

Poly(2-alkyl-2-oxazoline) Containing Multiphase Systems

by

Qin Liu

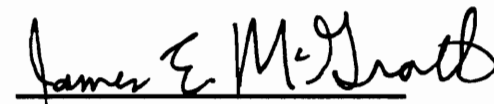
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(Abstract)

This research is focused on the polymerization of 2-alkyl-2-oxazoline homopolymers and 2-alkyl-2-oxazoline containing copolymers with well defined structures. In addition, the potential of selected materials as polymer blend compatibilizers was briefly evaluated. The polymerization of 2-alkyl-2-oxazoline was investigated with regard to the effects of initiator structures on molecular weight control and molecular weight distribution, living characteristics, and mechanisms and kinetics. The structure of initiators was shown to greatly affect the molecular weight control and molecular weight distribution of poly(2-ethyl-2-oxazoline). The living nature of poly(2-ethyl-2-oxazoline) in chlorobenzene initiated by benzyl iodide, benzyl chloride/NaI, or chloroethyl ethyl ether/NaI has been established by Mn-conversion plots and sequential monomer addition experiments. However, the molecular weight distributions of these polymers were not as narrow as Poisson distributions. Mechanistic and kinetic studies of 2-ethyl-2-oxazoline polymerizations suggested that, at very early stages of polymerization, the active species is covalent. After that very early

stage of polymerization, ionic species are present and the overall propagation rates increases. The rate determining step was found to be the initial propagation step(s) using benzyl iodide as the initiator, and initiation and/or the initial propagation step(s) in the case of iodobutane as an initiator. A kinetic study of 2-methyl-2-oxazoline polymerization in CD_3CN also indicated slower initiation than propagation rates using both butyl mesylate and butyl iodide as initiators. Based on the knowledge of 2-alkyl-2-oxazoline homopolymerizations, poly(2-alkyl-2-oxazoline) containing copolymers were prepared using macroinitiator methods, with poly(2-alkyl-2-oxazoline) being either the macroinitiator or the second component synthesized.

Narrow distribution poly(dimethylsiloxane) oligomers terminated with benzyl chloride endgroups were prepared by living anionic ring-opening polymerization of hexamethylcyclotrisiloxane followed by termination with a benzyl chloride containing chlorosilane reagent. Cationic ring-opening polymerization of 2-ethyl-2-oxazoline using these macroinitiators in combination with NaI generated a series of well defined block copolymers.

Poly(butyl vinyl ether) and poly(methyl vinyl ether) oligomers with Poisson distributions and precisely terminated on one end with a chloroethyl ether functional group were prepared by living cationic polymerization of alkyl vinyl ethers using a chloroethyl vinyl ether/HI initiating system with ZnI_2 as catalyst and terminated by lithium borohydride. The chloroethyl ether functional groups were

used in conjunction with sodium iodide to polymerize 2-ethyl-2-oxazoline blocks. In order to insure effective initiation and to narrow the copolymer molecular weight and composition distributions, the chloride to iodide conversion was made prior to the addition of monomer. A series of these diblock materials was prepared wherein the molecular weight distributions ranged from 1.3 to 1.4.

The bulk, solution and surface properties of these copolymers were investigated by NMR, DSC, XPS and surface tension measurements. Both types of materials described above are currently being utilized for studying the parameters important for steric stabilization of inorganic particles in polar media.

A less defined series of materials was also prepared. Using poly(butyl vinyl ether-co-chloroethyl vinyl ether) random copolymers as macroinitiators, 2-methyl-2-oxazoline was polymerized, resulting in poly(butyl vinyl ether-2-methyl-2-oxazoline) graft copolymers. Poly(2-methyl-2-oxazoline- ϵ -caprolactone) block copolymers were prepared using hydroxy-terminated poly(2-methyl-2-oxazoline) as macroinitiators. Poly(butyl vinyl ether-g-2-methyl-2-oxazoline) (PBVE-g-PMOX) or poly(2-methyl-2-oxazoline-b- ϵ -caprolactone) (PMOX-b-PCL) were screened as potential blend compatibilizers for poly(ϵ -caprolactam) (Nylon 6) and isotactic poly(propylene). Analysis of these blends by SEM indicated that PBVE-g-PMOX might function as a blend compatibilizer for Nylon 6/poly(propylene) blend while PMOX-b-PCL would not.

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Dedicated to

My parents, Weiyi Liu and Yangxian Zhu, and my husband, Zhizhang Chen, for their encouragement, inspiration, love and support.

