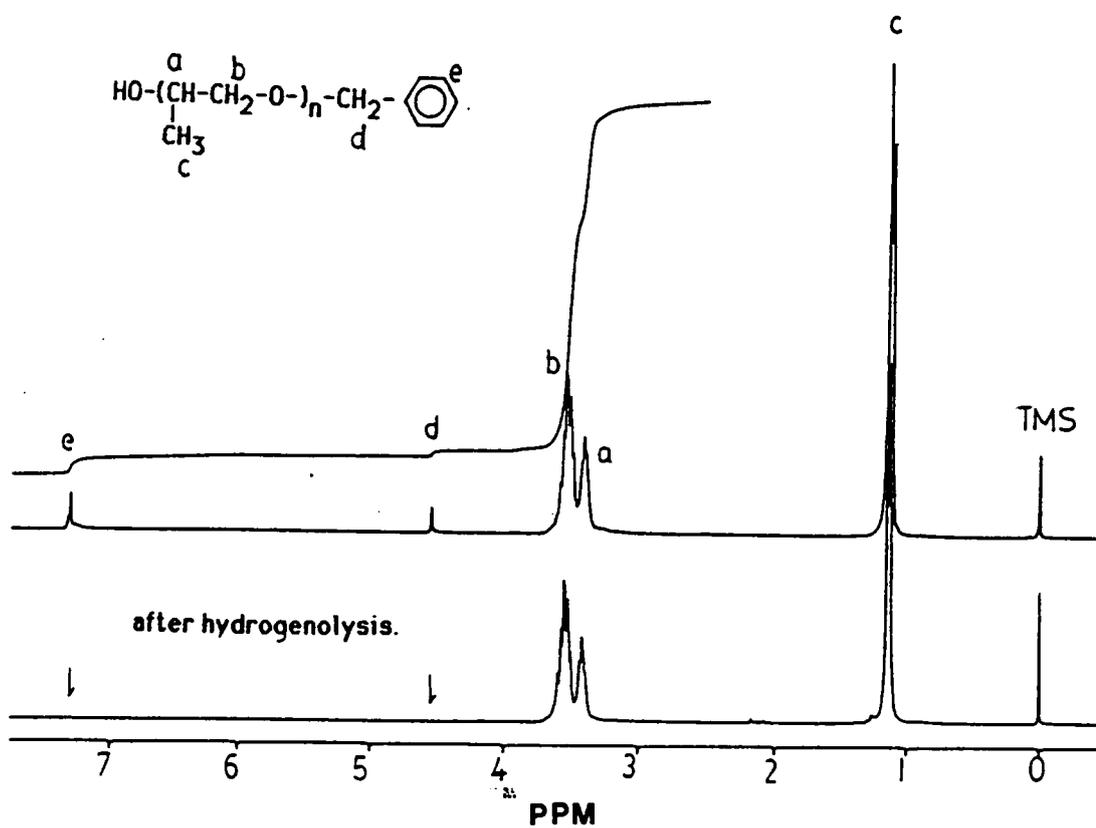


Figure 38. Proton-NMR spectra of benzyl terminated poly(propylene oxide) before and after hydrogenolysis

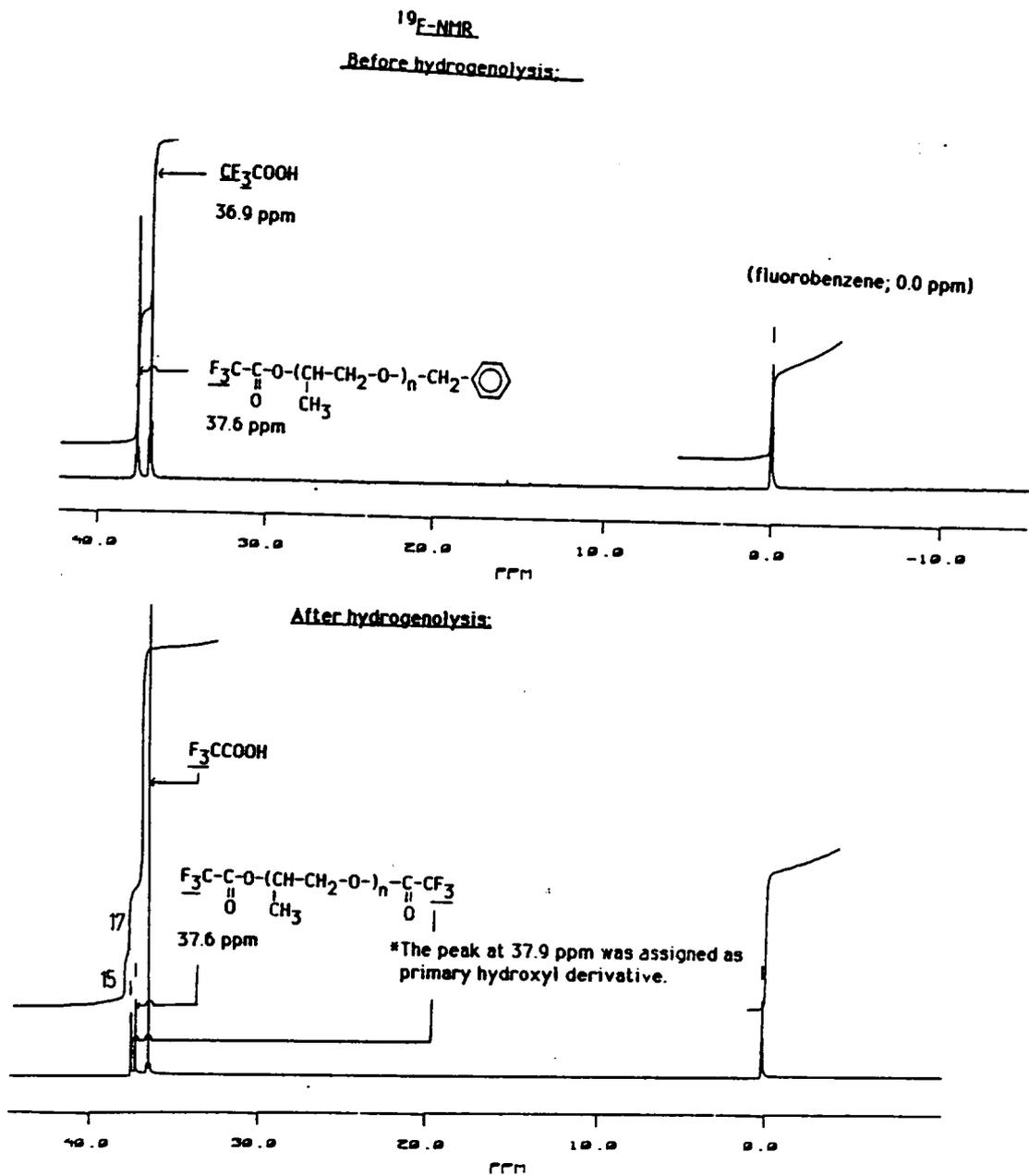


Figure 39. Fluorine-NMR analysis of end groups of poly(propylene oxide) after derivatization by trifluoroacetic anhydride

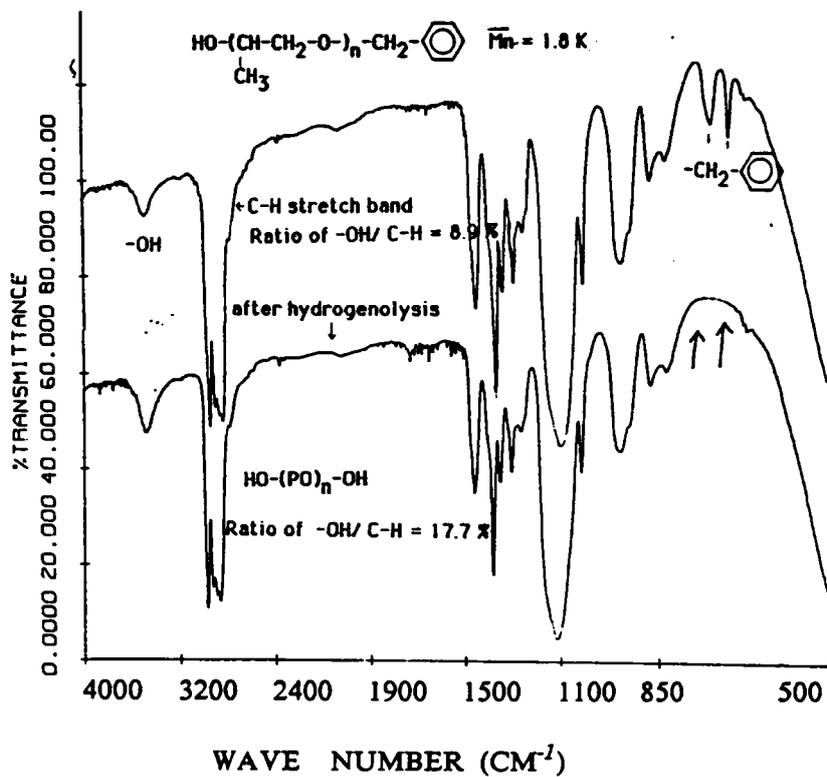


Figure 40. FT-IR spectra of poly(propylene oxide) before and after hydrogenolysis of benzyl ether group

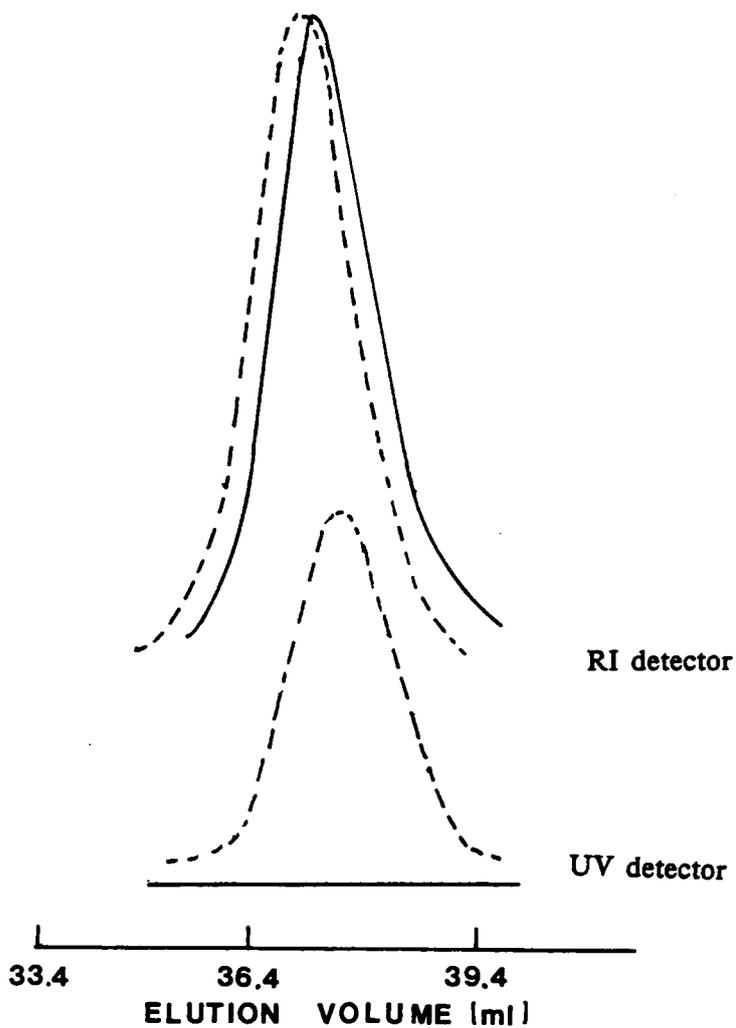


Figure 41. GPC traces of benzyl ether terminated poly(propylene oxide) and its hydrogenated product: dotted line = before hydrogenolysis, solid line = after hydrogenolysis, $[M_n] = 1750-1850$ g/mole, $MWD = 1.08$

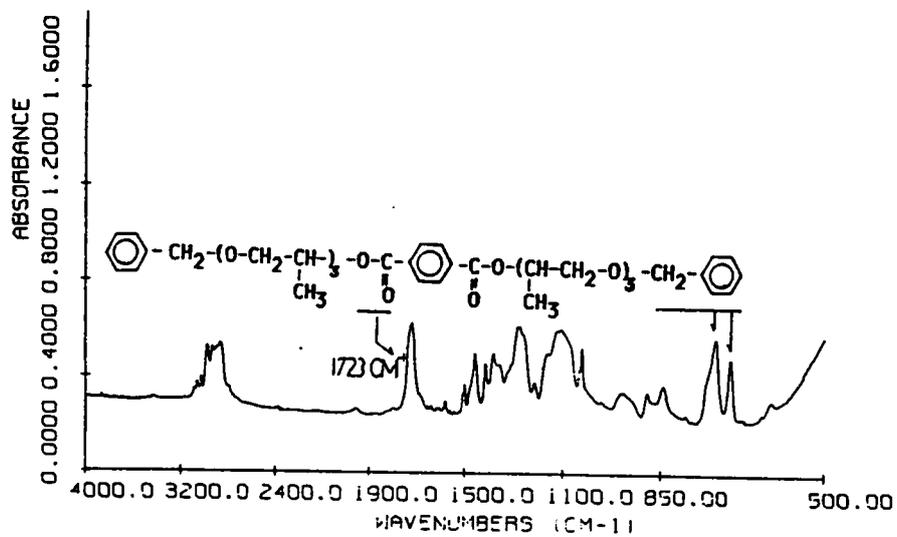


Figure 42. FT-IR spectrum of difunctional benzyl ether terminated propylene oxide oligomer

IV.1.5.5. Amine terminated poly(propylene oxide).

(a) By Modified Catalyst

In a similar fashion, amine terminated poly(propylene oxide) has been prepared by employing appropriate initiators and/or by the modification of the "terminal" hydroxyl groups. The polymerization of propylene oxide with nitrophenyl modified aluminum porphyrin catalyst is schematized in Figure (43), leading to difunctional aniline terminated polymer. By terminating the growing chain with a protonic compound, poly(propylene oxide) would be obtained with different terminal functional groups, i.e., hydroxyls and amines.

The calculated and measured number average molecular weights of the synthesized polymers are tabulated in Table(17) together with molecular weight distributions. As can be seen from the table, the number average molecular weights as determined by gel permeation chromatography are in good agreement with the values calculated from the charge ratio of [propylene oxide] to [nitrophenol].

Alternatively, the number average molecular weights of the polymers could be calculated by the integration of the aromatic and aliphatic protons in the proton-NMR spectra. The aromatic protons adjacent to the nitro group and ether bond appear as a doublet centered around 7.0ppm and 8.2ppm, respectively. Upon reduction via catalytic hydrogenation, these peaks completely relocate to 7.6ppm and 7.7ppm, indicating quantitative conversion of hydrogenation.

The polymer was analyzed by FT-IR before and after hydrogenation. From FT-IR spectra, transmittance at 1650cm^{-1} , indicative of N-O asymmetry, disappeared after hydrogenation and the doublet at $3460\text{-}3350\text{cm}^{-1}$ and the single peak at 1650cm^{-1} appeared due to N-H stretch of primary amine(Figures(44,45)). The primary amine terminated PPO was titrated by a potentiometric titrator, which again estimated the molecular weight of PPO consistent with GPC and calculated values.

Table 17. Experimental results of amine terminated poly(propylene oxide) synthesis

RUN	[I]/[C]	[Mn] ^{calc.(1)}	[Mn] ^{gpc(2)}	[Mn] ^{nmr(3)}	[Mn] ^{titr.}	MWD
1	1	5500	4800	6500	6100	1.10
2	3	3100	2800	2700	3300	1.13
3	5	2000	2000	1900	2150	1.16
4	10	1300	1300	1290	1150	1.20

* [I] and [C] represent initiator(nitrophenol) and porphyrin catalyst, respectively.

* The polymerizations were carried out in bulk at room temperature.

* The yield of polymerization was quantitative.

(1) The theoretical molecular weights were calculated based upon initial charge ratios of monomer to initiator.

(2) Obtained from GPC before hydrogenation.

(3) Estimated from the ratios of hydrogen number of aromatic group and methyl group in polymer chain.

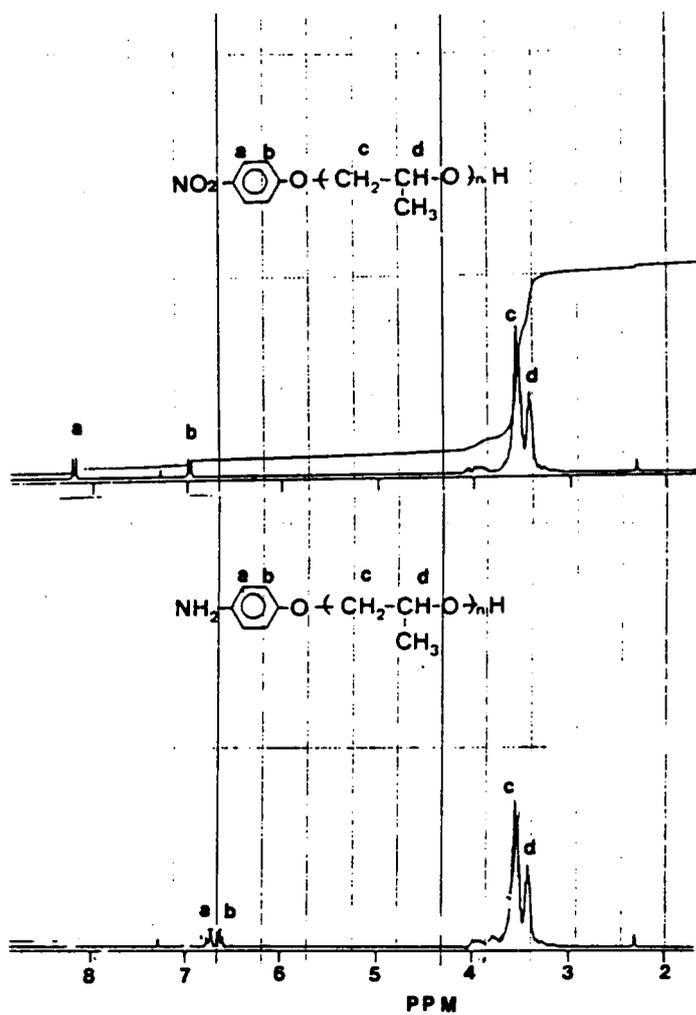


Figure 44. Hydrogenation of aromatic nitro group monitored by proton-NMR

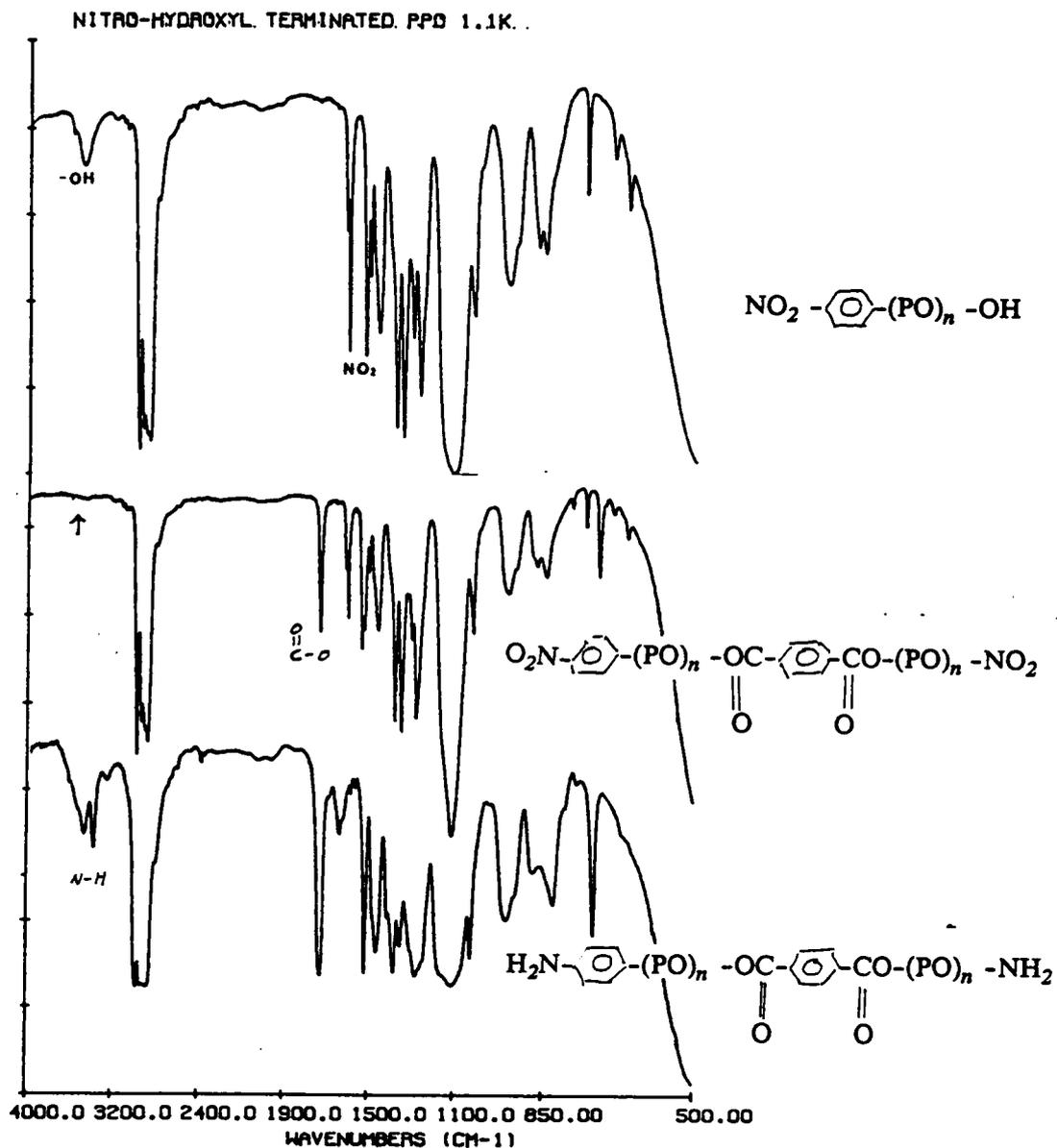


Figure 45. Synthesis of aromatic amine terminated poly(propylene oxide) monitored by FT-IR

(b) Post reactions by isatoic anhydride

Primary amine termini could be derived from a hydroxyl end groups by post reactions. One such method is through the interaction of hydroxyl group with isatoic anhydride in the presence of tertiary amine catalysts, typically imidazole or diazobicyclo undecene. A model compound was synthesized from the reaction of butane diol and isatoic anhydride in an aprotic solvent e.g., DMF. The reaction yielded the corresponding diamine compound along with the evolution of two equivalents of carbon dioxide. The reaction is outlined in Figure(46) providing applied reaction conditions. The product recovered by precipitation from large amounts of methanol is a white crystal with a melting point of 102°C. The peaks in the proton-NMR spectrum could be properly assigned to each hydrogen, as shown in Figure(47).