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Chapter I

Introduction

As the requirement for materials becomes more stringent and diversified, the constitution of materials becomes more complex. Often multicomponent systems provide properties that are not obtainable from single component systems. The oldest examples are metal alloys. Then there are composites, polymer blends, and copolymers. Copolymers such as thermoplastic elastomers have been used alone, or used as additives to various systems. The latter application involves various interfaces: polymer-polymer (blend compatibilizer), polymer-air (surface modifier), polymer-water (emulsion particle stabilizer), ceramic-solvent (particle stabilizer). As the need for functional polymeric materials increases, copolymers for the latter application become more important. These applications require diverse copolymer structures (chemical, compositional, etc.) and well defined block or graft copolymers are often very desirable. The preferred technique, or perhaps the only technique available, for preparing well defined block or graft copolymers is living polymerization¹. The term "living" polymers was first used by Szwarc² to describe polystyrene prepared via "termination free" anionic polymerization. Since then living polymerization has extended into other types of polymerization mechanisms, such as cationic polymerization and group transfer polymerization. Many characteristics are associated with living polymerization. They

include: (1) fast initiation relative to propagation ($k_i > k_p$), and (2), the concentration of active species remains constant throughout the polymerization. As a result, the number average degree of polymerization is proportional to monomer conversion, and the molecular weight distribution follows a Poisson distribution^{3,4}. Living polymerization techniques provide possibilities for sequential polymerization, and quantitative incorporation of functional groups via initiation and termination. Thus, block and graft copolymers with controlled molecular weights and narrow polydispersity can be prepared.

Living polymerizations are mostly observed in anionic polymerization. For many years, researchers have been searching for perfect living cationic polymerization systems. There are generally two types of monomers synthesized by cationic polymerization, namely, heterocycles and electron rich vinyl compounds. In the field of cationic ring-opening polymerization, as stated by Penczek and Kubisa⁴, none of these systems fulfill all the requirements for a living system. The term living polymerization is used by many authors to simply indicate that the active species are "long lived". This causes confusion in terms of what people can expect from a so-called "living" system when limitations or deviations from a true living system are not pointed out. It is important to define a system as precisely as possible so that useful applications can be developed based on knowledge of the capabilities and limitations of the systems. In the field of cationic polymerization

of vinyl monomers, living polymerization has long been regarded as extremely difficult, although not impossible^{5,6}. Since the growing carbocations are inherently unstable, many side reactions, such as chain transfer and termination, may occur. Living cationic polymerization of vinyl compounds did not become a reality until the early 1980's⁶.

For a long time, ring-opening polymerizations of many 2-oxazoline monomers have been regarded as "living". However, a detailed evaluation according to the definition of living polymerization has not been reported. In addition, changes in monomer, initiator, solvent, temperature, or combinations of these factors often alter the living nature of a system to some extent or completely. Since there are many attractive features of 2-oxazoline polymerizations and 2-oxazoline polymers, it is important to define their polymerization systems more precisely. Poly(2-ethyl-2-oxazoline) and poly(2-methyl-2-oxazoline) are polar, water soluble, and relatively easy to make. In addition, their propagating species are "long lived"⁷. Combinations of these polymers with other nonpolar or polar polymers may provide a spectrum of materials including surface modifiers, nonionic surfactants, blend compatibilizers, and ceramic particle stabilizers. In this research, the polymerization of 2-ethyl-2-oxazoline and 2-methyl-2-oxazoline were investigated with the objective of preparing well defined poly(2-oxazoline) segments. Specifically, the following aspects were studied: the effects of initiator structure on molecular weight control

and molecular weight distribution, the living nature of these polymerization systems using Mn-monomer conversion plots and sequential monomer addition experiments, and mechanisms and kinetics of these polymerizations using on-line NMR spectroscopy. The synthesis of poly(2-alkyl-2-oxazoline) containing copolymers was based on both a fundamental and a practical approach. Living techniques for preparing poly(dimethylsiloxane) and poly(alkyl vinyl ethers) were utilized to obtain functional oligomers with controlled molecular weights and very narrow molecular weight distributions. Both 2-alkyl-2-oxazolines and alkyl vinyl ethers are polymerized by cationic catalysts. Theoretically the possibility exists that their block copolymers might be prepared via sequential polymerization. However, due to the unique chain ends of living poly(alkyl vinyl ethers), the block copolymers so synthesized have unstable linkages⁵⁰. Using the functional oligomers as macroinitiators and based on the knowledge gained from 2-alkyl-2-oxazoline homopolymer studies, well defined poly(2-alkyl-2-oxazoline) containing block copolymers were prepared. Their molecular weight distribution, composition, and phase separation behavior were characterized by GPC, NMR, solid state NMR, DSC. The surface properties of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers were studied using XPS. These well defined block copolymers are intended for fundamental investigations of the stabilization of concentrated ceramic particle suspensions and compatibilization of immiscible blends. From a utility point of view,

less defined but practical graft copolymers of butyl vinyl ether and 2-methyl-2-oxazoline were prepared, where butyl vinyl ether constituted the backbone and was polymerized using an aluminum hydrogen sulfate catalyst with ca. 3 mole percent of chloroethyl vinyl ether. The pendent chlorine groups are used in conjunction with sodium iodide as initiators for the polymerization of poly(2-methyl-2-oxazoline) grafts. Their potential applications as compatibilizers for poly(ϵ -caprolactam) (Nylon 6) and poly(propylene) blends were investigated using SEM.

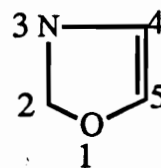
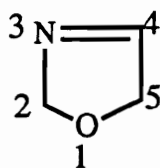
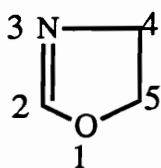
Chapter II

Literature Review

2.1 Cationic Polymerization of 2-Oxazolines

2.1.1 Introduction

Oxazolines belong to the family of compounds known as cycloimino ethers. They are five-membered heterocyclic compounds containing nitrogen, oxygen and one double bond in the ring^{8,9}. Depending on the location of the double bond, three types of oxazoline rings are possible:

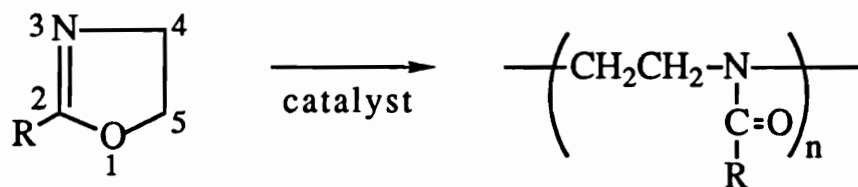


Among those oxazolines, only the 2-oxazoline and its derivatives have been widely used in organic and polymer synthesis^{8,9}. The substituents can be present on the 2, 4, and/or 5 position of the 2-oxazoline ring. Earlier work on the polymerization of 2-aryl- and 2-alkyl-2-oxazolines dates back to the mid-1960's¹⁰⁻¹⁴. Cationic catalysts, such as stannic chloride, boron trifluoride etherate, methyl p-toluenesulfonate induced the polymerization of 2-methyl-2-oxazoline and 2-phenyl-2-oxazoline¹⁰⁻¹³, but anionic catalysts such as potassium methylate and n-butyl lithium or free radical initiators were not effective¹⁰. In fact, selective anionic, free radical, or cationic polymerizations of 2-p-styryl-2-oxazoline have been demonstrated recently¹⁵. Oxazoline salts of the monomer with strong

acids, alkyl iodides, dialkyl sulfates are also effective initiators. Simple carboxylic acids and their anhydrides are not suitable because the corresponding anions are too nucleophilic¹². Further investigations on the polymerization of 2-oxazolines have been concentrated on the kinetics and mechanisms of the polymerization. Synthesis of poly(2-oxazoline) containing copolymers continues to be developed along with the applications of these homo and copolymers.

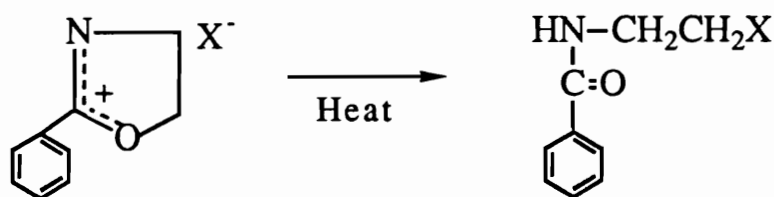
2.1.2 Mechanisms and Kinetics

Based on hydrolysis products and infrared spectra of the polymers, it was proposed that 2-substituted-2-oxazolines polymerized with ring opening between the 1-5 bond to form the N-acyl-substituted polyethyleneimine structures^{10,11}:



As supporting evidence for this mode of ring opening, ¹H NMR spectra showed the deshielding of the 5-position protons in 2-methyl-2-oxazoline/BF₃ complex (4.76ppm) relative to that in the monomer (4.24ppm)¹¹. Studies on the bulk polymerization of 2-phenyl-2-oxazoline initiated by salts of the monomer with perchloric acid (HClO₄) and p-toluenesulfonic acid(p-C₇H₇SO₃H) were the most effective catalysts in terms of polymerization rate. On the other hand, the salts with hydrogen chloride (HCl), trichloroacetic acid

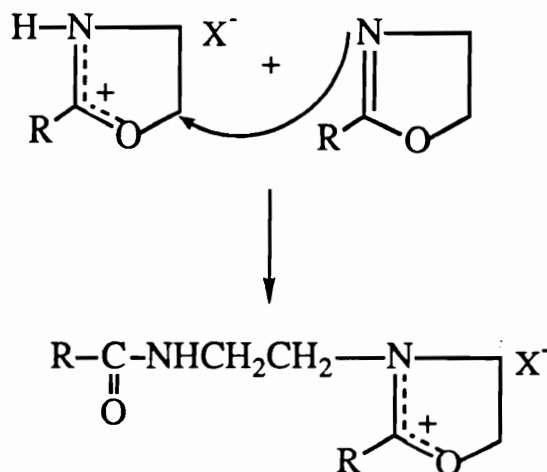
(CCl₃COOH) and nitric acid (HNO₃) did not initiate the polymerization¹⁶. These observations appear to agree with the thermal stability of various salts. For example, the salt with perchloric acid is stable at 150°C, while the salt with HBr, HCl, CCl₃COOH and HNO₃ rearranged to ring-opened structures at temperatures over 100°C¹⁶:



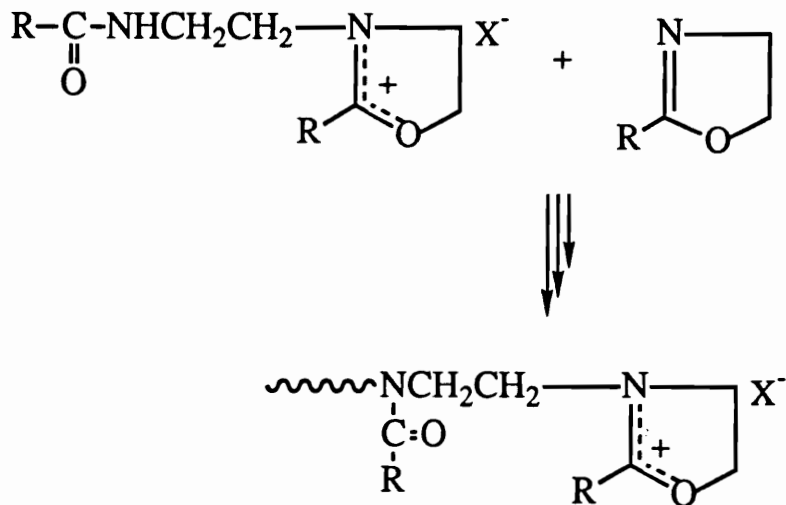
In addition, it was observed that when the salt with perchloric acid was used as a catalyst, the number average molecular weight of poly(2-phenyl-2-oxazoline) increased linearly with the feed molar ratio of monomer to the catalyst¹⁵, which indicated that the polymerization system was termination and chain transfer free. Similar behavior was also noted by Litt et al.¹³. Based on these observations, Kagiya and Matsuda proposed two types of polymerization routes involving different initiators¹⁶ (Scheme 2.1.1 a and b). When X = ClO₄⁻ or HSO₄⁻, route 1 applies; when X = I⁻ or Br⁻ route 2 applies. Similar mechanisms were proposed by Saegusa and his co-workers based on the polymerization of unsubstituted 2-oxazoline initiated by methyl tosylate and methyl iodide^{17,18}. In their study, the formation of oxazolinium tosylate was observed by ¹H NMR, leading to the conclusion that the polymerization initiated

Scheme 2.1.1 a Polymerization Mechanism of
2-Oxazolines (Route 1) via Ionic Propagating Species¹⁶