These results indicate that the hydroxyl group may be quantitatively converted to an aromatic amine functional group. Poly(tetra methylene oxide) diols with 1,000, 2,000, 2,900 number average molecular weights were converted to their amine derivatives via the same method. A proton-NMR analysis of resulting poly(tetramethylene oxide(PTMO)) reveals that the reaction was quantitative and thereby the corresponding amine terminated product was prepared. The integration of the aromatic and aliphatic hydrogens in the polymer chain allows one to calculate the reaction conversion. Poly(tetramethylene oxide) oligomers are waxlike semi-crystalline materials which melt at above room temperature. However, after the end groups are modified by the a fore-mentioned reaction, the oligomer of 1,000 number average molecular weight became a viscous liquid at room temperature. This phenomena may be due to the presence of ester groups and possibly, by the fact that two bulky terminal end aromatic amine groups impose a considerable irregularity on relatively short oligomeric chains. Usually,

this reaction yields a quantitative conversion in 2-4 hours at 110-120°C. However, when this approach is applied to the poly(propylene oxide), the conversion was significantly reduced due to a low reactivity of sterically hindered secondary hydroxyl end groups.

Although an extended reaction time up to 24 hours was allowed for the reaction, the conversion determined by ¹H-NMR analysis has been in the range of 72-78%. The ¹H-NMR spectrum of the polymer along with the corresponding peaks assignments is provided in Figure(48).

(c) Post reactions with p-fluoro nitrobenzene.

The ortho amine obtained by the previous approach may be relatively less reactive than an amine group in para position, since hydrogen bonding interactions are expected between ester carbonyl and hydrogens of ortho-amine groups and because of the electron withdrawing motion of the ester groups. In addition, the difunctional amine terminated poly(propylene oxide) prepared from previous approaches contains hydrolytically unstable ester groups in the chain. Difunctional amine terminated poly(propylene oxide) without unstable ester group may be obtained through following approach: First, a hydroxyl group of poly(propylene oxide) was converted to a lithium alkoxide by a stoichiometric amount of n-butyl lithium in toluene at 80-100°C. Then, upon addition of p-fluoro nitrobenzene, nucleophilic substitution occurs. The mechanism of these substitution reactions involves two steps: an addition followed by an elimination. The presence of electron-withdrawing nitro group provides sufficient resonance stabilization of the anion, thus allow it to form a reaction intermediate. Nitro groups are most effective for this nucleophilic substitution when they are para to the leaving group(fluorine).

MODEL REACTION

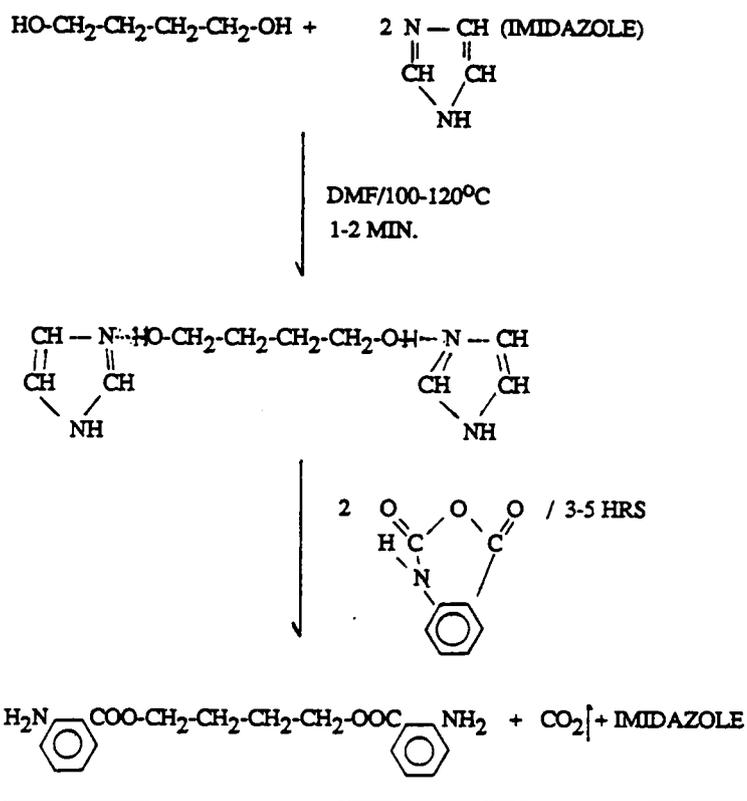


Figure 46. Model reaction for the modification of hydroxyl to aromatic amine by isatoic anhydride: The product was recovered by precipitation from methanol with a quantitative yield, MP = 101-103°C

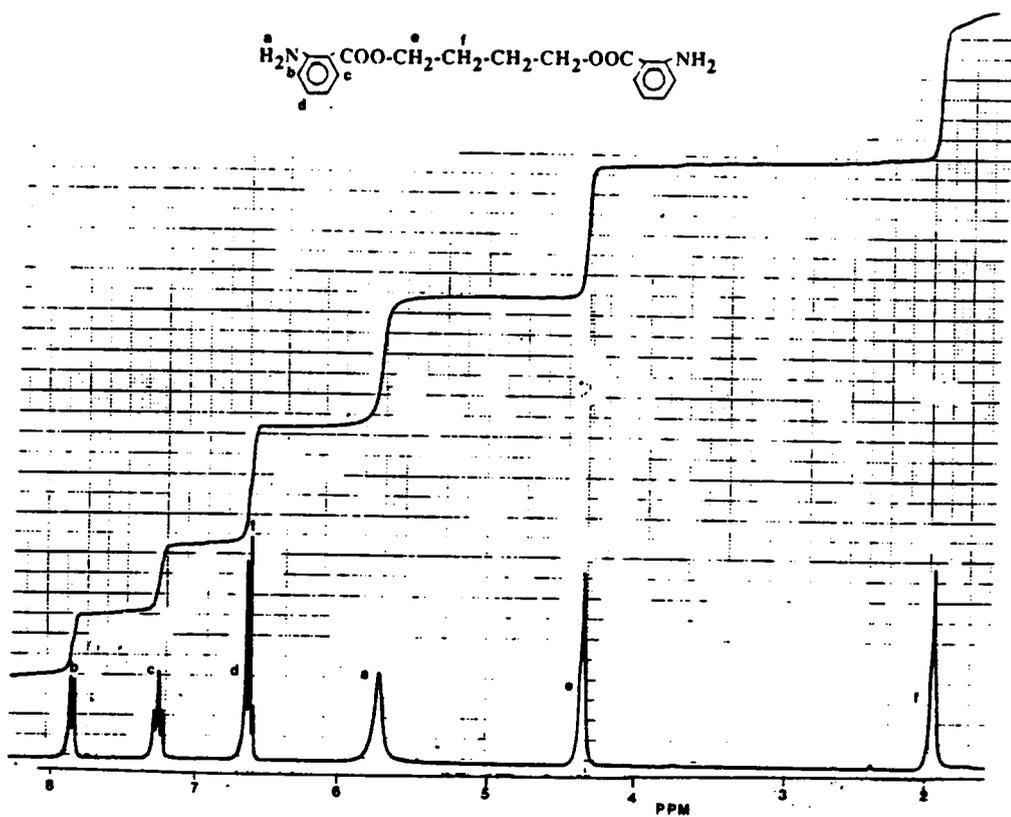


Figure 47. Proton-NMR spectrum of butane diamine from model reaction

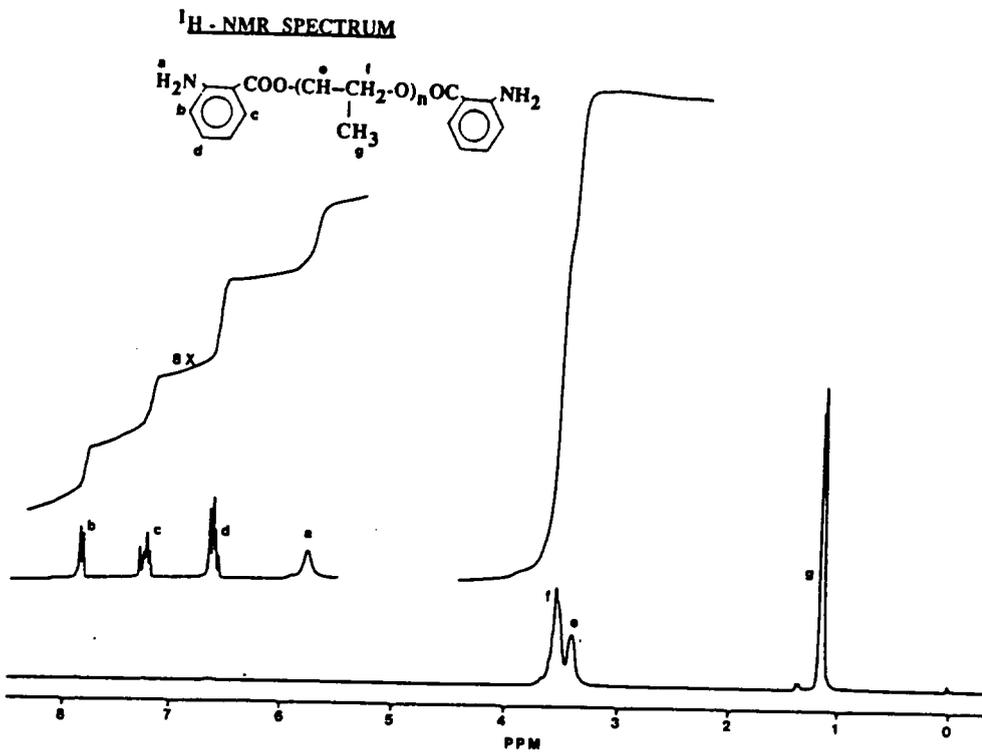
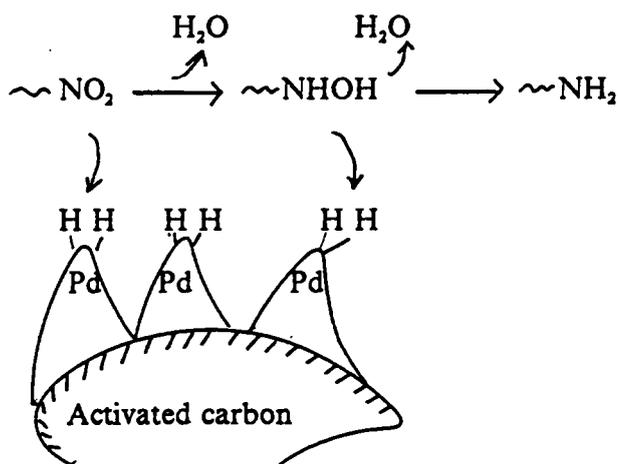


Figure 48. Proton-NMR spectrum of modified poly(propylene oxide) by isatoic anhydride

As illustrated in the the FT-IR spectrum in Figure(49), the hydroxyl group of poly(propylene oxide) is quantitatively substituted with an aromatic nitro group. The doublet peak at 1590cm^{-1} is the indicative of N-O asymmetry stretching. Subsequently, the p-nitro group was reduced by catalytic hydrogenation. The hydrogenation of nitro group is the most facile route to aromatic amines. Three equivalents of hydrogen are required to convert one equivalent of the aromatic nitro group to the amine. The reduction is believed to occur on the surface of solid catalyst(10% palladium on activated carbon) where hydrogen molecules are absorbed and activated.



Since the reaction mixture constitutes an essentially three phase system: (hydrogen(G), polymer solution(L), solid catalyst(S)), vigorous agitation is vital to maintain frequent contact among these components and lead to a high conversion.

Aliphatic alcohols such as ethanol or methanol, and hexane are preferred solvents for hydrogenation because of the high solubility of hydrogen gas in these solvents. As a matter of fact, hexane is the better solvent than ethyl alcohol for hydrogen. However,

it is speculated that its solvating power is not sufficient to afford a fully extended polymer chain, which is necessary to bring the end group into better contact with hydrogen on the catalytic surface.

Normally, the hydrogenation is conducted at an elevated pressure(45psig) to enhance the solubility of hydrogen in the solvent. The amount of hydrogen dissolved in the solvent follows Henry's law, which postulates that the solubility is linearly dependent upon the pressure of the system. Also, the absorption equilibrium of hydrogen on a catalytic surface would be shifted in a more favorable direction with higher applied pressure. Correspondingly, the progress of the hydrogenation reaction may be monitored by the decrease of pressure inside the reaction vessel. The molecular weights of hydroxyl terminated poly(propylene oxide)s are compared with the titrated molecular weights of amine terminated polymer after the modification in Table (18).

(d) Coupling by DGEBA in a post reaction

Multifunctional amine terminated poly(propylene oxide) may be obtained by employing diglycidyl ether of bisphenol A(DGEBA) in a post reaction. This post coupling could allow one to prepare the star-like poly(propylene oxide) with a variety of multifunctional end groups. This route of coupling essentially affords the molecular design of poly(propylene oxide). However, the most significant feature of this approach is that quite high number of functionality can be achieved after terminating connected growing species. For example, coupling of three growing chains would result a hexa-functional polymers, as illustrated in Figure(50), in which reaction scheme and predicted structure of the polymer are described. Using proper ratios of [DGEBA] to [porphyrin catalyst], a desired number of polymer chains may be coupled, leading to multifunctionality. If the ratio is 2:3 as in the figure, statistically, three chains may be combined, resulting in trifunctional aromatic nitro terminated polymer. This is analogous to the synthesis of

star shaped polystyrene by divinyl benzene incorporation at the end of anionic polymerization of styrene.

This approach was followed by the GPC analysis of the polymer before and after the coupling reaction. Before the injection of DGEBA into the reactor, the poly(propylene oxide) had a molecular weight and molecular weight distribution of 8,200 g/mole and 1.13, respectively. However, after the coupling by DGEBA (67 mole% of aluminum porphyrin catalyst in the reactor), the GPC trace observed from both RI and UV(254nm) detectors in Figure(51) estimated the number average molecular weight of 20,500 and 20,900 g/mole, respectively with the molecular weight distribution of 1.41. The increase in molecular weight and broadening of molecular weight distribution predict that statistically ca. 2.6 polymer chains may have been coupled by the reaction.

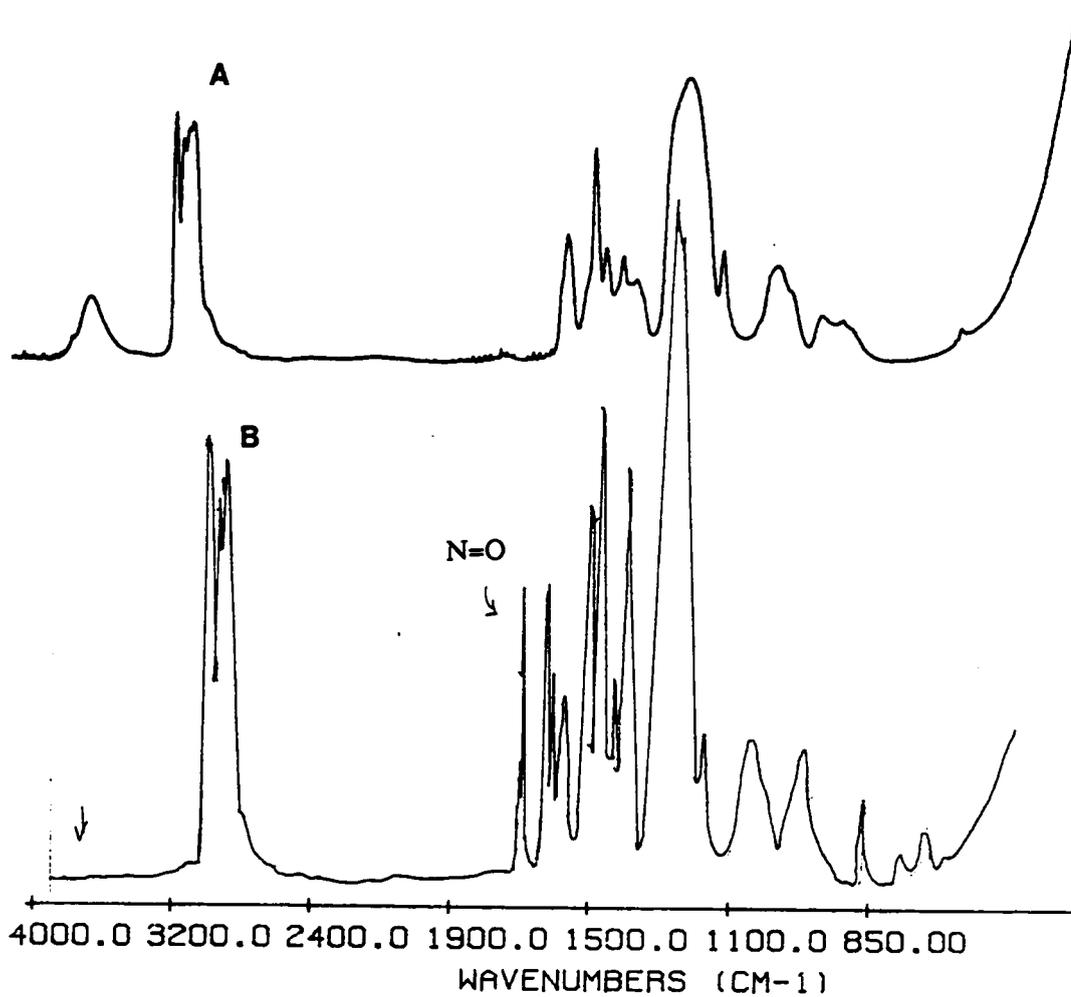


Figure 49. FT-IR spectra of hydroxyl terminated PPO(A) and after modified with p-fluoro nitrobenzene(B)

Table 18. Experimental results of modification by p-fluoro nitrobenzene

Run	Mn(i)	Mn(ii)
1	1,950	2,230
2	4,200	4,560
3	10,500	12,300

(i) Mn(i) : number average molecular weight of hydroxyl terminated poly(propylene oxide) obtained from the titration of hydroxyl end group by phthalic anhydride method.

(ii) Mn(ii): number average molecular weight of resulting amine terminated poly(propylene oxide) obtained from the titration of amine groups by hydrochloric acid after modification.

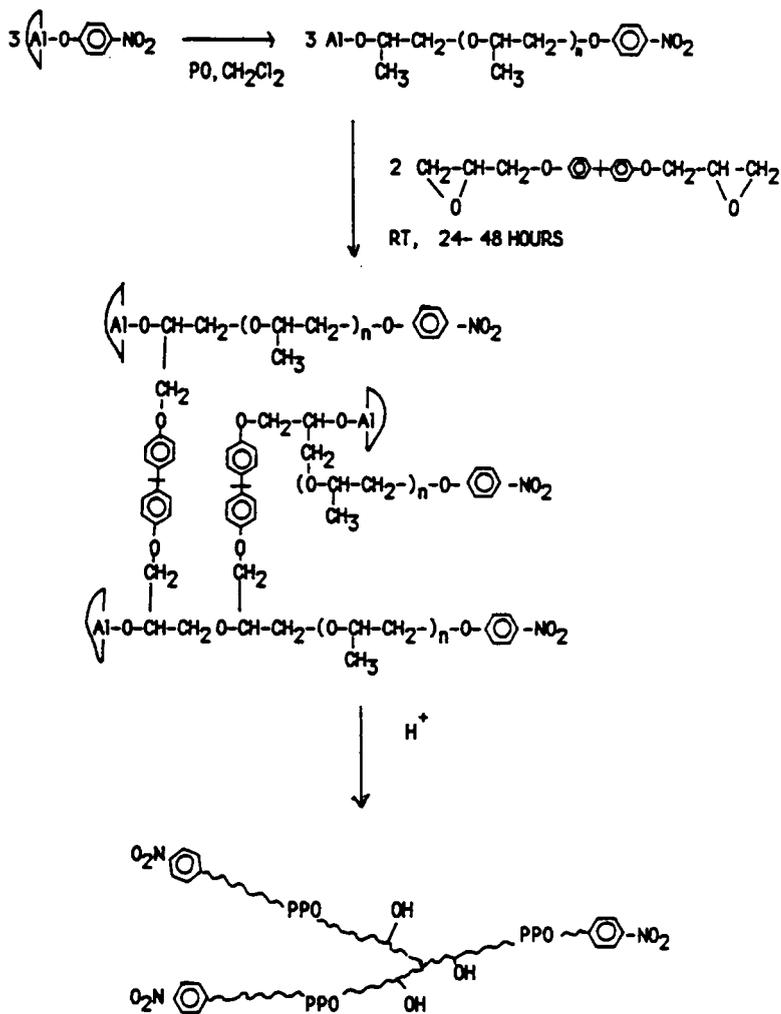


Figure 50. Reaction scheme for star-like post coupling by DGEBA

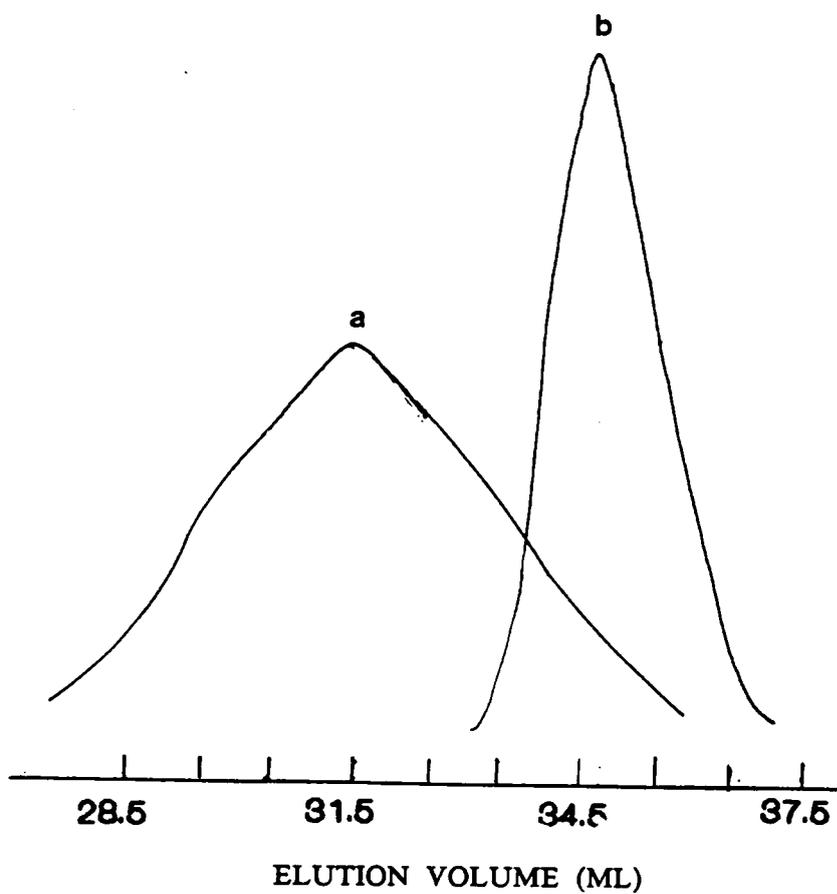


Figure 51. GPC trace of poly(propylene oxide) before(b) and after(a) coupling: (b)[Mn] = 8,200 g/mole MWD = 1.13 (a)[Mn] = 20,900 g/mole MWD = 1.41

In summary, poly(propylene oxide) with controlled molecular weights and functional end groups has been synthesized. The polymeric materials are fully identified by spectroscopic analysis, gel permeation chromatography, a titration of end groups, indicating that the molecularly designed the poly(propylene oxide) has been achieved in terms of chain length, topology, functional groups and narrow polydispersity. Terminal groups of this polymer have included hydroxyl, amine, carboxylic, etc.. Also, molecular weight has been reasonably controlled by utilizing a chain transfer reactions.

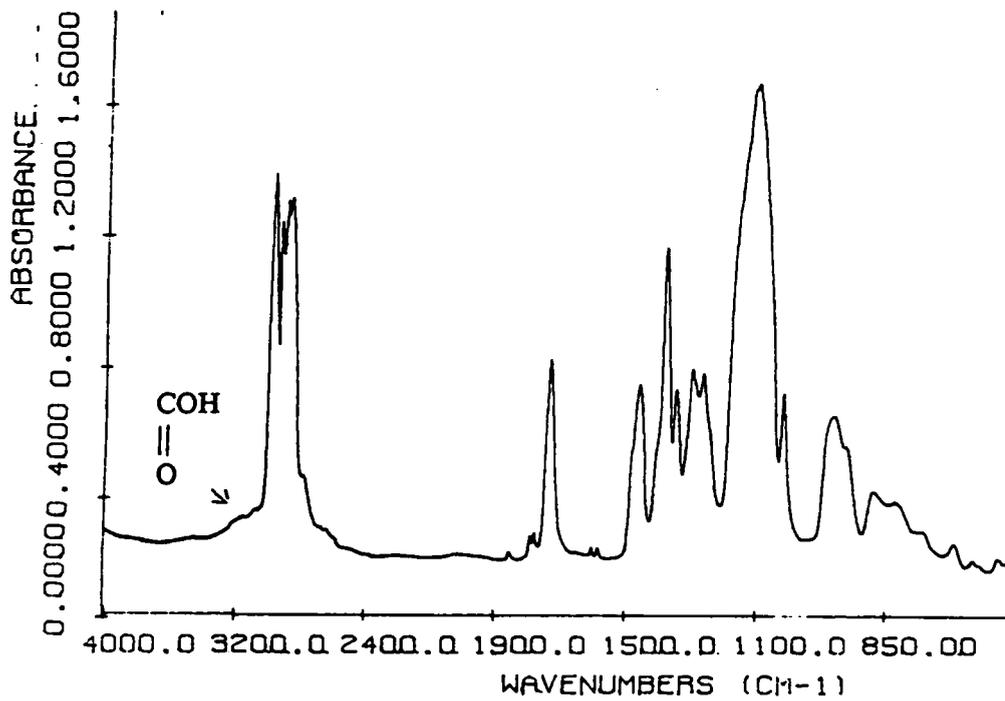
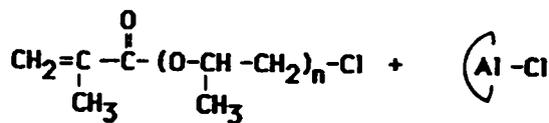
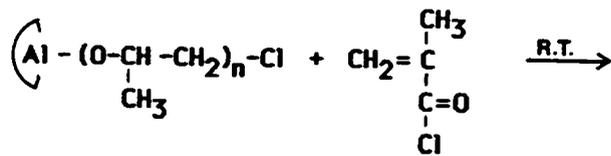


Figure 52. FT-IR spectrum of carboxylic acid terminated poly(propylene oxide)

1. Monofunctional:



2. Difunctional:

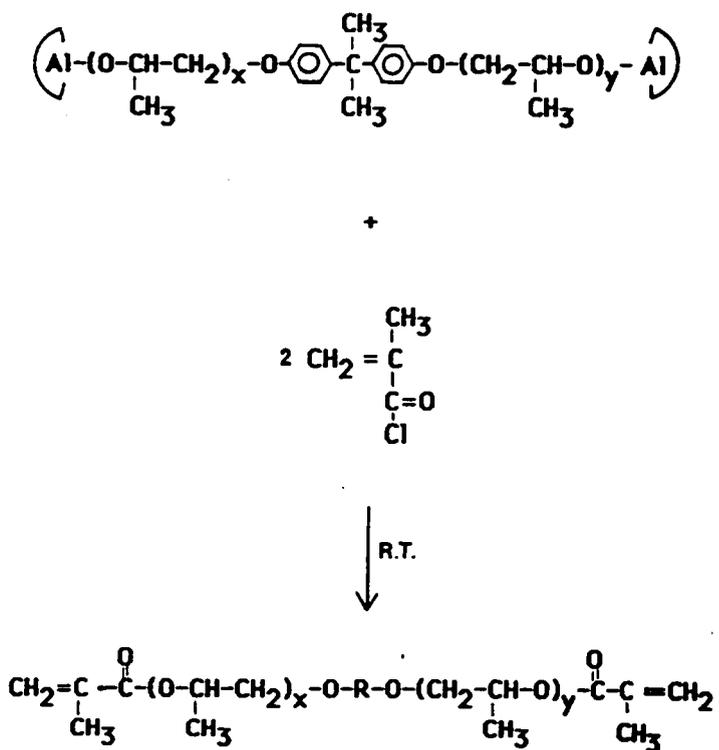


Figure 53. Reaction scheme for synthesis of methacrylate terminated poly(propylene oxide)

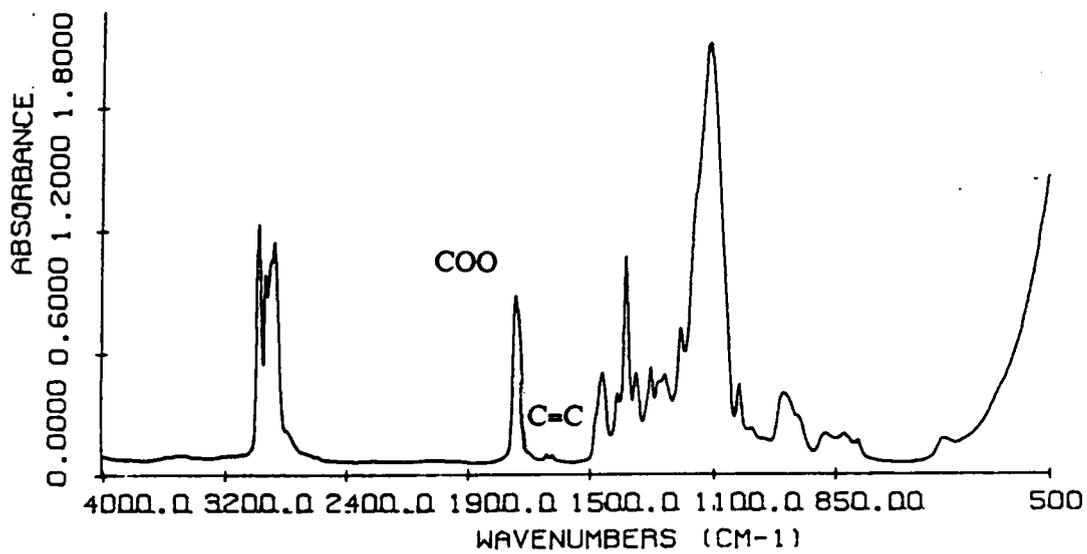


Figure 54. FT-IR spectrum of methacrylate terminated poly(propylene oxide)

IV.2. THERMAL DEGRADATION BEHAVIOR OF POLY(PROPYLENE OXIDE)

IV.2.1. Introduction

The thermal degradation behavior of poly(propylene oxide) has been investigated by using thermogravimetric analysis(TGA). The study has been motivated by the relatively unstable nature of this material at elevated temperatures. Generally, irreversible changes in the chemical structure and weight loss have been observed beyond the degradation temperature. It is now generally recognized that stabilization of this polymer to degradation is necessary and should be established if the useful life is to be extended sufficiently to meet design requirements. Polymers degrade by a wide variety of mechanisms. However, the most common cases arise from reactions with oxygen in its various form with an acceleration by heat or radiation.

Polymer stabilization is undergoing a transition from an art to a science as mechanisms of degradation become more fully developed. A scientific approach can only be achieved when an understanding of the reactions which lead to degradation exists. It is the purpose of this study to examine the effect of variables on the thermal degradation behavior of this poly(propylene oxide). Subsequently, stabilization may be implemented based upon the understanding of this system.

IV.3.2. Variables Affecting Thermal Degradation

There are several important variables affecting the thermal stability of poly(propylene oxide). For instance, the tacticity is one of the factors significantly af-

fecting thermal degradation behavior[151]. This may be due to the fact that isotactic poly(propylene oxide) constitutes a semi-crystalline material, which is so compact that oxygen cannot penetrate as easily into the polymer. Therefore, it is expected that oxidation of such a material is restricted to the disordered or amorphous region. However, the effect of the crystalline structure will not be observed at an elevated temperature of ca. 150°C or higher, since the crystalline melting point of isotactic poly(propylene oxide) is only 70-80°C. As previously mentioned, poly(propylene oxide) with monofunctional hydroxyl end groups has been prepared over a wide range of molecular weights. The dynamic and isothermal thermogravimetric diagrams of two polymers with molecular weights of 4,900 and 89,000 g/mole have been obtained, as illustrated in Figures(55,56). As can be seen from the comparison, high molecular weight poly(propylene oxide) demonstrates an improved thermal stability to some degree over the low molecular weight species. However, considering the fact that the higher molecular weight PPO possess less than one twentieth of the end groups relative to the low molecular weight sample, only a part of the degradation process may be attributed to the chain end initiation mechanism.

Dynamic thermogravimetric analysis of commercial poly(propylene oxide) was conducted in different environments of pure oxygen, air and dry nitrogen. The TGA diagrams are presented in Figure(57). The degradation of the polymer at high temperatures was accelerated with the aid of oxygen. Nevertheless, the poly(propylene oxide) under an inert environment degraded ca. 40-50°C above the degradation temperature of the polymer in air. This fact may suggest that the mechanism of degradation is primarily due to the pyrolysis of the thermally unstable ether(C-O) bond. The presence of oxygen only accelerates the degradation by the means of generating radicals. From the comparison of the thermal degradation temperature of poly(propylene oxide) and polypropylene(PP), PP has the higher degradation point by ca. 50-100°C. This indicates

that the initial breakage of the chemical bonds may start from the ether linkages since both polymers contains somewhat thermally unstable tertiary carbons(hydrogens).

Mass spectroscopic analysis of poly(propylene oxide) in Figure(58) revealed that thermal degradation yields some volatile fraction, consisting of acetaldehyde, acetone, propene, and propylene oxide. The acetone is isomeric with propylene oxide. The composition of these volatile fragment was previously reported by Madorsky et.al.[173]. The mole fractions of the major components were as follows; acetaldehyde(40.3%) acetone(17.0%) propylene oxide (4.7-5.2%), propene(8%) and so on. Kilic and McGrath[154] have postulated that the thermal degradation of poly(propylene oxide) follows zeroth order kinetics with respect to the remaining polymer weight. It has been well recognized the random scission of chains is a typical mechanism of zeroth order kinetics. Considering the poly(propylene oxide) is yielding monomerlike fragments when it is exposed to elevated temperature, it may be speculated that the depolymerization immediately follows at the end of randomly scissorred polymer chains.

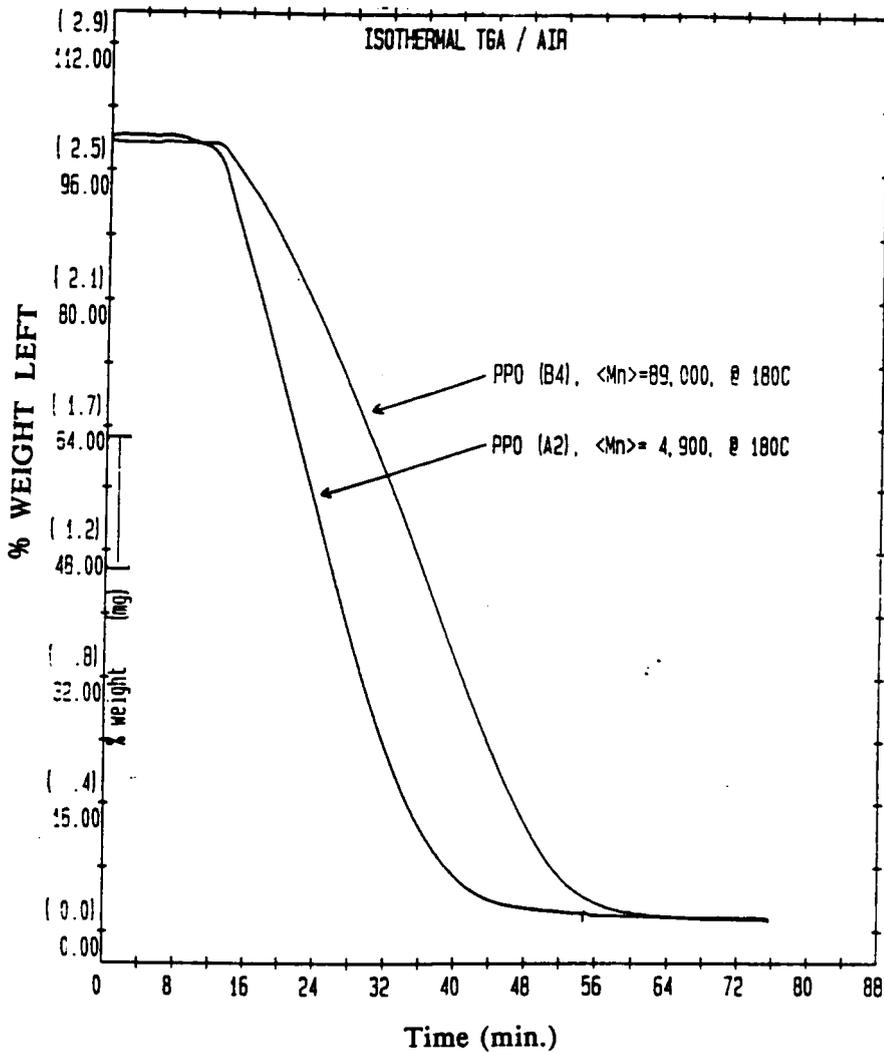


Figure 55. Effect of molecular weight on isothermal degradation of poly(propylene oxide) at 180°C: Both poly(propylene oxide)s were prepared by using aluminum porphyrin initiators

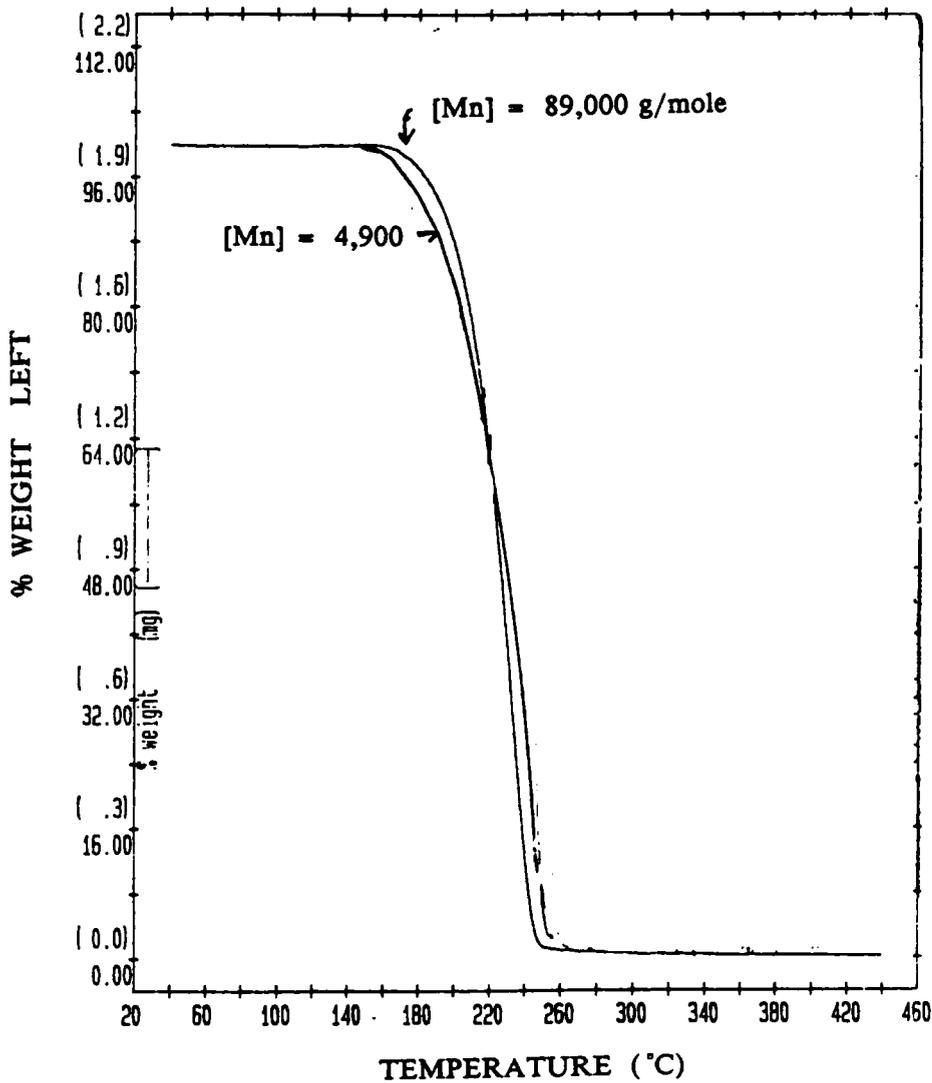


Figure 56. Effect of molecular weight of poly(propylene oxide) observed by dynamic TGA thermogram: Both poly(propylene oxide)s were prepared by using aluminum porphyrin initiators

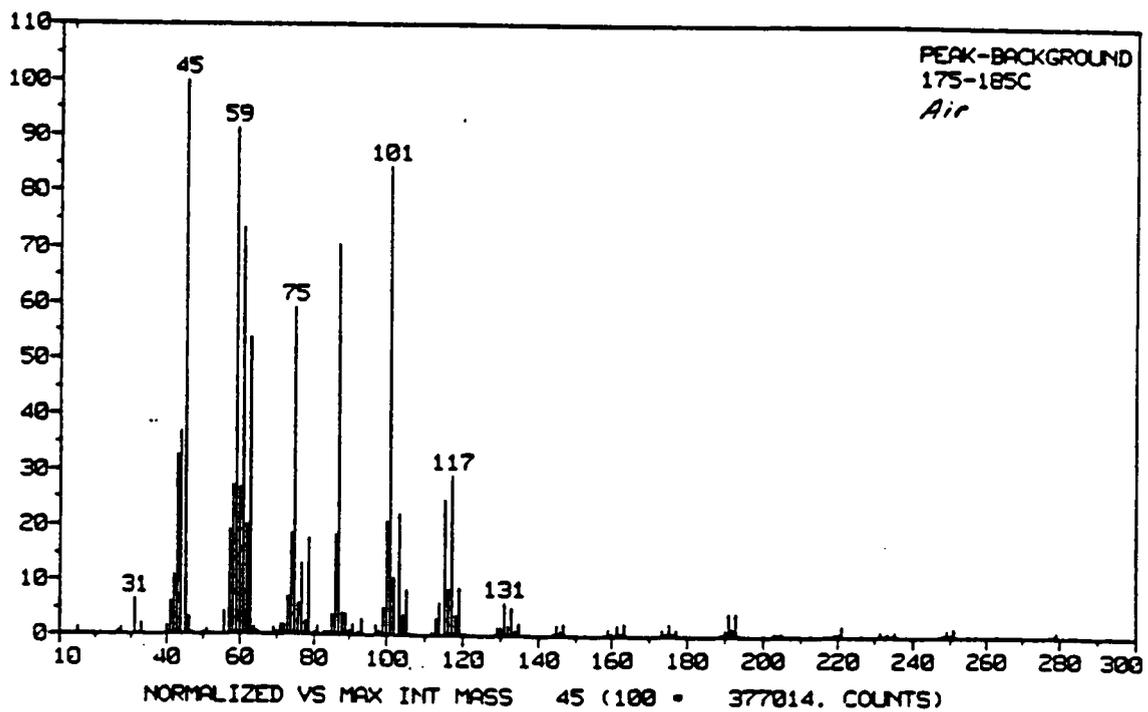


Figure 57. Mass spectrum of volatile fragments of commercial poly(propylene glycol) exposed at 185°C in air

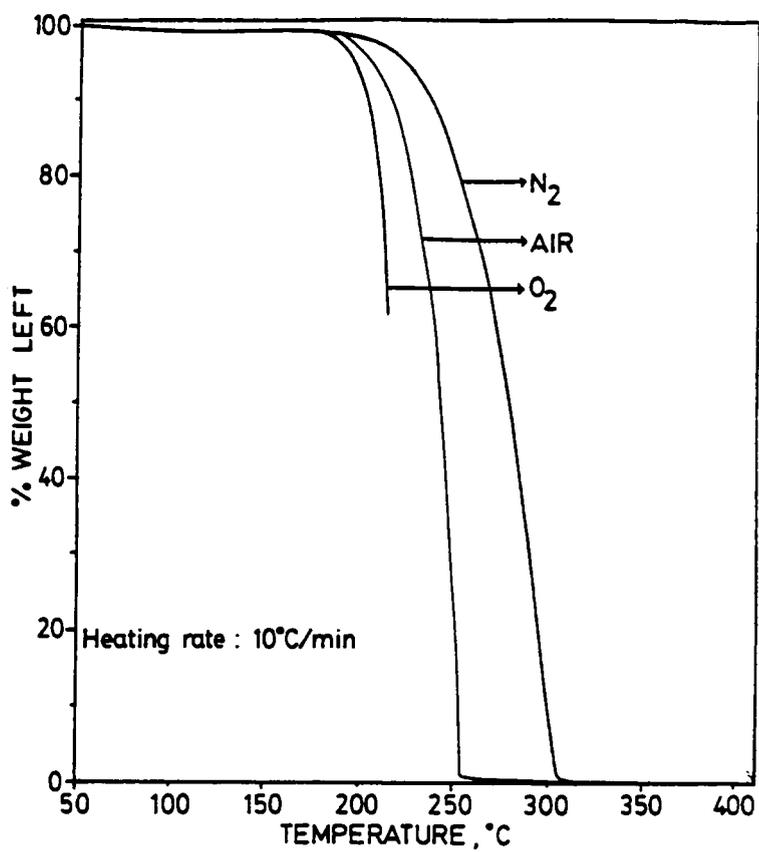


Figure 58. Effect of atmosphere on thermal degradation of commercial poly(propylene glycol)

IV.2.3. Effect of Functional Groups on Thermal Degradation

Dynamic thermograms of commercial hydroxyl terminated poly(propylene oxide) ($[Mn] = 1000, 2000$ g/mole) and poly(propylene oxide) with various functional end groups were obtained. These samples were all prepared by aluminum porphyrin catalysts. Figure(59) illustrates some typical TGA diagrams of poly(propylene oxide) with various functional groups. Table(19) summarizes the initial degradation temperatures over the 3-8 % weight loss region. Commercial poly(propylene glycol) begins to lose weight around 185-190°C. Monofunctional hydroxyl terminated poly(propylene oxide) prepared by the coordination polymerization with the aluminum porphyrin catalyst demonstrated improved thermal stability. This may be due to the fact that the commercial anionic route of polymerization inherently generates 3.0-3.5 meq of unsaturated end groups per gram of product.