Initiation

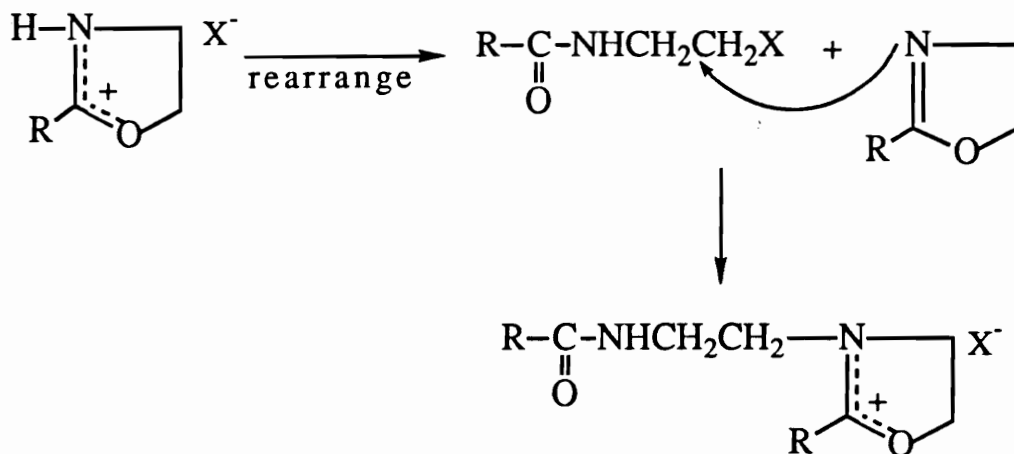


Propagation

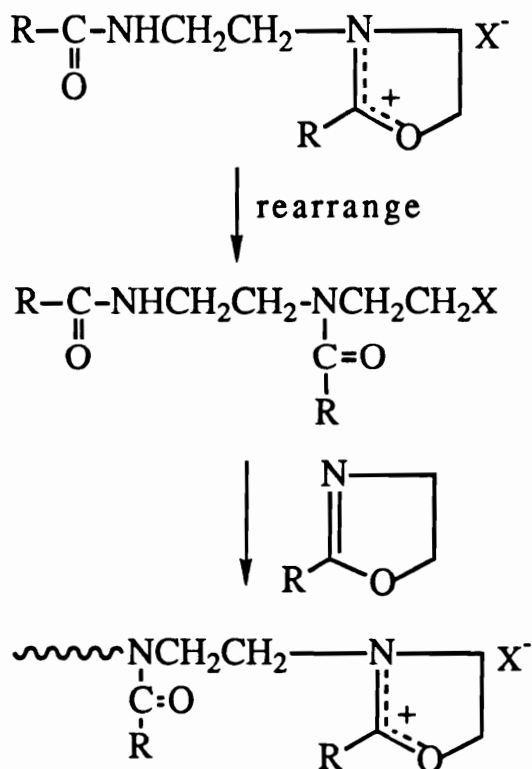


Scheme 2.1.1 b Polymerization Mechanism of
2-Oxazolines (Route 2) via Covalent Propagating Species¹⁶

Initiation



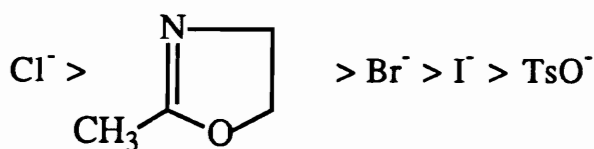
Propagation



by methyl tosylate proceeded through a route similar to that in Scheme 2.2.1 a, while the absence of the oxazolinium ion in the polymerization initiated by methyl iodide implied that the polymerization went through a route similar to Scheme 2.2.1 b.

Investigation of the polymerization of 2-methyl-2-oxazoline in acetonitrile initiated by benzyl chloride, benzyl bromide, methyl p-toluenesulfonate and methyl iodide^{19,20,21} also suggested two types of polymerization routes. With tosylate and iodide as counter-anion, the propagating species in the polymerization of 2-methyl-2-oxazoline was "exclusively an oxazolinium ion"²¹. The presence of oxazolinium ion was also detected with bromide as the counter-anion. With chloride as counter-anion, the polymerization was found to proceed through covalent species.

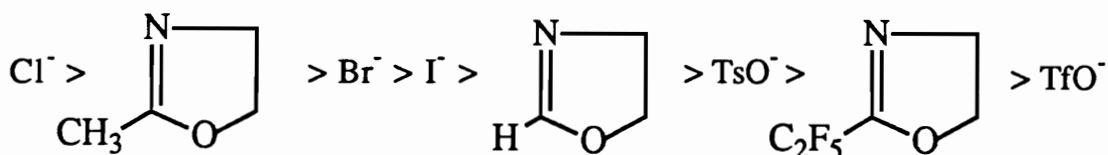
The existence of two types of propagating species was believed to be due to the difference in nucleophilic reactivity²¹. The nucleophilicity in the order of:



explained the formation of covalent species when Cl^- was the counter-anion and the existence of oxazolinium ion when Br^- , I^- or TsO^- was the counter-anion.