These observations are consistent with lower stability of poly(propylene oxide) with unsaturated end groups, such as allyl or acrylate. Lower degradation temperatures of 20-30°C were observed for poly(propylene oxide) with those end groups.

The aromatic nitro terminated poly(propylene oxide) showed remarkably improved thermal stability compared to commercial hydroxyl and amine terminated poly(propylene oxide)s. Thermal stability increased ca. 150°C by introducing the aromatic nitro end groups. After hydrogenating the aromatic nitro end groups to aniline groups, a comparison of thermal stability was made among aromatic amine, aliphatic amine and aliphatic hydroxyl terminated poly(propylene oxide)s. As listed in Table(19), the effect of the aromatic amine group on thermal degradation behavior was comparable to that of aromatic nitro end group. In the early stage of this study, it was speculated that the thermal degradation behavior of the hydroxyl terminated poly(propylene oxide) may have been caused by depolymerization. The reaction is initiated at the chain ends

and depolymerization then proceeds sequentially along the backbone. On the basis of this assumption, hydroxyl groups of the polymer were eliminated by end capping with benzoyl chloride, yielding phenyl terminal groups. However, the dynamic thermogram of this polymer did not show significant difference in thermal stability.

The poly(propylene oxide) with aromatic moieties leaves a char yield after degradation of the aliphatic polymer chain. The weight fraction of residue corresponds to those of the end group portion. The aromatic group is more stable than the aliphatic hydrocarbon due to its resonance stabilization.

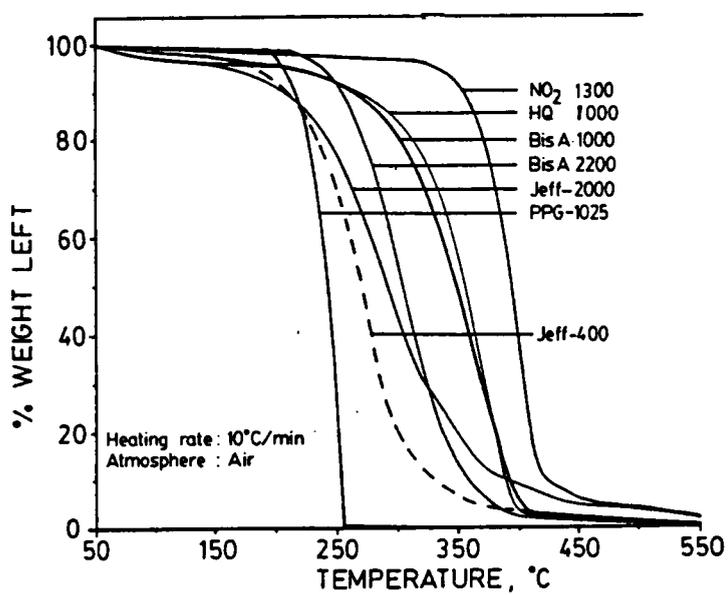
The hydroxyl terminated propylene oxide polymers derived from phenolic initiators such as bisphenol A or hydroquinone exhibited improved thermal stability up to 250°C for molecular weights of 1,000 g/mole. This has not been the case for the polymer derived from aliphatic hydroxyl initiators such as hexane diol or ethylene glycol. The difference may be explained by the presence of the some phenolic hydroxyl, which did not entirely participate in the chain transfer reaction.

An interesting comparison was made between the aliphatic hydroxyl and the aromatic nitro terminated poly(propylene oxide) in air and nitrogen atmospheres in Figure(60). Surprisingly, the polymer with aromatic nitro group under oxidative environment(air) demonstrated even higher thermal stability than the other under inert condition(nitrogen). This again verifies that the aromatic nitro group behaves as an active stabilizing agent against thermal degradation regardless of environments. Aromatic nitro groups are known to be free radical scavengers. An equimolar mixture of aromatic nitro terminated PPO(1.1K) and commercial PPO(1K) was subjected to thermogravimetric analysis. The dynamic thermograms of the individual components are also plotted on the same Figure(60). The blended polymer exhibits enhanced thermal stability, comparable to that of aromatic nitro terminated one. The difference in the initial degradation temperature 20-30°C is due to the dilution effect of the functional group

by 50%. From this observation, it is evident that the aromatic nitro group provides stabilization not only for the chain to which it is attached but also to the aliphatic hydroxyl terminated polymer of the blend. This remarkable stabilization effect of the aromatic nitro group may be explained by the radical trapping function of the nitro group. The nitroxide radical may inhibit the propagation of decomposition by eliminating alkyl radicals in the initial stage. Thus, it prevents the thermal degradation of the polymer significantly. This type of stabilizer includes di-tert-butyl nitroxide and 2,2',6,6'-tetramethyl-1,4-pyridone nitroxide.

The aromatic amine terminated polymer also demonstrated considerably improved thermal stability. The aromatic amine group was obtained through the reduction of an aromatic nitro group by catalytic hydrogenation. A similar degradation temperature was observed in both cases, however, the stabilization mechanisms may not be analogous. It has been speculated that one or two labile hydrogens of the aromatic amine behave as antioxidants for both short and long term protection.

The amine group provides an alternative reaction to the rate controlling step in the propagation phase of autoxidation. The greater ease of hydrogen removal from these hydrogen donating antioxidants, in comparison to hydrogen abstraction from hydrocarbon polymers may be the key feature of this type of stabilization. Isothermal TGA diagram is given in Figure(61) for the aromatic amine terminated poly(propylene oxide) in comparison with commercial amine terminated poly(propylene oxide)(Jeffamine). The polymer with aromatic amine groups sustained undegraded for an hour of exposure to 225°C under oxidative environment, while the commercial poly(propylene oxide)s were mostly degraded under the given conditions.



SYMBOL	FW	STRUCTURE
NO ₂	1300	<chem>NO2-C6H4-O-PPGn-H</chem>
A/BIS	2000	<chem>NO2-C6H4-O-PPGn-C6H4-C(=O)-C6H4-PPGm-H</chem>
HQ	1000	<chem>HO-PPGn-C6H4-PPGm-H</chem>
BIS A	1000 2200	<chem>HO-PPGn-C6H4-C6H4-PPGm-H</chem>
PPG	1025 2000	<chem>HO-PPGn-H</chem>
JEFF	400 2000	<chem>NO2-PPGn-NO2</chem>

Figure 59. Dynamic TGA diagrams of poly(propylene oxide)s with various end groups

Table 19. Effect of various reactive end groups on thermal stability of poly(propylene oxide)

POLYMER	MOLECULAR WEIGHT	DEGRADATION [†] TEMPERATURE, °C
$\text{H}-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-\text{H}$	1000	190-210
(COMMERCIAL PPG)	2000	190-210
$\text{H}-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$	700	180-180
$\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$	800	170-200
$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{H}$	5000	180-200
$\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OH}$	2300	178-190
$\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{NO}_2$	2400	270-290
$\text{HO}-(\text{PO})_n-\text{C}_6\text{H}_4-\text{C}(\text{C}_6\text{H}_4)-\text{C}_6\text{H}_4-(\text{PO})_n-\text{OH}$	1000	250-270
	2000	220-240
$\text{HO}-(\text{PO})_n-\text{C}_6\text{H}_4-(\text{PO})_n-\text{OH}$	1000	250-270
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{NH}_2$	2000	350-365
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$	2000	350-365
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{NH}_2$	2300	225-245
PHYSICAL BLEND OF COMMERCIAL PPG AND BISPHENOL A (15 WT. %)	2000	260-280
PHYSICAL BLEND OF COMMERCIAL PPG AND ANTIOXIDANT (IRGANOX 1 WT. %)	2000	230-250
PHYSICAL BLEND OF COMMERCIAL PPG AND ANTIOXIDANT (IRGANOX 5 WT. %)	2000	265-275

[†] DEGRADATION TEMPERATURES OF EACH OLIGOMER HAVE BEEN MEASURED IN THE 3-8% WEIGHT LOSS REGION DURING THE DYNAMIC TGA SCANS (10°C/MIN).

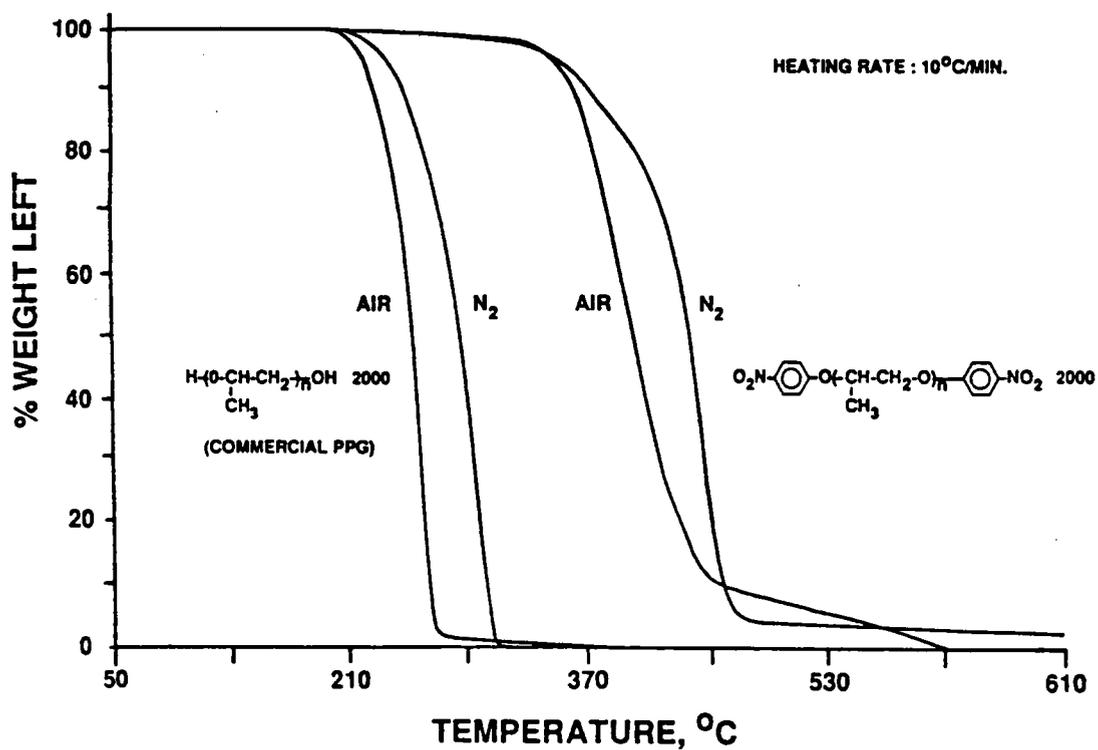


Figure 60. Dynamic thermal degradation of commercial PPO and aromatic nitro terminated PPO under air and nitrogen

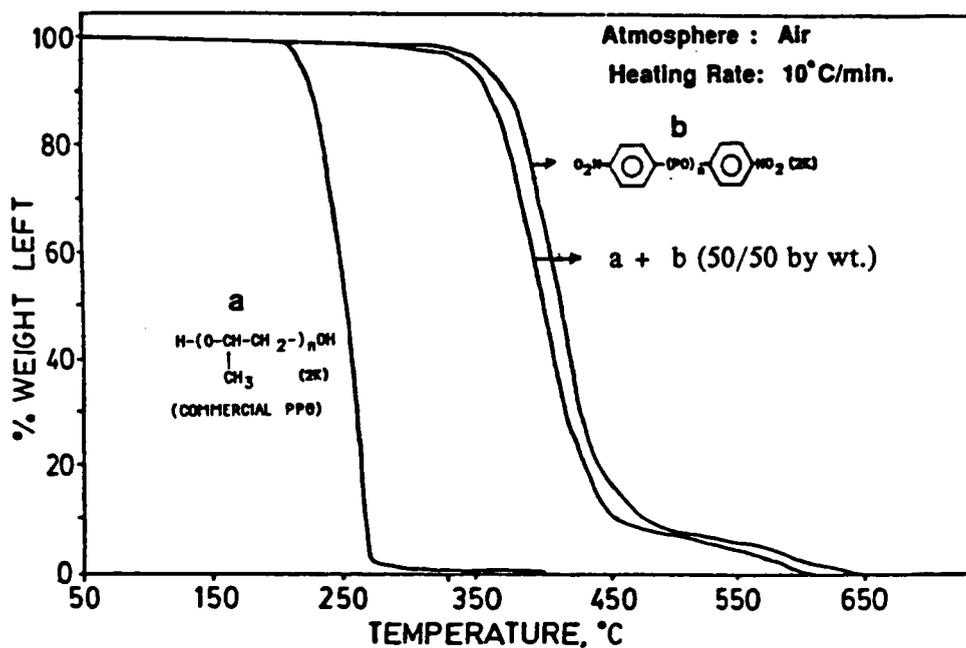


Figure 61. TGA diagram of an equimolar mixture of commercial PPO and aromatic nitro terminated PPO

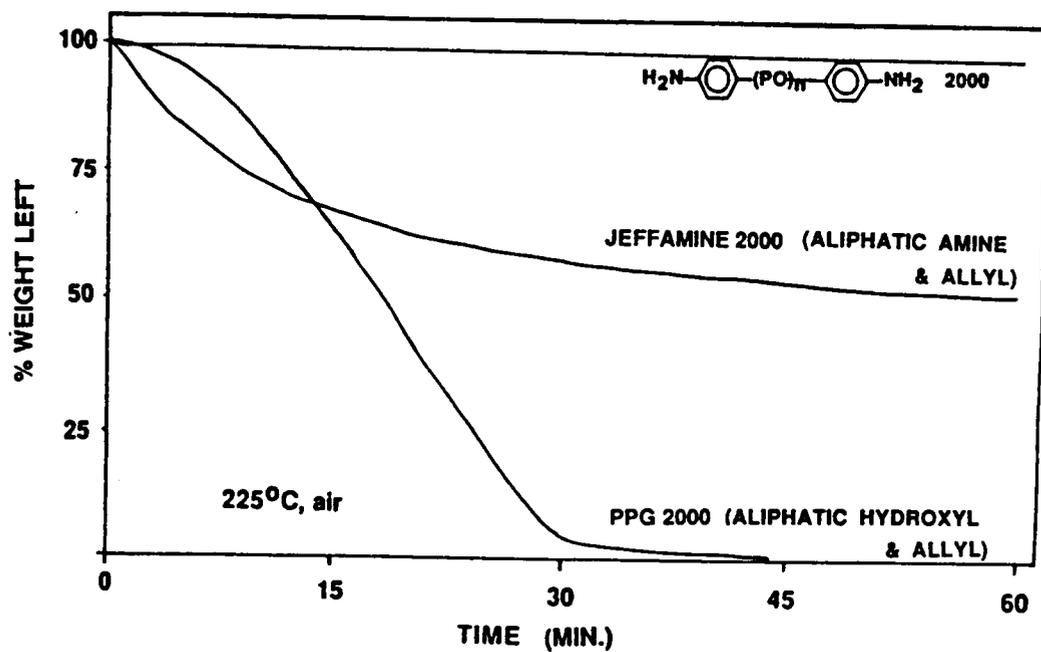


Figure 62. Isothermal TGA diagram of aromatic amine terminated poly(propylene oxide) at 225°C in air

IV.2.4. Concentration Effect

The effect of the concentration on thermal stabilization was examined. As presented in Figure(63), the initial degradation temperatures are considerably dependent upon the concentration of this functional group. Difunctional amine terminated poly(propylene oxide)s with 2300, 6000, 9000 molecular weight demonstrated initial degradation points of 350, 310 and 270°C, respectively. The temperature at which weight loss occurs increases with the concentration of aromatic nitro or amine group. However, this temperature seems to converge at 350°C as [Mn] is lowered.

Figure(64) shows the separate effect of the aromatic nitro group on thermal degradation behavior. Physical blends of commercial poly(propylene glycol) with nitrophenol, bisphenol A and several antioxidants have been prepared and the thermal degradation behavior was monitored by TGA. Physical mixtures of commercial poly(propylene glycol) and nitrophenol showed very interesting degradation behavior. Thermal degradation of poly(propylene oxide) was retarded by nitrophenol, up to 289°C, which is the boiling point of the nitrophenol. The specimen quickly lost its weight by degradation beyond this temperature.

IV.2.5. Stabilization of Poly(propylene oxide)

In general, stabilization of polymeric material has been achieved by either the addition of antioxidants or by structural modifications. First, antioxidants intended to provide protection must be capable of migrating freely throughout the polymer mass to reach a number of initiation sites which are generated at an elevated temperature.

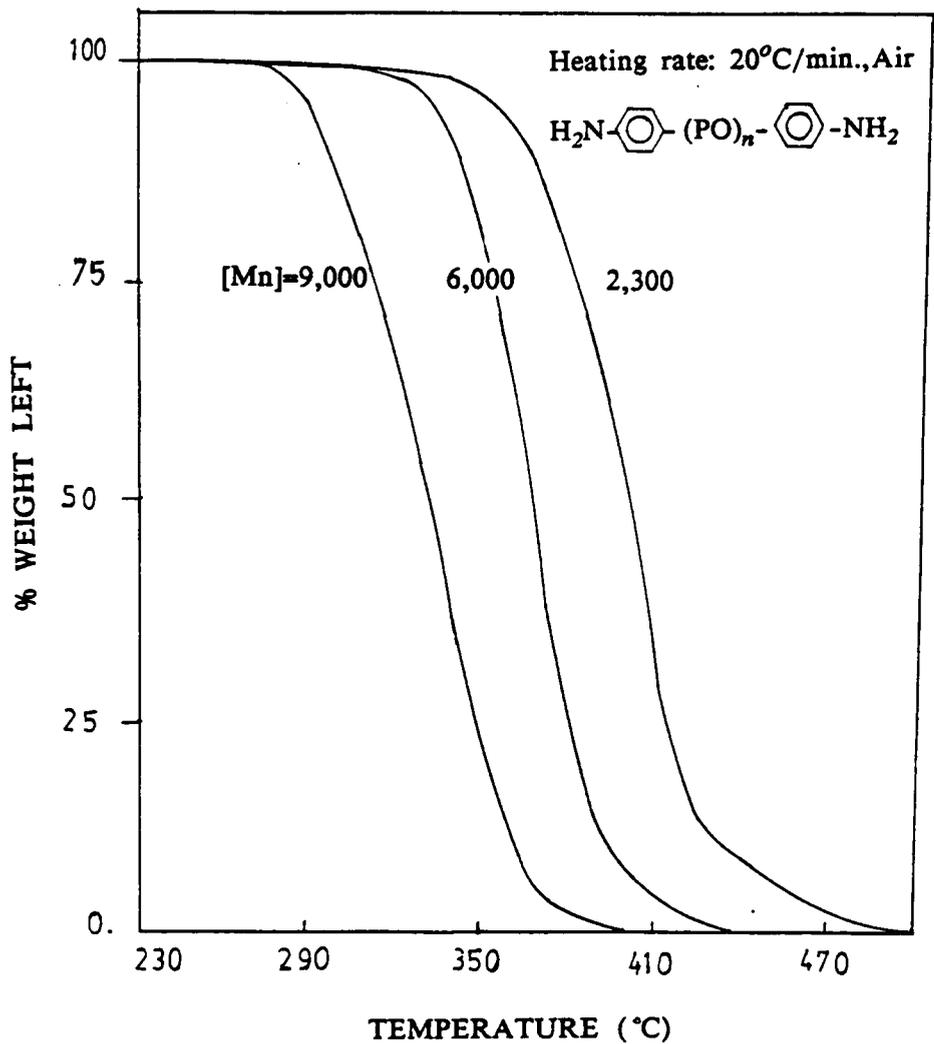


Figure 63. Effect of poly(propylene oxide) molecular weight and aromatic amine end group concentration on thermal stabilization

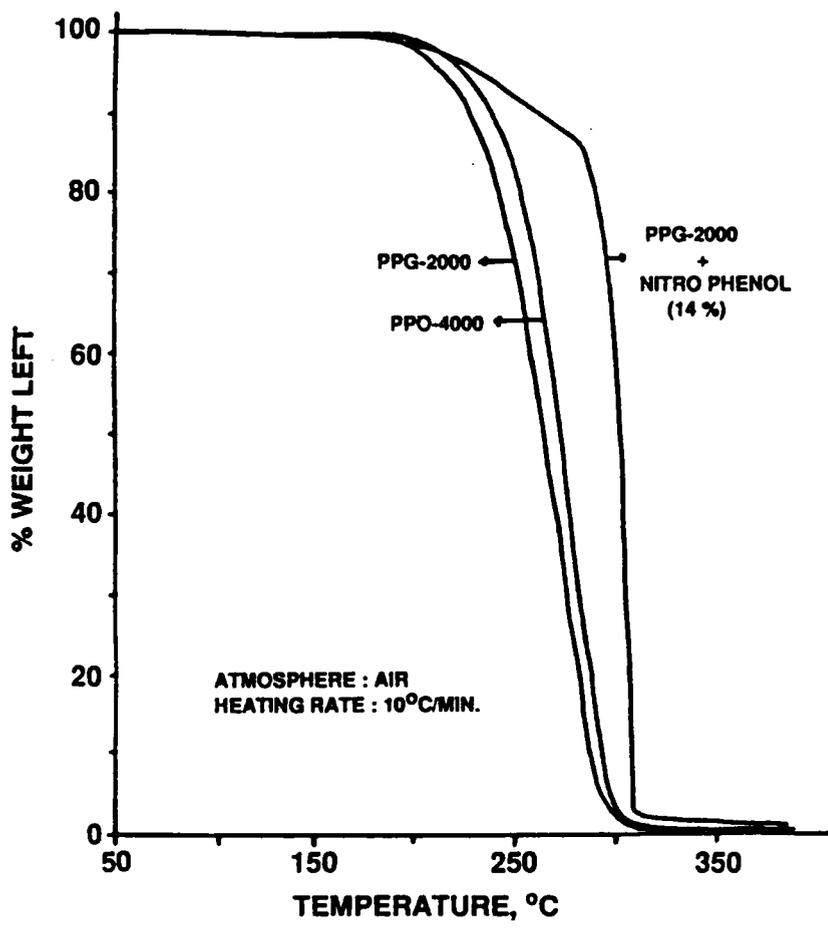


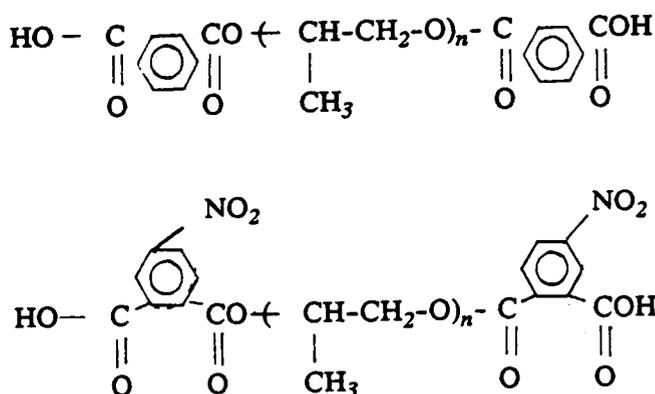
Figure 64. Dynamic TGA diagram of physical mixture of p-nitro phenol and commercial poly(propylene glycol)

However as discussed previously, low molecular weight antioxidants eventually diffuse from the system in the form of vapor at the elevated temperatures.

Another approach may include the grafting of antioxidant onto backbone of polymer chain. By doing so, the antioxidant will be retained as a part of the polymeric material. These are the key features of stabilization accomplished with the poly(propylene oxide), since the antioxidant compounds will be remaining even above their boiling points. Furthermore, utilizing unreactive functional groups such as the aromatic nitro group is very much appropriate, since it will not affect the functionalities of these reactive oligomers with hydroxyl or carboxylic end groups.

A difunctional hydroxyl terminated poly(propylene oxide) was synthesized by using nitro xylene α, α' diol as an initiator (Figure(64)). The thermal stability was improved through the incorporation of aromatic nitro group in the chain by ca. 100°C in a 5000 molecular weight poly(propylene oxide), as shown in Figure(65).

A similar observation was made for a carboxylic acid terminated poly(propylene oxide). The hydroxyl terminated poly(propylene oxide) was modified with phthalic anhydride and 5-nitro-phthalic anhydride to generate the carboxylic acid end groups. Again, the polymer with the nitro terminal groups showed higher thermal stability by ca. 100°C than the one without nitro groups.



Difunctional hydroxyl terminated poly(propylene oxide) derived from aluminum porphyrin/bisphenol A or hydroquinone modified catalyst systems also showed enhanced thermal stability. This may be due to a certain amount of a remaining phenolic hydroxyl end. This effect diminished rapidly as the molecular weight increased, since the phenolic hydroxyl group disappears by chain transfer reactions.

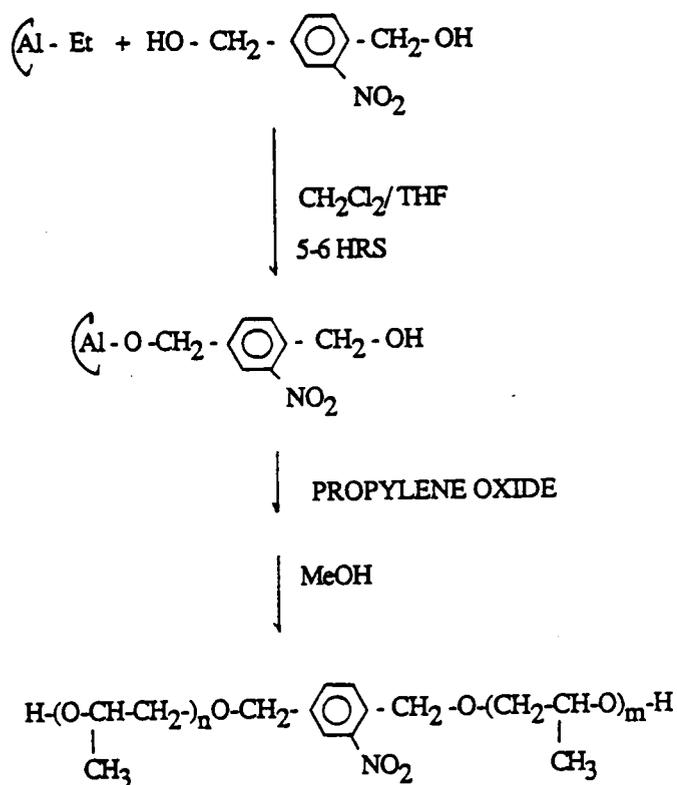


Figure 65. Synthesis of thermally stable poly(propylene oxide) via grafting anti-oxidant moiety in the polymer chain

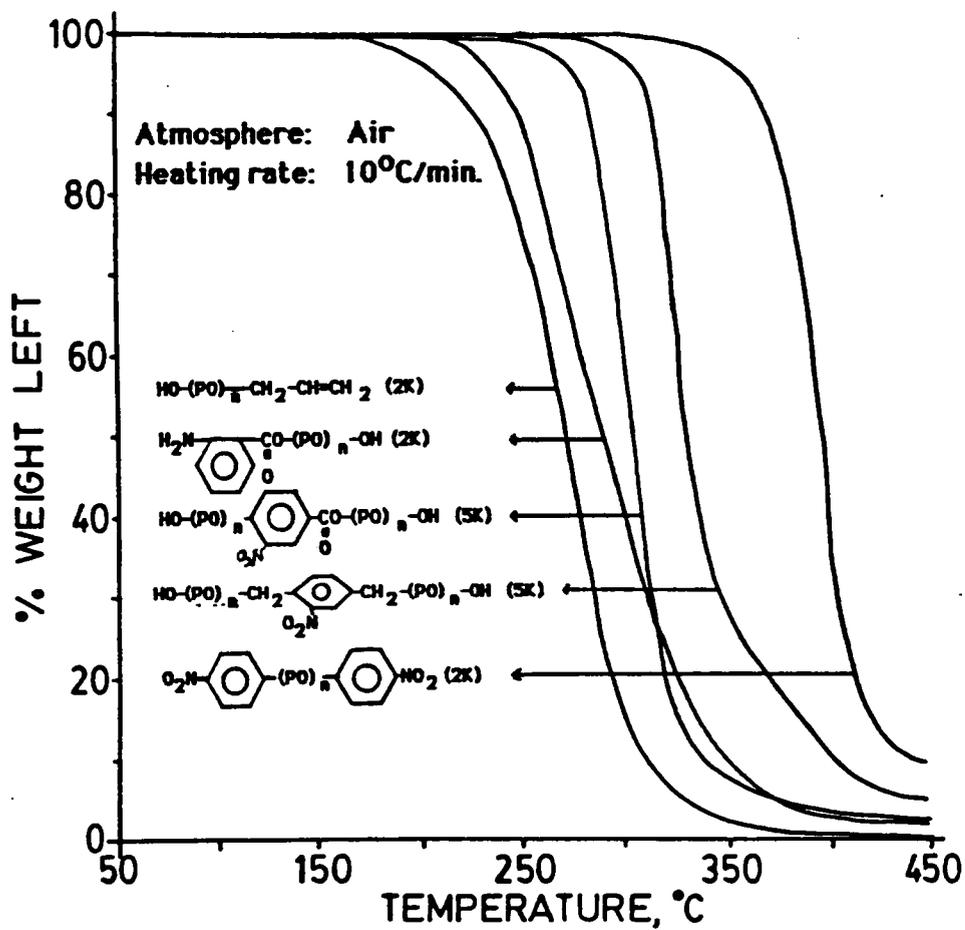


Figure 66. Dynamic TGA thermogram of stabilized poly(propylene oxide) with pendant nitro group

IV.3. COPOLYMERS OF POLY(PROPYLENE OXIDE)

IV.3.1. Poly(propylene oxide)-Poly(caprolactone) Block Copolymers

It has been possible to prepare oligomers and polymers of controlled molecular weights and narrow molecular weight distributions through the utilization of bisphenol A or 1,3,5,- benzene tricarboxylic acid-like chain transfer agents which are effective at interacting with the aluminum porphyrin initiator and can produce di- or tri-functional materials. It has been also feasible to prepare higher molecular weight secondary hydroxyl systems of controlled molecular weight which have little, if any, unsaturation.

The rate of polymerization with significant amount of a chain transfer agent (ten fold excess aluminum porphyrin catalyst concentration) such as bisphenol A, became quite acceptable if elevated temperatures were utilized. In principle, one may be able to directly synthesize poly(caprolactone)- poly(propylene oxide) by sequential addition of the two monomers; i.e., propylene oxide is charged and polymerized, then ϵ - caprolactone is added. In an exploratory study, such an attempt was made and a diblock copolymer of propylene oxide(10K) and ϵ -caprolactone(5k) was obtained quantitatively. The copolymer has a molecular weight of 16,000 g/mole with a polydispersity of 1.4 as observed from GPC. However, a problem arose in the separation of the porphyrin catalyst residue from the copolymer. The block copolymer containing more than approximately 50% by weight of the poly(propylene oxide) segment could not be isolated via precipitation from methanol.

For this reason, the well known stannous octanoate route was chosen for initiating caprolactone in the presence of the hydroxyl terminated poly(propylene oxide) oligomer as shown in Figure(67). The resulting material exhibited an interesting crystalline-

rubbery crystalline triblock character. In Tables(20,21), reaction conditions, yields, compositions, molecular weights and molecular weight distributions of triblock copolymers have been summarized. As can be observed, good agreement in molecular weight was obtained up to 50% concentration of the lactone materials. However, in this method, one can observe a continuing apparent broadening of the unimodal molecular weight distributions, which may due to the ester-ester interchange reaction during the polymerization of caprolactone. The copolymers are easily moldable above the T_m of the polycaprolactone. The strength properties at room temperature are, no doubt, a function of the amount of crystallinity in the polycaprolactone segment and this was demonstrated by utilizing Instron for stress-strain measurement, as shown in Figure(68).

The mechanical behavior of the triblock copolymers have been investigated and the copolymers containing caprolactone more than 50 % by weight showed interesting two phase behaviors, illustrative of the potentially mixed amorphous glass transition at low temperature, followed by a relatively stable modulus temperature plateau, up to the crystalline melting point of the polycaprolactone. From the DMTA diagram of the triblock copolymer(Figure(69)), $\tan \delta$ increases almost linearly with the concentration of poly(propylene oxide), whereas the plateau modulus was reduced. The glass transition temperature(T_g) and crystalline melting point(T_m) of the caprolactone block were shifted to lower temperatures as the poly(propylene oxide) content was increased. Similar trends have been observed from DSC or Rheovibron experiments(Figure(70)). The transition temperatures of series of triblock copolymers are listed in Table(22). The triblock copolymers were examined by small angle x-ray spectrophotometer(SAXS) to determine the interdomain spacing. The sample with the higher caprolactone content displayed the smaller distance between crystalline domains. The SAXS patterns and estimated interspacing distances are given in Figure(71).

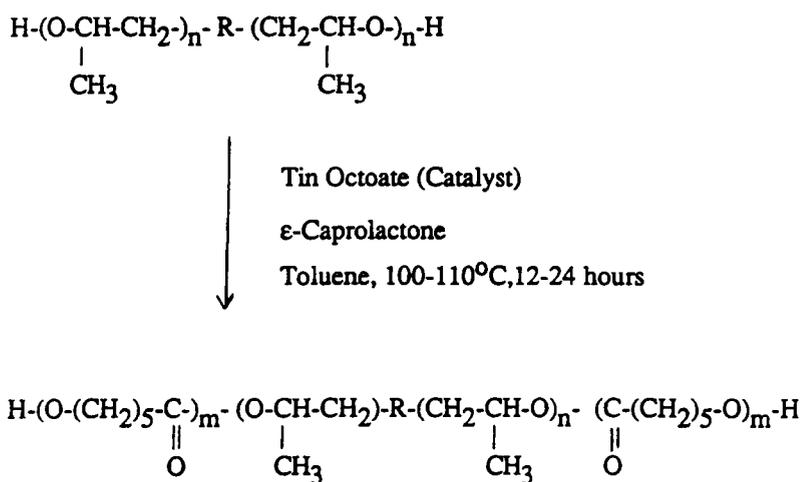


Figure 67. Synthesis of triblock copolymers of propylene oxide and caprolactone

Table 20. Experimental conditions for the synthesis of triblock copolymers of propylene oxide and caprolactone

Sample	Reaction Temp.	Reaction Time	Yield
PCL-PPO-PCL			
8k-35k-8k	108 °C	12 hours	92 %
18k-35k-18k	108 °C	24 hours	96 %
33k-35k-33k	108 °C	40 hours	98 %
66k-35k-66k	108 °C	40 hours	99 %

Table 21. Experimental results of triblock copolymer synthesis

PCL-PPO-PCL	[Mn](calc.)	[Mn](GPC)	MWD	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$
0K-35K-0K	35K	36K	1.12	0.526
8K-35K-8K	51K	52.8K	1.29	0.649
18K-35K-18K	71K	68.9K	1.41	1.059
33K-35K-33K	101K	84.8K	1.42	1.501
66K-35K-66K	167K	104K	1.53	1.930

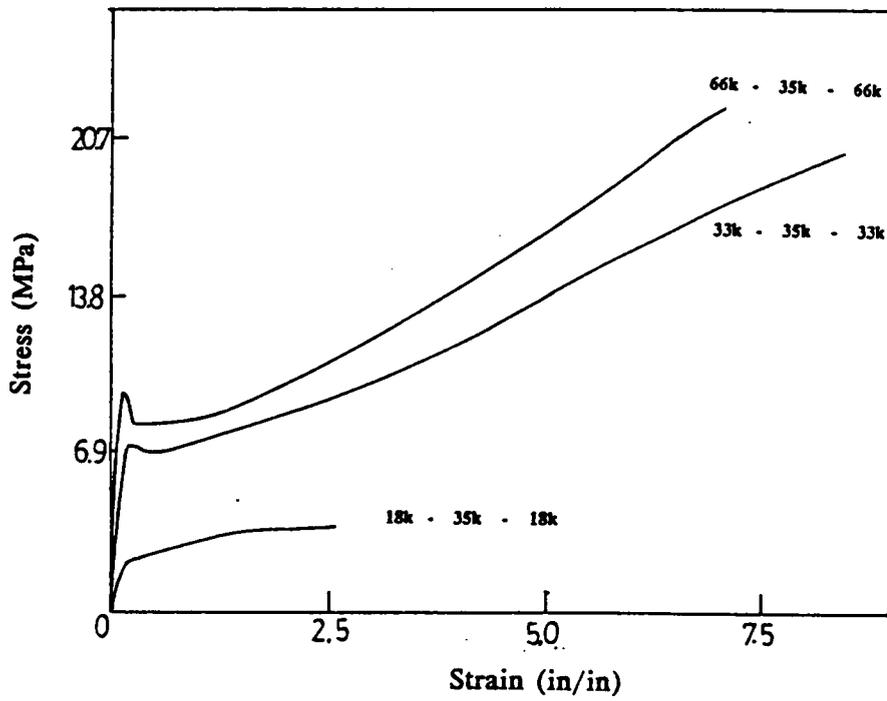


Figure 68. Stress-strain behavior of triblock copolymers of propylene oxide and caprolactone

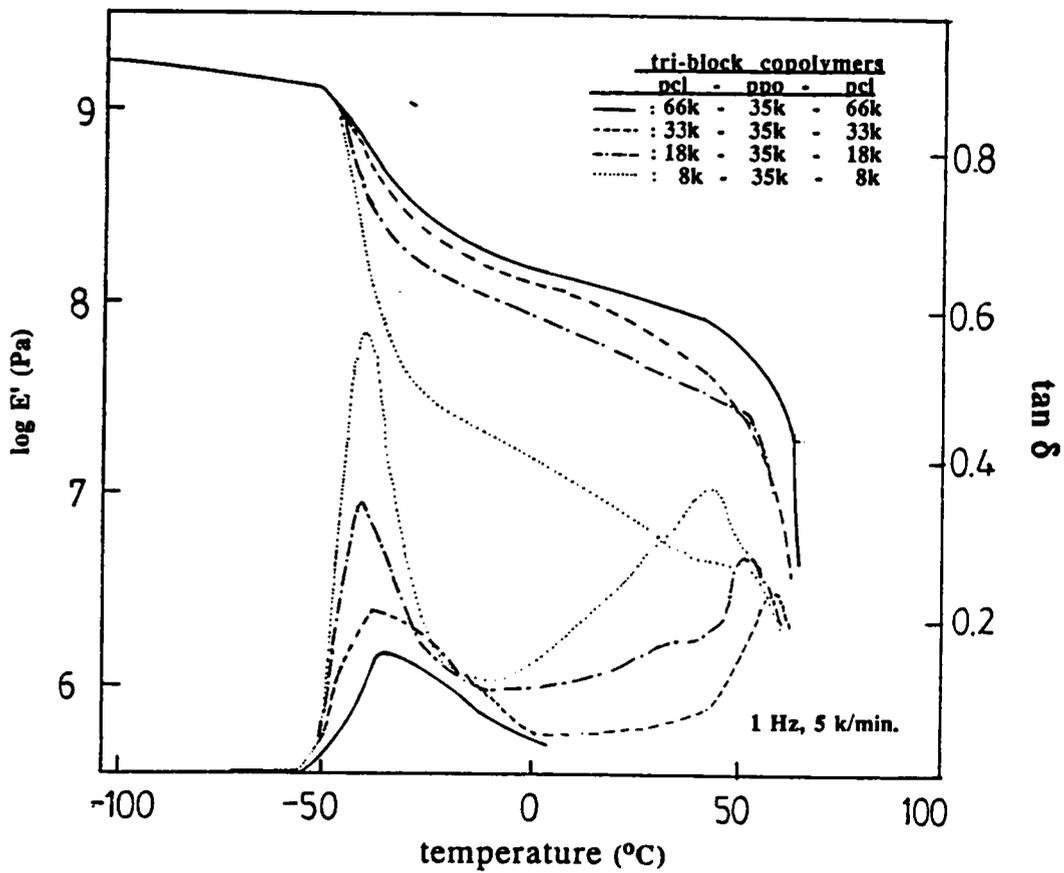


Figure 69. DMTA of triblock copolymers of propylene oxide and caprolactone

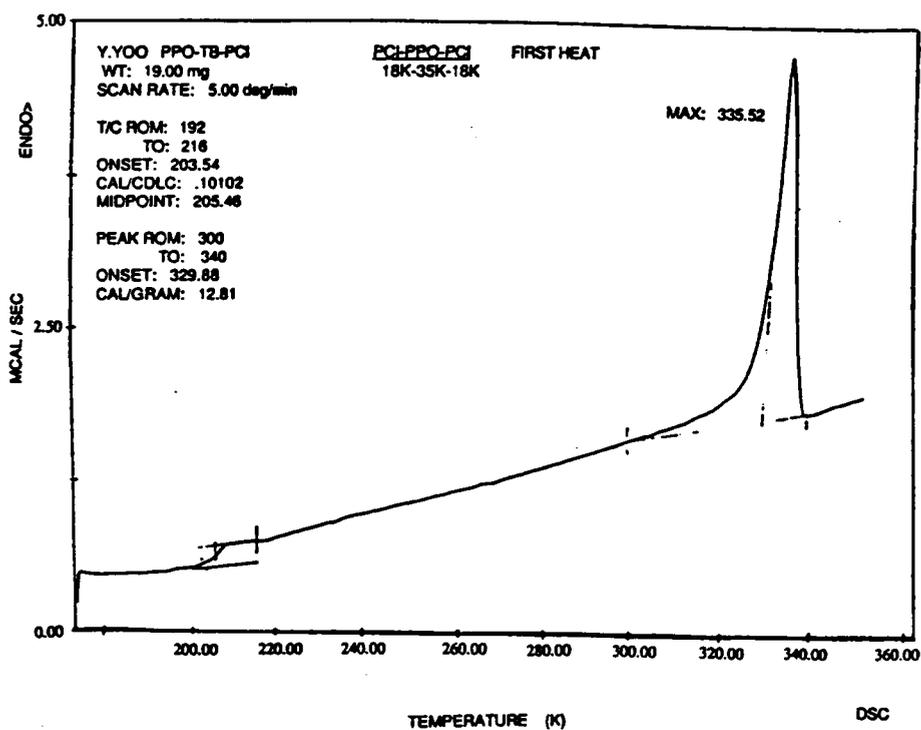


Figure 70. Differential scanning calorimetry of triblock copolymers of propylene oxide and caprolactone

Table 22. Summary of thermal analysis

Triblock copolymer	T _g (°C)				T _m (°C)			
	DSC	DMTA	TMA	RHV	DSC	DMTA	TMA	RHV
PCL-PPO-PCL								
PPO control	-71	-	-	-	-	-	-	-
8k-35k-8k	-68	-42	-52	-58	62	58	58	54
18k-35k-18k	-67	-41	-50	-58	63	61	60	55
33k-35k-33k	-65	-37	-48	-51	64	64	66	55
66k-35k-66k	-65	-35	-48	-49	65	66	67	57
PCL control	-	-	-	-	66	67	-	61

DSC: 5k/min., DMTA: 1Hz strain=x1,5k/min.
 RHV: Rheovibron 11Hz TMA: 5k/min.
 DSC PPO control: 10k/min.