More recent investigations on the polymerization of 2-perfluoroalkyl-2-oxazolines have indicated these two types of polymerization mechanism as well^{22,23}. With methyl tosylate or

methyl nosylate (p-nitrobenzenesulfonate) as initiator, the propagating species was a covalent ester. However, with a methyl trifluoromethanesulfonate (triflate) initiator, the propagating species was the oxazolinium triflate. Again, these two types of propagating species are believed to be caused by the relative nucleophilicity of monomer and counter-anion. The tosylate anion is more nucleophilic than 2-perfluoroalkyl-2-oxazoline monomers, thus it reacted with the oxazolinium intermediate and formed the tosylate ester. Triflate anion is much less nucleophilic than the monomer and did not react with the oxazolinium cation. Thus the resulting propagating species is the oxazolinium cation with a triflate counter-anion²². Based on the results of the mechanistic studies, the order of relative nucleophilicity among monomer and counter-anion was summarized as²²:



It has also been suggested that polar medium and lower temperature favor propagation through the oxazolinium ion. However, the effects of solvent and temperature are believed to be minor compared with the nucleophilicity of counter-anion relative to that of monomer²⁴.

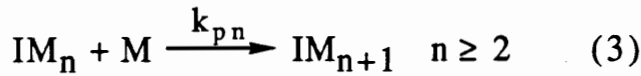
Quantitatively, propagation rate constants for the above mentioned systems further demonstrate the presence of two polymerization mechanisms. The rate constants cited hereafter were

obtained based on the following assumptions: there is no termination or chain transfer in the polymerization. Evidence for this assumption included: (1) the molecular weight of poly(2-phenyl-2-oxazoline) initiated by 2-phenyl-2-oxazolinium perchlorate in bulk as well as in DMAC increased linearly with a decrease in feed initiator concentration^{16,25}; (2) the molecular weight of poly(2-methyl-2-oxazoline) initiated by methyl tosylate in CD₃CN measured by vapor pressure osmometry was the same as the calculated value within 10% error¹⁹. This assumption is indirectly supported by chain transfer constants for bulk polymerization initiated by 2-p-chlorophenyl-2-oxazolinium perchlorate²⁶. At 130°C, with $[M_0]/[I_0] = 9810$, the chain transfer constant for 2-(n-heptyl)-2-oxazoline is about 1/300. For 2-isobutyl-2-oxazoline at 160°C, with $[M_0]/[I_0] = 500$, monodisperse polymer was obtained. At higher $[M_0]/[I_0]$ ratios, the chain transfer constant was estimated to be near 1/800. For bulk polymerized 2-ethyl-2-oxazoline initiated by methyl tosylate, about 3.5 branching points per chain were detected with $[M_0]/[I_0]=4000$ ²⁷. Since the ratios of $[M_0]/[I_0]$ in the kinetic studies reported were well below 300, the assumption of no chain transfer is valid. The termination free assumption is also supported by the observation that the amount of propagating species, oxazolinium ion, equals the amount of consumed initiator¹⁹. The generic scheme used for derivation of the rate constants, in spite of the propagating species, is summarized as follows^{19,25}:

Initiation:



Propagation:



where I and M stand for initiator and monomer. Based on the scheme, the following kinetic equation can be expressed as^{19,25}:

$$-d[I]/dt = k_i[I][M] \quad (4)$$

$$-d[M]/dt = k_i[I][M] + k_{p1}[P_1^*][M] + k_{pn}[M] \sum_{n=2} [P_n^*] \quad (5)$$

where $[P_1^*]$ and $[P_n^*]$ are the concentration of propagating species with various sizes. When it is assumed that $k_{p1}=k_{pn}$, the total number of propagating species will be:

$$[P^*] = [P_1^*] + \sum_{n=2} [P_n^*] \quad (6)$$

Since there is no termination nor chain transfer,

$$[P^*] = [I]_0 - [I] \quad (7)$$

is valid. Substituting eqs.(6) and (7) into eq.(5) and then integrating lead to:

$$\ln ([M]_0/[M]) = (k_i - k_p) \int_0^t [I] dt + k_p [I]_0 t \quad (8)$$

where $[I]_0$ and $[M]_0$ denote the initial concentrations of initiator and monomer, respectively. Rearrangement of eq.(8) gives:

$$\frac{\ln([M]_0/[M])}{\int_0^t [I] dt} = (k_i - k_p) + k_p \frac{[I]_0 t}{\int_0^t [I] dt} \quad (9)$$