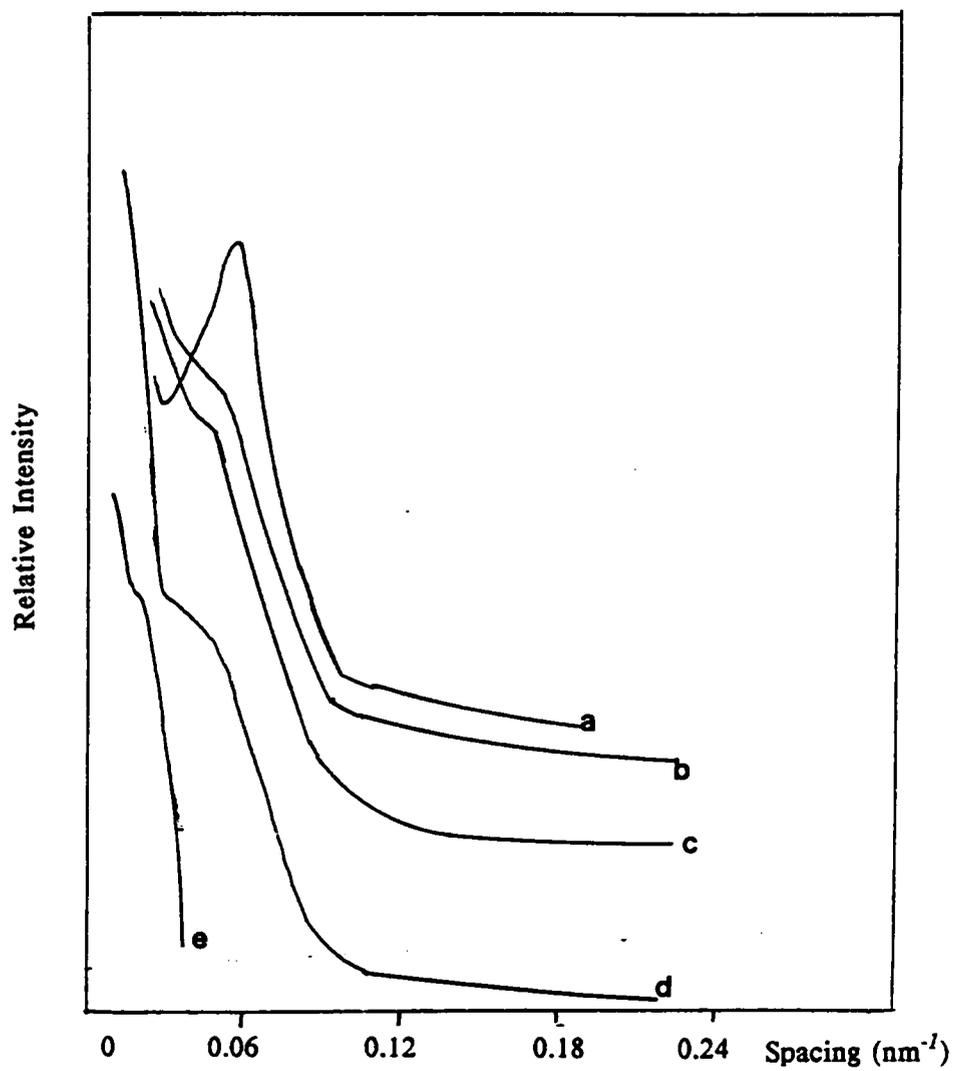


Figure 71. Small angle X-ray scans of triblock copolymers: (a)PCL control (b)66k-35k-66k (c)33k-35k-33k (d)18k-35k-18k (e)8k-35k-8k

IV.3.2. Poly(propylene oxide) Based Polyurea Segmented Copolymers

Difunctional amine terminated poly(propylene oxide)s of various molecular weights were prepared as previously discussed. As outlined in Figure(71), the synthesis of poly(propylene oxide) based polyurea was carried out via following two step process: First, methylene diphenyl diisocyanate(MDI) was weighed in the three neck flask and dissolved in dimethyl acetamide(DMAC). Amine terminated poly(propylene oxide) was added dropwise using a dropping funnel to obtain the prepolymers capped with isocyanate groups. This sequence of addition prevents the formation of high molecular weight in the initial stage of the polymerization. Therefore, a significant increase in the viscosity of the solution was not observed. In addition, a low temperature(ca. 25°C) was maintained in order to prevent side reactions such as biuret formation, which can be formed by the nucleophilic attack of isocyanate on the urea linkage, especially at an elevated temperature. In the second step, the ethylene diamine, chain extender was added as a solution in DMAC. First, 70-80% of the ethylene diamine was charged at a reasonably fast rate and the rest of the solution was added dropwise to ensure the correct stoichiometry of the amine to the isocyanate, since a few percent of the isocyanate is expected to be converted to amine due to trace amount of moisture in the solvent (usually 30-50 ppm water, as tested by Karl Fisher Titrator). Upon addition of ethylene diamine to the reaction, the viscosity of the reaction mixture remarkably increased. After complete addition of chain extender, the reaction was allowed to continue about 1-2 hours after complete addition of chain extender. The solution was homogeneous throughout the polymerization. The solids content in the solution was usually 7-15 wt/volume%. The resulting polyurea was recovered via precipitation from water or a water/methanol co-solvent. The polyurea contained 20% hard segment (wt. fraction of MDI and diamine chain extender based on total reactants).

Intrinsic viscosities and mechanical properties of the poly(propylene oxide) polyureas are listed in Table(23). The polymers demonstrated higher viscosities and tensile strength than the corresponding polymers derived from commercial Jeffamines under similar experimental conditions. This may be attributed to an acceptable difunctionality of the poly(propylene oxide) which was obtained from the aluminum porphyrin catalyst. The polyureas are readily soluble in solvents such as DMAC or NMP, which indicates that the polyureas are essentially free of any crosslinking and have little branching, if any. The linear characteristics of the poly(propylene oxide) urea will provide superior mechanical strength, since the absence of side branching affords more crystallization in the hard segment. It is also found that these linear urea systems possess better physical properties than polyurethane due to a greater degree interchain hydrogen bonding between the urea linkages. However, if would branching is present, the efficiency of the hydrogen bonding would be greatly reduced.

The thermal behavior of poly(propylene oxide) based polyureas was investigated. DSC thermograms of polyureas and the corresponding oligomers with molecular weight of 2000, and 4,000g/mole shown are in Figure(73). The consistent glass transition temperatures of each polymer and oligomer were monitored at a heating rate of 10 °C/min. Poly(propylene oxide) is a viscous liquid even at high molecular weights of approximately 100,000 g/mole. The poly(propylene oxide)s obtained by the aluminum porphyrin catalyst has a low isotactic configuration(<40 %) therefore possesses a completely amorphous morphology. Consequently, no crystallization exotherm was observed in DSC. The poly(propylene oxide) oligomers show glass transition temperatures of -75 and -56°C for the 2,000 g/mole molecular weight Jeffamine and aromatic amine terminated polymer prepared in our laboratory, respectively. However, the Tgs' of the corresponding polyureas increased ca. 16°C when the 2000 g/mole oligomer was employed as the soft segments, in both cases. Only an 8°C increase was observed in case of the

polyurea derived from the 4,000 [Mn] oligomers. As can be seen from these comparisons, high molecular weight soft segments enhance the microphase separation of these copolymers, while significant amounts of phase mixing are observed when lower molecular propylene oxide oligomer was incorporated. The mechanical strength of the polyurea elastomers were significantly dependent upon soft segment chain length, as can be seen in Table(23). The longer soft and hard segment could afford a better phase separation thus yields a higher tensile strength.

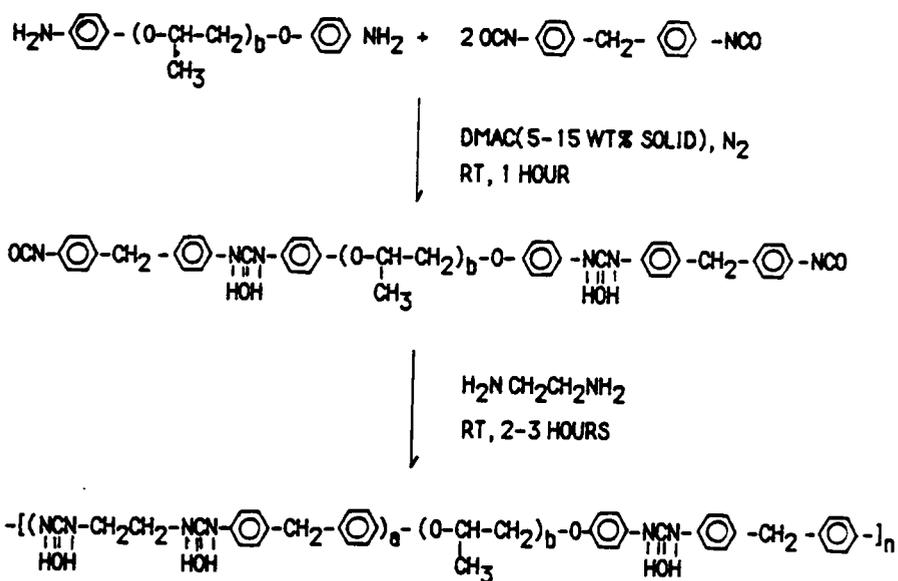


Figure 72. Reaction scheme for the synthesis of poly(propylene oxide) based polyurea

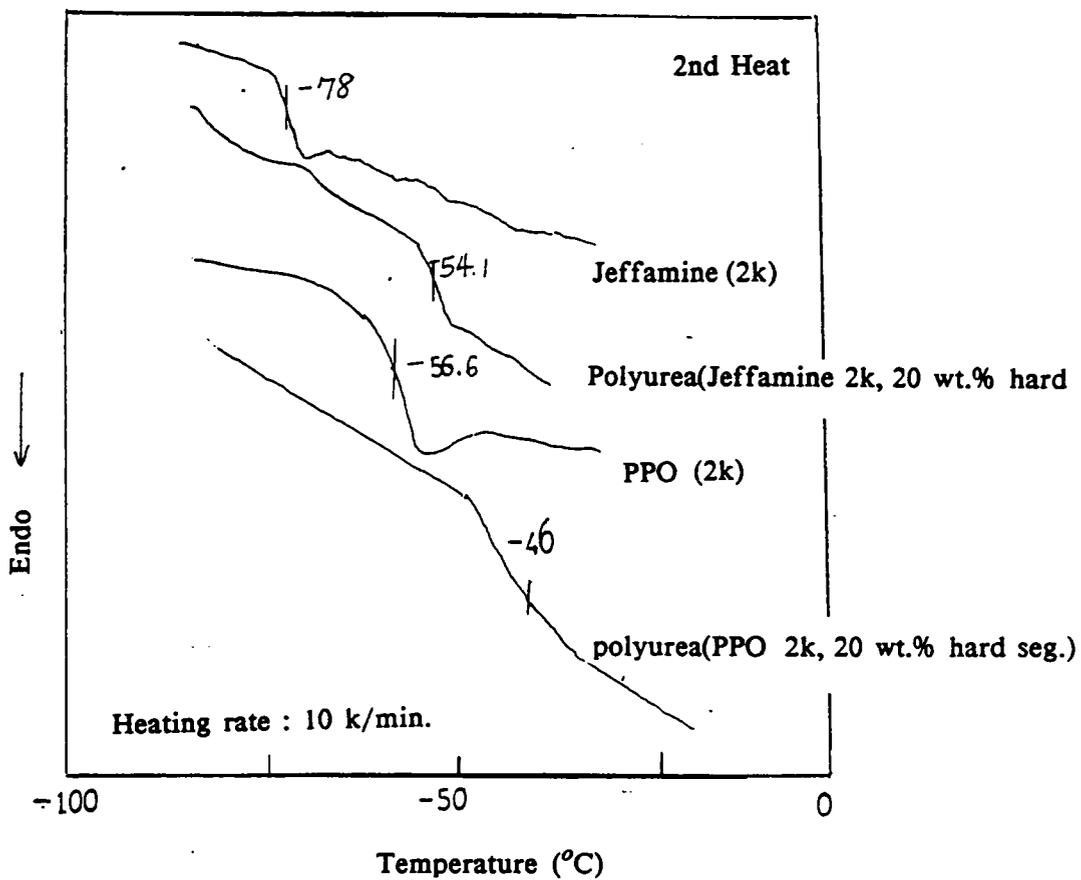


Figure 73. Differential scanning calorimetry of poly(propylene oxide)s and polyureas

Table 23. Properties of poly(propylene oxide) based polyureas

Polyurea	Tensile Strength (MPa)	Elongation at Break (%)	$[\eta]_{\text{dmac}}^{25^\circ\text{C}}$
Jeff. 2.0k-20	6.95 ± 0.74	1017.8 ± 107.4	0.59
PPO- 1.3k-20	6.01 ± 0.08	326.7 ± 17.7	-
PPO -2.0k-20	10.07 ± 0.64	1633.2 ± 80.3	0.78
PPO -2.8k-20	32.32 ± 1.34	1378.1 ± 19.8	-
PTMO-3.0k-20	40-50	-	-

i) Hard segment was consist of MDI and ethylene diamine.

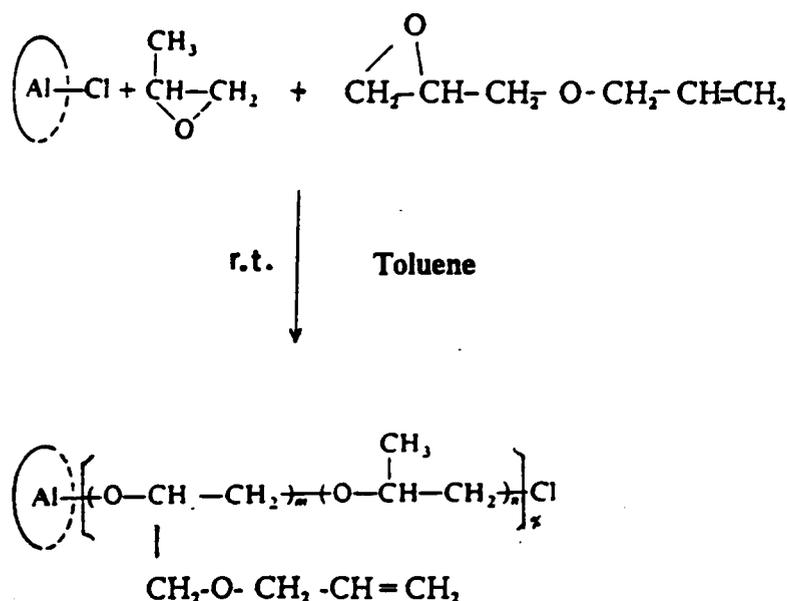
ii) Hard segment content was 20 wt %

iii) Jeffamine is the commercial aliphatic amine terminated poly(propylene oxide)

IV.3.3. Statistical Copolymers

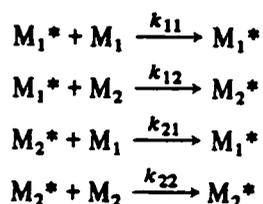
IV.3.3.1. Statistical copolymers of propylene oxide and allyl glycidyl ether.

The aluminum porphyrin catalysts turn out to be quite efficient initiators for the polymerization of the three-membered epoxides, lactones, and phthalic anhydride[109-130]. Copolymerizations of mixed monomers often provide unique features due to the versatile structure of the resultant polymeric materials. For this reason, propylene oxide was copolymerized with allyl glycidyl ether via several initiator systems. Consequently, the polymer would contain crosslinkable sites provided from the allyl glycidyl ether monomers. The copolymer had been utilized as a major ingredient for high impact elastomers. The copolymerizations were carried out by using aluminum porphyrin catalysts in toluene, which could result in statistical copolymers with following structures:



The copolymerizations proceeded, quantitatively yielding statistical copolymers of propylene oxide and allyl glycidyl ether. Typical experimental conditions and results of the copolymerizations are outlined in Table(24). The GPC trace by UV detector at 218 nm, as given in Figure(74), showed a fair agreement with the predicted values from the [Monomer]/[catalyst] ratio indicating allyl glycidyl ethers have been incorporated in the copolymers.

In order to determine the reactivity ratios, four different compositions of the comonomers (mixture of propylene oxide and allyl glycidyl ether) were employed in the copolymerizations, which were terminated at the initial stage of reaction (< 5% conversion). In the copolymerizations, two kinds of porphinatoaluminum alkoxides from the corresponding epoxide are involved as the growing species, assuming that ring opening takes place exclusively at the methylene-oxygen bonds for these non-symmetric epoxides. Therefore, the rate constants of the following four elementary reaction steps will govern the sequence distributions of the comonomers in the copolymer.



,where k_{11} is the rate constant for a chain ending in M_1 adding to monomer M_1 , k_{12} that for a propagating chain ending in M_1 adding to monomer M_2 , and so on.

Figure(75) illustrates a typical FT-IR spectrum of the allyl glycidyl ether-propylene oxide copolymer. The peak at 1655 cm^{-1} is indicative of C=C stretching of the unsaturated allyl moiety. The integration of the allyl peak and C-H wagging at known compositions of poly(propylene oxide) and allyl glycidyl ether constitutes a calibration curve,

as presented in Figure(76). From the FT-IR spectra of copolymers, the integrated ratios of C=C stretching at 1655 cm⁻¹ to C-H wagging at 1489 cm⁻¹ were calculated and the actual compositions were estimated from the calibration curve. The copolymer showed less allyl glycidyl ether contents than the initial charge. The results are given in Figure(77). Based upon the copolymer composition of comonomers (propylene oxide and allyl glycidyl ether) and corresponding copolymers, the reactivity ratios were calculated using the following formula.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

,where f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fraction of M_1 and M_2 in the copolymers.

In general, the reactivity ratio of the epoxide monomer toward the porphyrinato aluminum alkoxide decreases as the monomer carries the bulky pendant substituent, according to the study of Aida and Inoue[128]. This is attributed to the fact that the bulky monomer is more difficult to incorporate into the alkoxide growing species simply due to the steric hinderance. The effect of the allyl group may not significantly affect the reactivity of the epoxide since it has enough distance from the epoxide ring by the spacing methylene groups. The reactivity ratios of propylene oxide and allyl glycidyl ether are presented in Table(25), and compared to the those obtained from other initiator systems.

Table 24. Experimental conditions and results for the synthesis of statistical copolymers of PO and AGE

Run	Wt.% AGE	Solvent	Conv.	Time	Mn(th.)	Mn(gpc)	MWD
1	4	toluene	92 %	5 d	7,000	8,500	1.14
2	6	toluene	94 %	7 d	8,400	10,800	1.23
3	10	toluene	quant.	7 d	11,000	12,500	1.21

i) Molecular weights and molecular weight distributions were obtained from GPC chromatogram using PMMA standards.

ii) Reactions were carried out at room temperature to prevent the gelation during the polymerization.

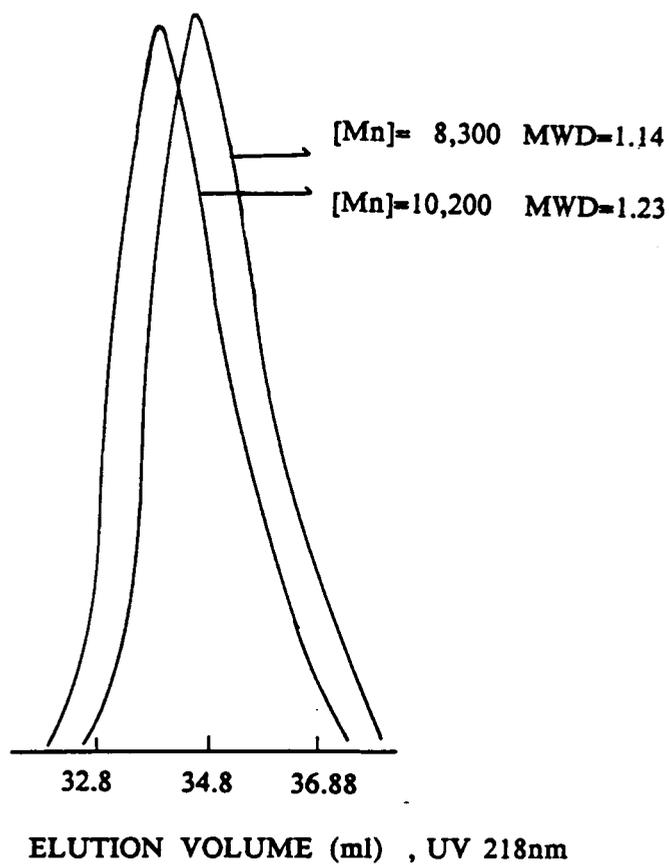


Figure 74. Typical GPC trace of statistical copolymers of PO and AGE prepared by aluminum porphyrin catalyst

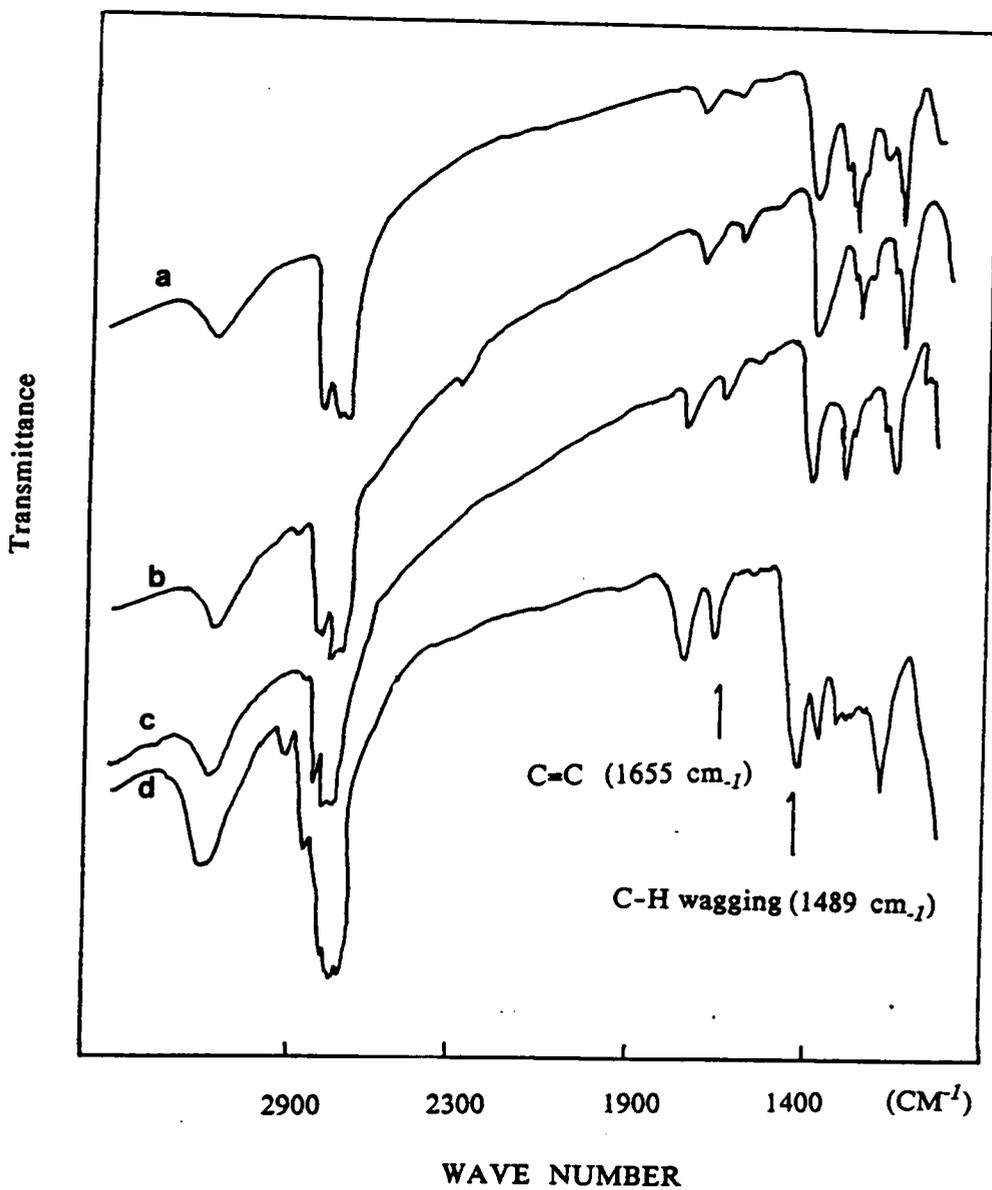


Figure 75. FT-IR spectra of statistical copolymers of PO and AGE with various compositions

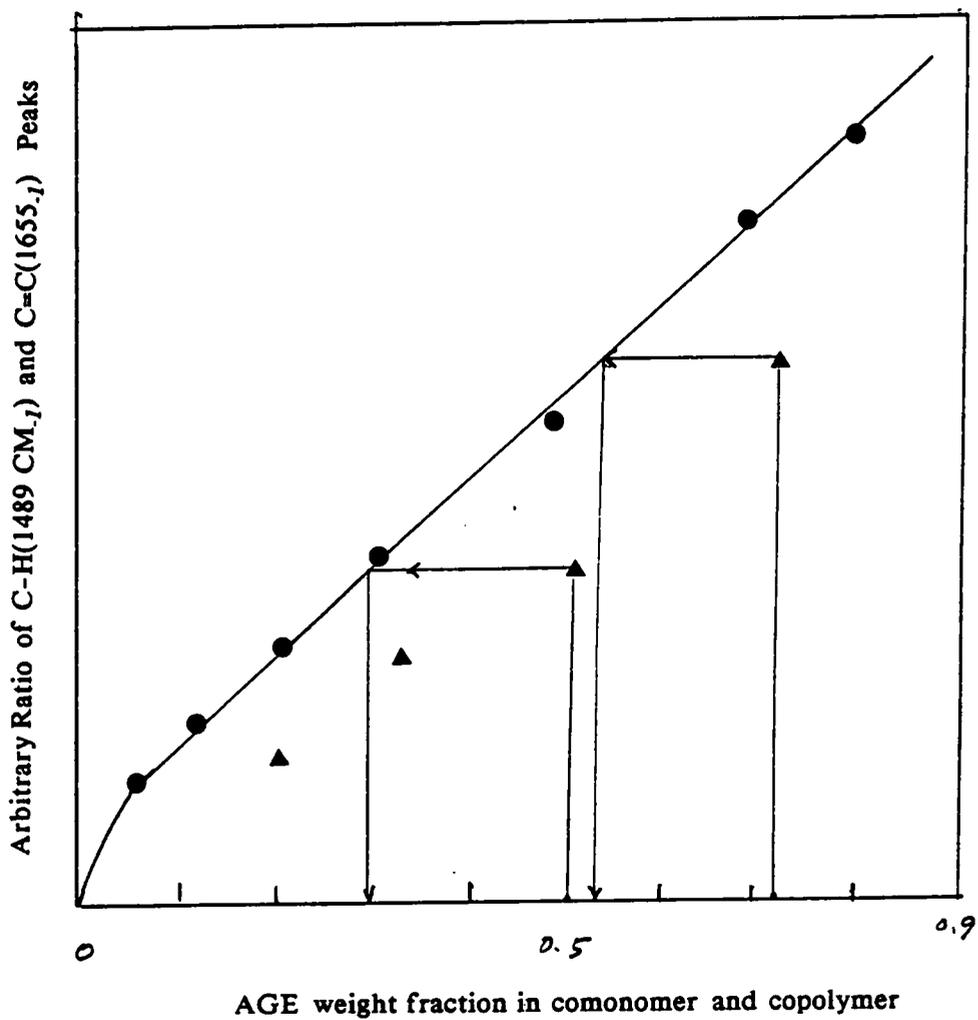


Figure 76. A calibration curve for the determination of copolymer composition

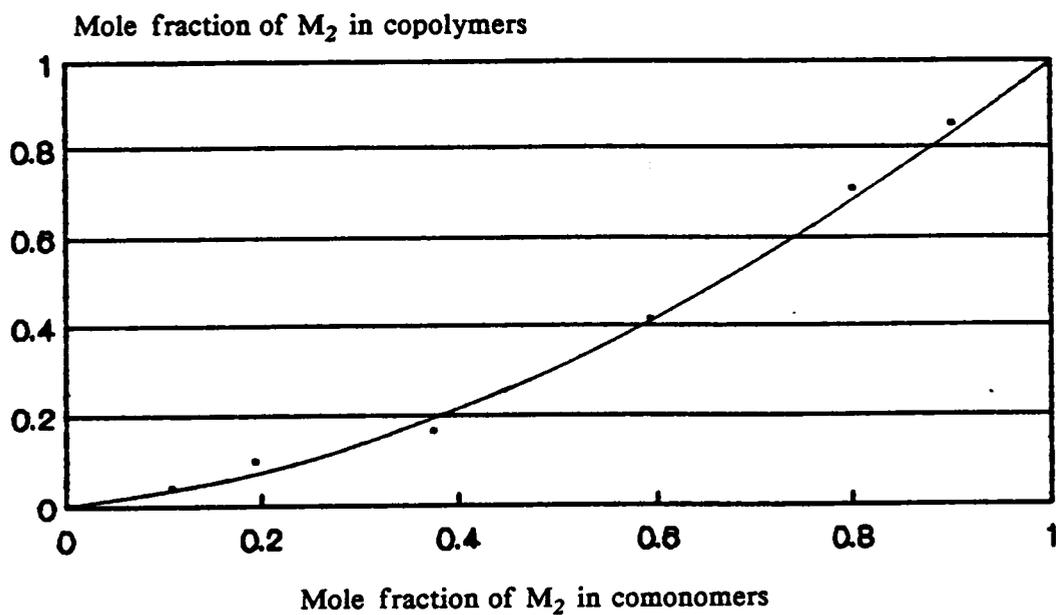


Figure 77. Mole fraction of AGE in initial charge vs in copolymer: M1 = PO, M2 = AGE, The copolymerization was carried out in toluene at room temperature and stopped at < 5% conversion.

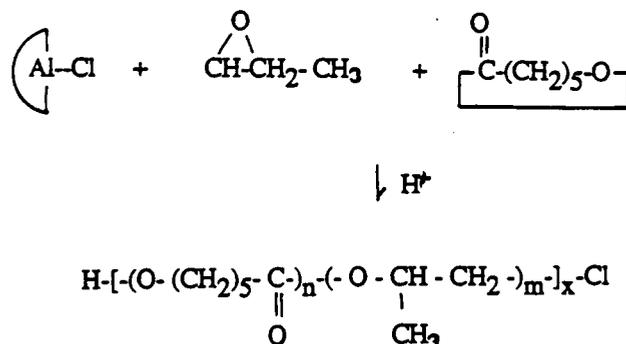
Table 25. Reactivity ratios of propylene oxide and allyl glycidyl ether

Catalyst	Solvent	M ₁	M ₂	r ₁	r ₂
TPPA1C1 (27 °C)	toluene	PO	AGE	2.35	0.78
R ₂ Al/AcAc R ₂ Zn [8] (50 °C)	benzene	PO	AGE	1.89	0.64
TPPA1C1 [125] (25 °C)	methylene chloride	PO	EO	0.3	0.5
TPPA1C1 [125] (25 °C)	methylene chloride	PO	BO	1.4	0.9

PO: propylene oxide
 AGE: allyl glycidyl ether
 EO: ethylene oxide
 BO: 1,2 butene oxide
 TPPA1C1: tetraphenyl porphyrin aluminum chloride

IV.3.3.2. Attempted synthesis of statistical copolymers of propylene oxide and caprolactone.

Copolymerizations of propylene oxide and ϵ -caprolactone were attempted, as shown below:



It was anticipated that this copolymerization might provide benefits over the respective homopolymers. For instance, the statistical copolymers, could be biodegradable, while the homopolymer of propylene oxide is not. In a similar manner, if 10-20 mole% of propylene oxide is randomly distributed over a homopolymer caprolactone backbone, the copolymer may have less crystallinity compared to the caprolactone homopolymers.

The oligomers compositions were determined by gravimetric analysis, taking advantage of the tremendous difference in the boiling points of these two monomers. It was found that the copolymer have higher propylene oxide contents compared to their corresponding comonomers (mixture of propylene oxide and caprolactone), which in turn indicates that the propylene oxide has a higher reactivity toward the porphyrinato aluminum alkoxide. The compositions of copolymers vs comonomer are plotted in Figure(78). The remarkably different reactivities predict a blocky structure of the

copolymers. The copolymers containing 10 and 20 mole percent of propylene oxide were synthesized with a quantitative yield. The proton NMR spectrum of the copolymer of propylene oxide and ϵ -caprolactone containing 20 mole percent of propylene oxide is shown in Figure(79). The integration of each peak generally agreed with the expected molar ratio of the propylene oxide and the caprolactone repeating units.

Thermal behavior of these copolymers was characterized by DSC. However, the copolymers containing poly(propylene oxide) 10-20 mole% did not show significant changes from caprolactone homopolymers with respect to crystalline melting point and heat of fusion, suggesting that these copolymers have essentially blocky characters.

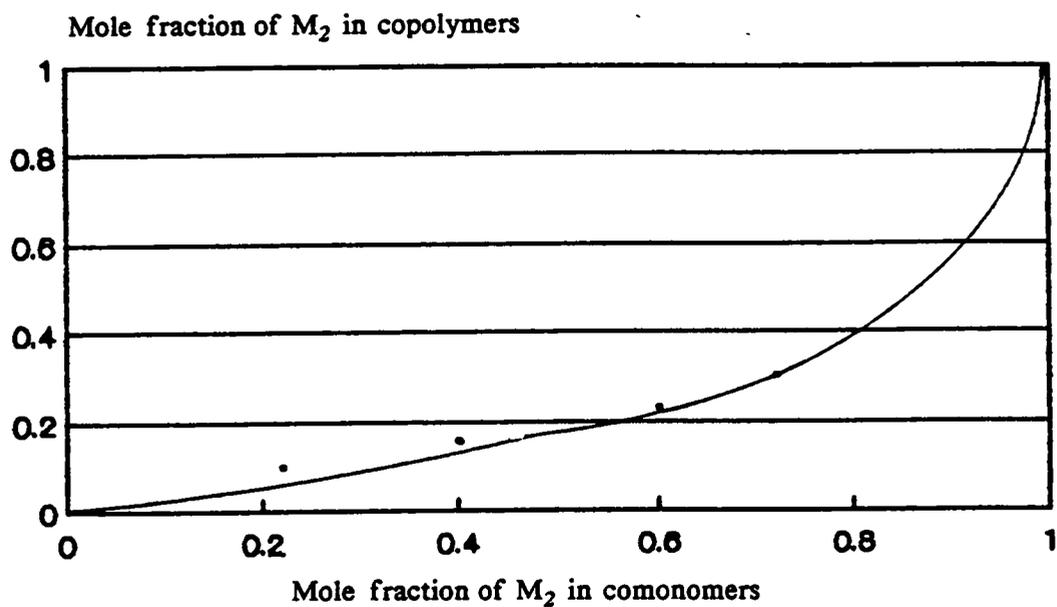


Figure 78. Mole fraction of M₂ in initial charge vs. in copolymer: The polymerization was carried out in methylene chloride at room temperature, M₁ = propylene oxide, M₂ = caprolactone

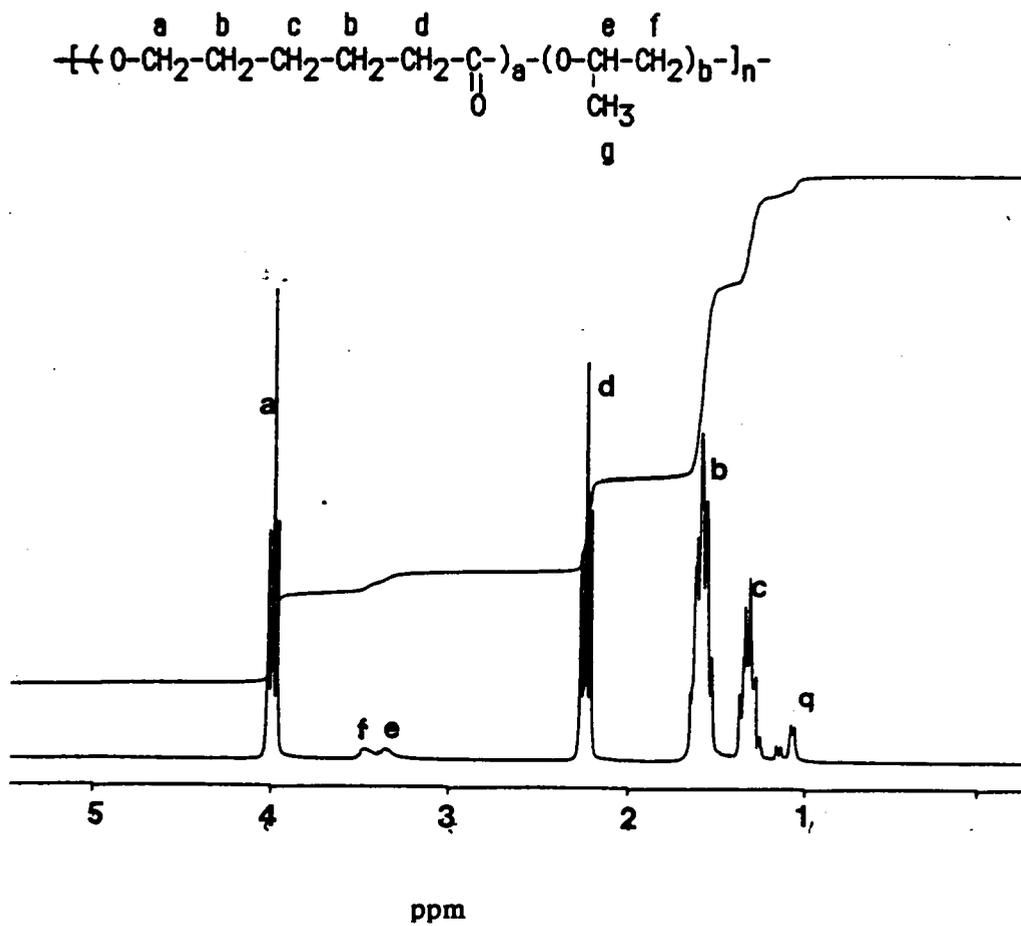


Figure 79. Proton-NMR spectrum of an attempted statistical copolymer of PO(20 mole%) and caprolactone(80 mole%)

CHAPTER V. CONCLUSIONS AND SUGGESTED FUTURE STUDIES

The synthesis of molecularly designed poly(propylene oxide) was accomplished by using aluminum porphyrin catalysts with respect to molecular weights, narrow molecular weight distributions, topologies and controlled functionalities. The poly(propylene oxide) was found to be formed by the exclusive cleavage of methylene oxygen bonds via a nucleophilic attack of the alkoxide growing species. This type of ring opening polymerization should yield a head-to-tail configuration with asymmetric monomers. The aluminum porphyrin catalyst system also allowed the synthesis of poly(propylene oxide)s with a high molecular weight of ca. 100,000 g/mole maintaining narrow molecular weight distribution. Furthermore, this system clearly displayed a living nature as indicated by the narrow molecular weight distributions observed from gel permeation chromatography and was free of termination. According to the preliminary kinetic studies, the propagation rate is proportional to the first order of both monomer and catalyst concentrations with an activation energy of 9.7-11.3 kcal/mole (40.0-45.8 kJ/mole).

Various functionalities were successfully incorporated into the poly(propylene oxide) as terminal end groups by modification of the aluminum porphyrin catalyst with co-initiators. Such modified systems can be used to synthesize well defined hydroxyl terminated poly(propylene oxide)s. Also, the polymer could be prepared with very narrow molecular weight distributions and the number average molecular weights could be controlled by the [monomer]/[chain transfer agent] ratios. Side reactions such as hydrogen abstraction that occur in the potassium hydroxide initiated anionic polymerization of propylene oxide were not observed when using this synthetic route. Multifunctional secondary hydroxyl terminated poly(propylene oxide)s were obtained by using DGEBA prereacted catalyst.

Primary amine and primary hydroxyl terminated poly(propylene oxide)s could be prepared by protecting those functionalities with aromatic nitro groups or benzyl ether groups and by subsequent hydrogenation. The latter step also removes the purple color of the porphyrin due to the destruction of the conjugation. Multifunctionality of those terminal groups was achieved by coupling two or three polymer chains with acid chlorides. Even higher functionality could be achieved via star-like post coupling of growing polymer chains by DGEBA. In addition, primary amine terminated poly(propylene oxide) could be obtained through post reactions of the hydroxyl groups by means of isatoic anhydride or p-fluoro nitro benzene/hydrogenation routes. Other functional groups such as allyl, carboxylic and methacrylate could also be incorporated at the end of poly(propylene oxide) chain. The structures of poly(propylene oxide)s with a variety of functional end groups were identified by spectroscopic analysis such as $^1\text{H-NMR}$, and Fourier Transform Infrared Spectroscopy. Such characterizations verified the presence of particular end groups along the polymer chains. Integration of the $^1\text{H-NMR}$ peaks provided very reliable number average molecular weights, which were in accordance with the values determined from both GPC and titration technique. Author's

unique approach enabled the synthesis of primary hydroxyl terminated poly(propylene oxide)s without resorting to a block copolymerization route. Current anionic polymerizations must use a significant amount of ethylene oxide to generate the primary hydroxyl end. Both hydrogenolysis of the benzyl ether group in poly(propylene oxide) and the reduction of an aromatic nitro group to amine resulted in quantitative yields.

By taking advantage of the well defined structures of the poly(propylene oxide)s, it was possible to study the effect of functional end groups on the thermal degradation behavior. Most interestingly, aromatic nitro and aromatic amine groups resulted in thermally stable poly(propylene oxide)s. On the other hand, unsaturated functional groups such as allyl, or acrylate had the opposite adverse effects. Hydroxyl terminated oligomers derived from bisphenol A like initiators also possess enhanced thermal stabilities, which may be due to the absence of unsaturation as well as possibly some remaining phenolic end groups. Among various functional groups, the positive effects of the aromatic nitro and aromatic amines were the most remarkable. Typically, difunctional aniline terminated oligomers exhibited enhanced thermal stability by ca. 150°C as observed by TGA. This stabilizing effect gradually diminishes as the concentration of the end group is diluted. Grafting aromatic nitro groups on the poly(propylene oxide) chain with the end groups inhibited oxidative thermal degradation.

Well defined poly(propylene oxide) also could be utilized in the synthesis of block and segmented copolymers. Difunctional hydroxyl terminated poly(propylene oxide)s of 35,000 g/mole molecular weight have been used as a center block in the copolymer of poly(caprolactone)-poly(propylene oxide) of various compositions. The block copolymers demonstrated phase separation as characterized by dynamic mechanical thermal analysis or rheovibron. Amine terminated low molecular oligomers obtained from the aluminum porphyrin catalysts system were also employed as soft segments in the synthesis of polyurea thermoplastic elastomers. The resulting polyurea exhibits im-

proved mechanical properties, thermal stability to its analogue derived from commercial Jeffamines, as new synthetic route affords virtually difunctional amine terminated oligomers.

The improved difunctionality of the oligomeric poly(propylene oxide)s yielded high molecular weights when utilized in step polymerizations as demonstrated by high intrinsic viscosity values. The polyurea based on PPO-4,000 exhibited a higher relaxation temperature of the hard segment and a lower glass transition temperature of the soft segment than the polyurea based on PPO-2000. This clearly reflects the difference in phase separation behavior due to the longer sequences of hard and soft blocks.

The synthetic approaches have been directly applied to prepare statistical copolymers containing polyethers and polyesters. Statistical copolymers of propylene oxide and allyl glycidyl ether have been synthesized by using the aluminum porphyrin catalysts. From the copolymerization kinetic studies, the allyl glycidyl ether showed lower reactivity than propylene oxide toward the growing aluminum alkoxide species.

The reactivity of both monomers were determined as $r_1 = 2.35$, $r_2 = 0.78$ from FT-IR spectra of the oligomers obtained at the initial stage of the polymerization. Attempts to prepare statistical copolymers of propylene oxide and ϵ -caprolactone were also investigated, which showed considerable difference in reactivity ratios. The propylene oxides preferentially incorporated into the growing chain leading to a blocky nature of these statistical copolymers.

In summary, a variety of well defined poly(propylene oxide)s with useful functionalities could be synthesized in a controlled manner. Second, a unique study on thermal degradation behavior of poly(propylene oxide) was conducted, which ultimately provided a knowledge on the stabilization of thermally sensitive polymers. Finally, the functionally terminated poly(propylene oxide)s could be utilized in copolymerizations, resulting in numerous polymeric materials.

In a continuation of efforts on this coordination polymerization , following future works are suggested. First, the study of the polymerization mechanism in aluminum porphyrin catalyst system would be worthwhile to pursue. Recently, the investigation has been initiated through the aluminum-NMR technique. It was hoped that the aluminum-NMR may elucidate various coordinated states of aluminum-porphyrin in the course of polymerization.

The porphyrins are very versatile compounds. The reactivity of metalloporphyrin may be significantly affected by the substituents bound to pyrrole carbon of the porphyrins. It would be valuable to examine the possible relationship between the substituents and catalytic activities of the aluminum porphyrins.

Since these synthetic approaches afford the molecular design of poly(propylene oxide) in terms of chain lengths and functionalities, these polymers and oligomers can be directly utilized in a number of polymer hybrid systems. The resulting hybrids systems may have relatively well defined structures, which will in turn allow the study on structure-property relationship. In addition, the aluminum porphyrin catalysts allow the direct synthesis of various statistical and block copolymers, which may be another subject of future studies.

CHAPTER VI. BABLIOGRAPHY

1. G. M. Powell III. and F. E. Bailey Jr., in A. Standen, ed., "Kirk-Othmer Encyclopedia of Chemical Technology", 2nd edition, Supple. vol.1, John Wiley & Sons Inc, New York, 1900, p597.
2. S. D. Gagnon, J. I. Kroschwitz, ed., "Encyclopedia of Polymer Science and Engineering", 2nd ed., Wiley Interscience, New York, 1986, 6, p276.
3. A. Streitweiser Jr. and C. H. Heathcock, "organic Chemistry" 2nd ed., Macmillan Publishing Company, New York, 1981.
4. C. Hepburn, "Polyurethane Elastomers", Applied Science Publishers, New York, 1982, Chapter 4.
5. Ibid, Chapter 3.
6. H. Ulrich in M. Grayson, ed., Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., vol. 23, Wiley-Interscience, New York, 1982, p576.
7. E. R. Mueller and W. H. Martin, Lubr. Eng., 1975, 31(7), p348.
8. Nye Clington and Paul Matlock in J. I. Kroschwitz, ed., "Encyclopedia of Polymer Science and Engineering", 2nd ed., Wiley-Interscience, New York, 1986, 6, p267.