From the slope and intercept of the plot according to eq.(9), k_i and k_p can be obtained. Independently, k_i can be determined by integrating eq.(4), which is:

$$\ln ([I]_0/[I]) = k_i \int_0^t [M] dt \quad (10)$$

When $[M]_0/[I]_0$ is rather high (for instance, 100), above equations can be simplified into eqs.(11) and (12) for earlier and later stages of polymerization respectively²⁵:

$$\ln([M]_0/[M]) = 1/2 k_i k_p [I]_0 [M]_0 t^2 \quad (11)$$

$$\ln([M]_0/[M]) = k_p [P^*](t - t') \quad (12)$$

where t' denotes times when $k_i[I][M]$ can be neglected. The rate constant can be estimated accordingly. According to eqs.(9) and (10), two sets of data for initiator and monomer concentrations, as functions of time, are required to obtain the rate constants. The disappearance of monomer has been monitored by IR spectroscopy^{11,25}. A more quantitative determination of monomer as well as initiator concentrations was developed by Saegusa and his coworkers using ¹H NMR¹⁷⁻²⁰.

The rate constants as a function of initiator structure and temperature for various monomers are summarized in Tables 2.1.1 through 2.1.3. Significant differences in initiation and propagation rate constants can be observed for monomers polymerized under the same conditions except for initiator structures. These differences were believed to be due to different propagation mechanisms^{17,18,21}.

It is interesting to note that there are two propagation rate constants for the polymerization of 2-methyl-2-oxazoline. The rate constant of the first step propagation, k_{p1} , is smaller than that of the remaining propagating steps, k_{pn} . The explanation was that the reactivity of the initiation product was different from that of the propagating species having at least two repeat units in a row²⁰. The N-acyl carbonyl group of the neighboring unit may interact with the oxazolinium ring in the latter species which is absent in the initiation product. In reviewing the rate constants in both Tables 2.1.1 and 2.1.2, there seems to be no correlation between the relative k_i and k_p values and the initiator and monomer structures. The initiation rate

Table 2.1.1 Polymerization Rate Constants of 2-Methyl-2-Oxazoline as a Function of Initiator and Temperature*

Initiator	Temp. (°C)	$k_i \cdot 10^4$ (L/mol.s)	$k_{p1} \cdot 10^4$ (L/mol.s)	$k_{pn} \cdot 10^4$ (L/mol.s)
Benzyl Chloride ²¹	40	0.01		0.03
	85	0.47		0.59
	95	0.89		1.0
	105	1.6		1.7
Benzyl Bromide ²¹	35	1.1		0.81
	40	1.3		1.2
	47	1.6		2.2
Methyl Iodide ²⁰	30	0.98	0.38	0.47
	40	2.68	0.90	1.14
	50			2.85
CH ₂ =CHO ₂ CCH ₂ I ⁵¹	35	0.81		0.76
Methyl Tosylate ¹⁹	31	0.90	0.40	0.49
	40	1.82	0.77	1.17
	50	4.0	1.58	3.1
((CH ₂ CH ₂ O) ₃ SO ₃ Me) ₂ ³³	80	0.25		21
Methyl Chloroformate/ KI ⁵²	80			6.3

* in acetonitrile

Table 2.1.2 Polymerization Rate Constants of Unsubstituted- and 2-Phenyl-2-Oxazoline as a Function of Initiator and Temperature

Monomer	Initiator	Temp. (°C)	$k_i \times 10^4$ (L/mol.s)	$k_p \times 10^4$ (L/mol.s)
2-H-*	MeTOs ¹⁸	24	0.14	1.9
		31	0.29	4.6
		40	0.98	19
	MeI ¹⁸	40	1.6	0.18
		55		0.42
		70		1.2
2-Phenyl-	Oxazolinium ²⁵ perchlorate	120	0.007**	0.25**
		135	0.0234**	0.69**
		150	0.061**	2.39**