9. J. N. Cawse, J. P. Henry and M. W. Swartzlander in M. Grayson, ed., "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd ed., Wiley-Interscience, New York, 1980, 9, p432.
10. R. O. Kirt and T. J. Dempsey in M. Grayson, ed., *ibid*, Wiley- Interscience, New York, 1980, 19, p246.
11. A. H. Haines in J. F. Stoddart, ed., "Comprehensive Organic Chemistry", Pergamon Press, New York, 1979, 1, p853.
12. C. C. Price in S. Patai, ed., "The Chemistry of the Ether Linkage", Wiley- Interscience, New York, 1967, p499.
13. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectroscopic Identification of Organic Compounds", 4th ed., John Wiley & Sons, New York, 1981.
14. D. J. Merer, *J. Phys. Chem.*, 1967, 71, p1861.
15. G. Kraus and H. E. Railsback, *Polym. Prepr., Am. Chem. Soc., Polym. Chem. Div.*, 1973, 14(2), p1051.
16. J. L. Cohen and G. P. Fong, *Anal. Chem.*, 1975, 47, p313.
17. H. M. Stanley in, S. A. Miller, ed., "Ethylene and its Industrial Derivatives", Ernest Benn, LTD., London, 1969, p16.
18. *Chem. Week*, 1980, 127(14), p47.
19. W. Kuhn, *Hydrocarbon Process*, 1979, 59(10), p123.
20. N. Indicator and W. F. Brill, *J. Organic Chemistry.*, 1965, 30, p2074.
21. R. A. Sheldon and J. A. Van Doorn, *J. Catalyst*, 1974, 34, p242.
22. K. H. Simmrock, *Hydrocarbon Process*, 1978, 57(11), p105.
23. B. H. M. Kingston et. al., *Anal. Chem.*, 1969, 41, p86.
24. G. C. Sinke and D. L. Hildenbrand, *J. Chem. Eng. Data*, 1962, 7(1), p74.
25. N. G. Gaylord, ed., "Polyethers", Wiley-Interscience, New York, 1963, 1, p226.
26. *ibid.* p223.

27. A. J. Lowe. et. al., U. S. Patent 3,380,967, 1968.
28. I. R. Schmolka and L. R. Bacon, *J. Am. Oil Chem. Soc.*, 1967, 44, p559.
29. M. Hudlicky, "Reductions in Organic Chemistry", John Wiley & Sons, New York, 1984.
30. R. E. Ridenour and E. E. Flagg, *J. Organometal Chem.*, 1969, 16, p393.
31. C. C. Price in S. Patai, ed., "The Chemistry of the ether Linkage", Wiley-Interscience, New York, 1967, p499.
32. C. P. McClelland, *Chem. Eng. News*, 1945, 23(3), p247.
33. P. A. Levene, *J. Biol. Chem.*, 1927, 75, p325.
- 34a.S. D. Gagnon, J. I. Kroschwitz, ed., "Encyclopedia of Polymer Science and Engineering", 2nd ed., Wiley-Interscience, New York, 1986, 6, pp273-307.
- 34b.J. E. McGrath., "Ring Opening Polymerization: Kinetics, Synthesis, Mechanism, ACS Symposium Series", J. E. McGrath, ed., 1985, p286.
35. C. C. Price, in, E. J. Vandenberg, ed., "Polyether, ACS Symposium Series", 1975, 6, Chap. 1.
36. T. Aida and S. Inoue, *Macromolecules*, 1981, 14, p1166.
37. S. Perry and H. Hibber, *J. Am. Chem. Soc.* 1940, 62, p2599.
38. S. Inoue and T. Aida, in K. I. Ivin and T. Saegusa, ed., "Ring Opening Polymerization", Wiley-Interscience, New York, 1984, 1, Chap. 4.
39. W. M. Pasika, *J. Polymer Sci.*, 1965, A3, p4287.
40. R. E. Parker, *Chemical Review*, 1959, 59, p758.
41. S. Penczek et. al., *Adv. Polym. Sci.*, 1980, 37, p1.
42. T. Saegusa, "Ring Opening Polymerization", Wiley- Interscience, New York, 1984, 6, Chap. 1.
43. F.C. Schilling and A.E. Tonelli, *Macromolecule*, 1986, 19, p1337.
44. G. Gee et. al., *J. Chem. Soc.*, 1959, p1345.

45. G. Gee et. al., *ibid*, 1959, p1388.
46. S. Boileau, *Tetrahedron Lett.*, 1978, p1767.
47. S. Inoue, *Chem. Tech.*, 1976, 6, p588.
48. Y. Ishii., "Ring Opening Polymerization", S. L. Reegan, ed., Marcel Dekkar, New York, 1969, Chap. 1.
49. C. C. Price and M. K. Akkapeddi, *J. Am. Chem. Soc.* 1972, 94, p3972.
50. J. E. Figueruelo and A. J. Bello, *J. Macromol. Sci. Chem.*, 1969, A3, p311.
51. A. Deffieux and S. Boileau, *Polymer*, 1977, 18, p1047.
52. D. M. Simmons and J. J. Verblanc, *J. Polym Sci.*, 1960, 44, p303.
53. E. C. Steiner et. al., *J. Am. Chem. Soc.*, 1964, 86, p4678.
54. C. C. Price, *J. Am. Chem. Soc.*, 1966, 88, p4039.
55. J. Furukawa and T. Saegusa, "Polymerization of Aldehyde and Oxides", Wiley-Interscience, New York, 1963, Chap. 3.
56. S. D. Gagnon and J. I. Kroschwitz, ed., "Encyclopedia of Polymer Science and Engineering", 2nd ed., Wiley-Interscience, New York, 1986, 6, p237.
57. H. Becker and C. Wagner, *Acta Polymer*, 1982, 33, p34.
58. G. Gee and W. C. E. Higginson, *J. Chem. Soc.*, 1961, p4298.
59. E. J. Vandenberg, *J. Polym. Sci. Part A-1*, 1969, 7, p525.
60. M.E. Pruitt and J.M. Baggett, US Patent 2,706,181, 1955.
61. C. C. Price and M. Osgar, *J. Am. Chem. Soc.*, 1956, 78, p690.
62. C. Booth and W. C. E. Higginson, *Polymer*, 1964, 5, p497.
63. T. Aida, R. Mituta, Y. Yoshida, S. Inoue, *Die Makromol. Chem.* 1981, p1073.
64. T. Aida and S. Inoue, *Macromolecules*, 1981, 14, p1162.
65. T. Aida and S. Inoue, *Makromol. Chem. Rapid Commun.*, 1980, 1, p677.
66. T. Yashuda and S. Inoue, *Ibid*, 1982, 3, p585.
67. T. Aida and S. Inoue, *Macromolecules*, 1982, 15, p682.

68. E. J. Vandenberg, *J. Polym. Sci.*, 1960, 47, p486.
69. A. Sato et. al., *Makromol. Chem.*, 1975, 176, p1187.
70. S. Inoue et. al., *Makromol. Chem.*, 1962, 53, p215.
71. T. Hirano, *Makromol. Chem.* 1976, 197, p3237.
72. *Ibid.*, p3245.
73. W. Kuran, S. Pasykiewicz and J. Skupinkusa. *Makromol, Chem.* , 1976, 177, p11.
74. N. Takeda and S. Inoue, *Makromol. Chem.* 1978, 179, p893.
75. Z. Jedlinski, A. Dworak and M. Bero, *Makromol. Chem.* 1979, 19, p949.
76. Z. Jedlinski, A. Dworak and M. Bero, *Makromol. Chem.* 1970, 180, p949.
77. C. C. Price and D. Carmelite, *J. Chem. Am. Soc.*, 1966, 88, p4039.
78. M. Barlow, *J. Polym. Sci. Part A-2*, 1966, 4, p121.
79. G. Allen, C. Booth and C. C. Price, *Polymers*, 1967, 8, p414.
80. J. M. Bruce and S. J. Hurst, *Polymer*, 1966, 7, p1.
81. F. N. Hill, F. E. Bailey and J. T. Fitzpatrick, *Ind. Eng. Chem.*, 1958, 50, p5.
82. J. Furukawa and T. Saegusa, "Polymerization of Aldehyde and Oxides", Wiley, New York, 1963, p169.
83. C. Booth et. al., *Polymer*, 1964, 5, p479.
84. W. Kuran, A. Rokiki and J. Pienkowski, *J. Polym. Sci., Polym. Chem.* 1979, 17, p1238.
85. E. J. Vandenberg, *J. Polym. Sci. Part A-1*, 1969, 7, p525.
86. *Ibid.*, p540.
87. T. Ueskima, T. Fujii, R. sakata and J. Furukawa, *Makromol. Chem.*, 1966, 98, p58.
88. S. Kambara, M. Hatano and K. Sakaguchi, *J. Polym. Sci.*, 1961, 51, p57.
89. G. Sartori and G. Costa, *J. Elektrochem.* 1959, 63, p105.
90. E. J. Vandenburg, *J. Polym. Sci., Part A-1*, 1969, 7, p541.
91. A. Noshay and C. C. Price, *J. Polym. Sci*, 1959, 34, p165.

92. E. J. Vandernburg, *J. Polym. Sci.*, 1960, 47, p486.
93. C. L. Lebas and P. A. Turley, *Proceedings of the Sixth SPI Conference, Society of Plastics Industry*, New York, 1983, p43.
94. S. L. Wellons, M. A. Carey and D. K. Elder, *Anal. Chem.*, 1980, 52, p1374.
95. ASTM Standard, E 441-74, 1980, p949.
96. T. Segusa and E. Goothal, ed., "Ring Opening Polymerization", *Am. Chem. Soc.*, Washington, 1977.
97. F. Schilling and A. E. Tonelli, *Macromolecules*, 1986, 19, p1337.
98. A. Kumar, *Polymer*, 1980, 21, p317.
99. J. M. Hoover, Ph. D. Thesis, Blackburg, Virginia, 1987.
100. G. Odian, "Principles of Polymerization", 2nd ed., *John Wiley & Sons*, New York, 1981, p427.
101. S. Penczek, *Polym. Prepr., Am. Chem. Soc., Polym. Chem. Div.*, 1988, 29(2), p38.
102. B. D. Berlzin, "Coordination compounds of porphyrins and Phthalocyanines.", *John Wiley & Sons*, New York, 1981, Chapter 1-5.
103. K. M. Smith, *Porphyrins and Metalloporphyrins*, *Elesvier*, New York, 1975.
104. B. M. Hoffman and P. D. Sina, *J. Am. Chem. Soc.*, 1983, 105, p1776.
105. C. L. Hill and B. C. Schardt, *J. Am. Chem. Soc.*, 1980, 102, p6374.
106. J. T. Groves, W. J. Kruper and R. C. Hanshalter, *J. Am. Chem. Soc.*, 1980, 102, p6375.
107. W. Caughey and A. Corwin, *J. Am. Chem. Soc.*, 1955, 77, p1509.
108. C. Storm. et. al., *J. Am. Chem. Soc.*, 1966, 88, p2525.
109. T. Aida and S. Inoue, *Macromolecule*, 1981, 14, p1166.
110. T. Aida and S. Inoue, *Macromolecule*, 1981, 14, p1162.
111. T. Aida and S. Inoue, *Makromol. Chem.*, 1981, 182, p1073.
112. T. Aida and S. Inoue, *Macromol.*, 1982, 15, p682.

113. S. Inoue and T. Aida, *Makromol Chem., Macromol. Symp.* 6, 1986, p217.
114. T. Yasuda et. al. *Makromol Chem. Rapid Commun.*, 1982, 3, p585.
115. T. Aida, "Ph.D. Thesis", University of Tokyo, Japan 1984, Chap 2.
116. T. Aida and S. Inoue, *Makromol. Chem. Rapid Commun.*, 1980, 1, p677.
117. S. Inoue, *Makromol. Chem.*, 1978, 179, p1377.
118. T. Aida and S. Inoue, *Macromolecules*, 1982, 15, p682.
119. T. Aida and S. Inoue, *J. Am Chem. Soc.*, 1983,105, p1304.
120. T. Aida and S. Inoue, *Macromolecules*, 1985, 18, p1049.
121. T. Aida and S. Inoue, *Macromolecules*, 1982, 15, p682.
122. T. Aida, K. Wada and S. Inoue., *Macromolecules*, 1987, 20, p237.
123. S. Asano, T. Aida, S. Inoue, *Macromolecules*, 1985, 18, p2057.
124. T. Aida et. al., *Macromolecules*, 1988, 21, p1195.
125. T, Aida and S. Inoue., *J. Am. Chem. Soc.*, 1985, 107, p1358.
126. T. Yasuda, T. Aida and S. Inoue., 1984, 17, p2217.
127. T. Aida, S. Inoue, *J. Am. Chem. Soc.*, 1983, 105, p1304.
- 128.T, Aida, M. Ishikawa and S. Inoue, *Macromolecules*, 1986, 19, p8.
129. S. Inoue, *Bull. Chem. Soc, Japan.* 1978, 51, p3564.
130. F. Kojima, T. aida. S. Inoue., *J. Am. Chem. Soc.*, 1986, 108, p391.
131. W. J. Bailey, *Americal Chem. Soc. Symposium Series*, 286, 1985, Chap 4.
132. W. J. Bailey and B. Gapad, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., Preprints.* 1984, 27(1), p58.
133. W. J. Bailey, *Am. Chem. Soc. Div. Poltm. Chem., Preprints*, 1984, 27(1), p210.
134. T. Uryu, *J. Polym. Sci., Polym. Lett. Ed.*, 1983, 11, p275.
135. C. C. Price and M. Osgan, *J. Org. Chem.*, 1958, 23, p828.
136. M. Ishimori and T. Tsuruta, *Makramol. Chem.*, 1963, 66, p1477.
137. E. J. Vandenburg, *J. Polym. Sci.*, 1960, 47, p486.

138. R. A. Sheldon et. al., *J. Polym. Sci., Polym. lett.* 1965, 3, p23.
139. A. Sato, T. Hirano and T. Tsuruta, *Makromol. Chem.*, 1975, 176, p1187.
140. J. Furukawa, J. Akutsu and T. Saegusa, *Makromol. Chem.*, 1965, 81, p100.
141. T. Tsuruta, S. Inoue and J. Furukawa, *Makromol. Chem.*, 1962, 53, p215.
142. W. L. Hawkin., "Polymer degradation and stabilization", Springer-verlarg, New York, 1984, p3-5.
143. T. Kelen, "Polymer degradation", Van Nostrand Reihold Co, New York, 1983, Chapter11.
144. *ibid.*, Chapter 10.
145. W. Ostwald., *J. Soc. Chem. Ind. (London)*, 1913, 31, p1152.
146. N. Grassie ed., "Developments in Polymer Degradation" vol. 5, Applid science publisheds, New York, 1984.
147. J. R. Shelton., "Stabilization Against Thermal Oxidation", in "Polymer Stabilization", W. L. Hawkins ed., Wiley- Interscience, 1972, p29.
148. M. G. Chan and W. L. Hawkins, *Polym. Eng. Sci*, 1967, p3.
149. R. H. Hanson. et. al., *Trans. Inst. Rubber Ind.*, 1963, 39, p301.
150. L. A. Wall., M. R. Harvey and M. J. Tryon., *J. Phys. Chem.* 1956, 60, p1306.
151. L. D. Keith and F. J. Padden., *J. Appl. Phys.* 1971, 42, p 4585.
152. W. L. Hawkins ed, "Polymer stabilization", Wiley Interscience, New York, 1972, p140.
153. N. Grassie and B. J. D. Torrance, *J. Polym. Sci. Part A-1*, 1968, 6, p3303.
154. W. Dewinter, *Macromol. Sci., Rev. Macromol. Chem.*, 1966, 1, p329.
155. W. L. Hawkins, "Polymer degradation and Stabilization", Springe Verlag, New York, 1984, p40.
156. *Ibid.*, p42.

157. N. Grassie, ed., "Developments in Polymer Degradation", Applied Science Publishers, New York, 1984, chap. 6.
158. Y. Kamiya and E. Niki, "Oxidative degradation, in Aspects of Degradation and Stabilization of Polymers", M. H. G. Jellinek, ed., Elsevier, New York, 1978.
159. J. C. Ambelong et. al., "Rubber Rev., Rubber Chem. and Technol., 1979, p99. 1963, 36, p1497.
160. C. C. Price, J. Chem., Ed., 1965, 42(1), p13.
161. K. U. Ingold, "Inhibition of Oxidation": "Advances in Chemistry Series", Am. Chem. Soc., 1968, 77, p296.
162. D. H. R. Barton and J. Howlett, J. Chem. Soc., 1960, p144.
163. J. R. Thomas and C. A. Tolman, J. Am. Chem. Soc., 1962, 84, p2931.
164. K. U. Ingold and J. E. Puddington, Ind. Eng. Chem., 1959, 51, p1319.
165. J. R. Shelton and E. T. McDonel, J. Polym. Sci., 1960, 32, p75.
166. G. Scott, Eur. Polym. J., 1975, 11, p161.
167. G. Scott, Pure Appl. Chem., 1972, 30, p267.
168. J. R. Shelton, "Thermal Oxidation Of Polymers in Stabilization and Degradation of Polymers" : "Advances in Chemistry Series", Am. Chem. Soc., 1978, 169, p218.
169. W. L. Hawkins and H. Sautter, J. Polym. Sci. Part A-1, 1963, p3499.
170. W. L. Hawkins and H. Sautter, Chem. Ind. 1962, p1825.
171. W. L. Hawkins et. al., J. Apply. Polym. Sci., 1959, 1, p37.
172. M. E. Kaplan et. al., J. Polym. Sci. Part 2. 1973, 6, p357.
173. S. L. Madorsky and S. J. Straus, J. Polym. Sci., 1959, 36, p183.
174. K. Vovan, S. L. Malhotra and L. P. Blanchard, J. macromol. Sci. Chem., 1974, A8, p843.
175. S. Kilic and J. E. McGrath, Polymer Preprint, Am. Chem. Soc. Polym. Chem. Div., 1987, 28(1), p270.

176. T. Ozawa, *Bull Chem. Soc. Japan.*, 1965, 38, p1881.
177. A. W. Coata and J. P. Redfern, *J. Polym. Sci. Polym. Lett. Ed.*, 1965, 3, p917.
178. A. Noshay and J. E. McGrath, "Block Copolymers : Overview and Critical Survey", Academic Press, New York, 1977, Chapter 2.
179. J. E. McGrath, *J. Chem. Ed.*, 1981, 58, p914.
180. J. M. G. Cowie, "Carbon Chain Block Copolymers and Solvents, in: *Developments in Block Copolymers* ", I. Goodman ed., Applied Science. Publisher, N. Y. 1982, p1.
181. M. Morton and L. J. Fetters, *Macromol. Rev.* 1967, 2, p71.
182. A. Noshay and J. E. McGrath, "Block Copolymers, Overview and Critical Survey", Academic Press, New York, 1977, Chapter 4.
183. L. M. Robeson, *J. Appl. Polym. Sci.* 1973, 17(12), p3609.
184. M. Szwarc, M. Levy and R. Milkovich, *J. Am. Chem. Soc.* 1956, 78, p2656.
185. M. Szwarc, *Makromol. Chem.* 1960, 35, p132.
186. M. Szwarc, *Adv. Polym. Sci.*, 1965, 4, p1.
187. J. M. Lambert and E. J. Goethals, *Makromol. Chem.*, 1970, 133, p289.
188. A. V. Tobolsky and A. Rembaum, *J. Appl. Polym. Sci.*, 1964, 8(1), p508.
189. M. Morton, "Encycl. Polym. Sci. Tech.", 1971, 15, p508.
190. M. Morton and L. J. Fretters, *Macromol. Rev.* 1967, 2, p71.
191. R. J. Angelo et. al., *Polym.*, 1965, 6(3), p141.
192. E. Lanza et. al., *J. Polym. Sci. Phys. ed.*, 1973, 11(1), p95.
193. J. T. Patton, *Us. Patent* 3,101,374, 1955.
194. H. Fujii, T. T. Saegusa and J. Furukawa, *Makromol. Chem.*, 1963, 63, p147.
195. G. Finaz, P. Rempp and J. Parrod, *Bull. Soc. Chem. Fr.* 1962, 1962, p262.
196. J. J. O'Malley et. al. *Polym. Prepr., Am. Chem. Soc., Polym. Chem. Div.*, 1969, 10(2), p796.

197. J. J. Smith and W. T. Reiche., U. S. Patent 2,921,920, 1960.
198. G. L. Brode and J. V. Koleske, Otto Vogl, Junji Furukawa, ed., "Lactone Polymerization and Polymer Properties", in "Polymerization of Heterocyclics", Marcel Dekker, Inc. New York, 1973.
199. R. D. Lundberg, J. V. Koleske, and K. B. Wischmann, J. Polymer Science, Part A-1, 1969, 7, p2915.
200. L. R. G. Treloar, Rubb. Chem. Tech.,1974, 47(3), p625.
201. U. S. Patent 2,890,208, 1959.
202. H. Cherdron, H. Ohse, and F. Korte, Makromol. Chem., 1962, 56, p179.
203. H. bittiger, R.H. Marchassault and W.D. Niegisch, Acta Crystal. 1970, B26, p1923.
204. J. V. Kolske and R.D. Lundberg, J. Polym. Sci., Part 2, 1969, 7, p795.
205. G. Belorgey and R. E. Prudhomme, J. Polym. Sci. : Polym. Phys Ed., 1982, 20, p191.
206. T. P. Russel and R. S. Stein, J. Polym. Sci. Polym. Phys. Ed., 1983, 21, p999.
207. J. V. Koleske and R. D. Lundberg, J. Polym. Sci., Part A-2, 1969, 7, p795.
208. L. M. Robeson, J. Appl. Polym. Sci., 1973, 16, p3607.
209. M. M. Coleman and J. Zarian, J. Polym. Sci. Polym. Phys. Ed., 1979, 17, p837.
210. L. M. Robeson, J. Polym. Sci., Polym. Lett. Ed., 1978, 16, p261.
211. J. V. Koleske and G. R. Brode, "Lactone Polymerization and Polymer Properties : in Polymerization of Heterocyclics, O. Vogl and J. Furukawa ed., Marcel Dekker Inc., New York, 1973, p134.
212. F. E. Bailey and H. G. France, U. S. Patent 3,312,753, 1967.
213. F. X. Mueller and H. L. Hsieh, U. S. Patent 3, 585, 257, 1971.
214. D. D. Perrin, W. L. F. Armargo and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd ed.,Pergamon Press, New York, 1986.

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