* in CD₃CN

** in DMAC and units in L/mol.min

Table 2.1.3 Polymerization Rate Constants* of 2-Pentafluoroethyl-2-Oxazoline as a Function of Initiator and Temperature

Initiator	Temp. (°C)	$k_i \times 10^4$ (L/mol.s)	$k_p \times 10^4$ (L/mol.s)
Methyl triflate ²³	35	89	5.0
	45		11
	55		27
	65		56
Methyl ²³ nosylate	35	0.012	.029
	110		4.6
	120		7.9
	131		14

* in CD₃NO₂

constants are comparable to the propagation rate constants in the case of 2-methyl-2-oxazoline polymerization with most initiators. However the initiation rate constant is at least an order of magnitude smaller than the propagation rate constant in the polymerization of unsubstituted-2-oxazoline initiated with methyl tosylate in the same solvent and at same temperature as that in the 2-methyl derivative case. No explanation has been given to account for the difference. Therefore no prediction could be made for a different monomer using the same initiators. Solution polymerization of 2-phenyl-2-oxazoline initiated by oxazolinium perchlorate in N,N-dimethylacetamide also displayed a slower initiation rate than propagation rate. For example, the propagation rate constant of 2.39 L/mol·min. at 150°C is about 40 times greater than initiation rate constant of 0.061 L/mol·min.²⁵. The effects of these slow initiation rates on molecular weight control and molecular weight distribution have also not been reported.

Solvent Effects

The effects of solvent were demonstrated by a systematic study on the polymerization of 2-phenyl-2-oxazoline initiated by oxazolinium perchlorate in various solvents. The polymerization proceeded faster in polar solvents than in nonpolar solvents. In both polar and nonpolar solvents, the propagation rate constants increased with decrease in nucleophilicity as measured by the shift of an O-D bond of d₃-methanol in a solvent measured by IR²⁸.

Solvent effects were also studied from the perspective of compatibility between a solvent and polymer formation. It was found that in the polymerization of 2-n-pentyl-2-oxazoline, solvent with esters, ethers, tertiary amide groups did not interfere with the polymerization. Ketone, nitrile, secondary and primary amide, water as well as alcohol containing solvents did interfere with the polymerization. Sulfoxide, phenol, carboxylic acid and aromatic aldehyde containing compounds were found to be incompatible with the polymerization²⁹.

Reactivities of Monomers

In terms of propagation rates, the reactivities of 2-oxazoline monomers include two components: nucleophilicity and ring-opening reactivity. The nucleophilicity of 2-oxazoline monomers was evaluated via the reaction rates of monomers with the same substrate, such as methyl tosylate³⁰. In this manner, the nucleophilicity of three monomers was found to be in the following order: 2-methyl-2-oxazoline > unsubstituted-2-oxazoline > 2-phenyl-2-oxazoline.

Another component is ring-opening reactivity: the ease with which an incoming nucleophile reacts and opens a specific oxazolinium ring. N-methyl-2-phenyl-2-oxazolinium perchlorate is more reactive toward the nucleophilic ring-opening reaction than N-methyl-2-methyl-2-oxazolinium perchlorate. Reactivity is believed to be governed by electrophilicity at the 5-position of the

oxazolinium heterocycle³¹. In accord with this result, Saegusa and co-workers found that N-methyl-2-phenyl-2-oxazolinium tosylate reacted faster than N-methyl-2-methyl-2-oxazolinium tosylate with the same nucleophile³⁰. These two reactivities often do not go hand by hand. Thus, it is very hard to predict the overall polymerization rate. For example, nucleophilicity and ring-opening reactivity of 2-phenyl-2-oxazoline and 2-methyl-2-oxazoline are in the opposite order. The experimental order of the polymerization rate was found to be MeOX > PhOX³⁰.

2.1.3 Properties of Poly(2-oxazoline)s

Poly(2-alkyl-2-oxazoline)s, with the alkyl derivative being methyl or ethyl, are water soluble^{11,32}. With phenyl and other higher carbon (above butyl) derivatives, the polymers are water insoluble^{11,33}. Poly(2-ethyl-2-oxazoline) is amorphous as determined by X-ray diffraction measurements. Poly(2-oxazoline)s with linear acyl side chains larger than propenyl (n=4 to 6) have crystalline structures³⁴. The glass transition temperature of poly(2-ethyl-2-oxazoline) with very high molecular weight was found to be 56°C which increases to 72°C upon aging³². Miscibility studies of poly(2-oxazolines) with thermoplastic polymers have shown that poly(2-methyl-2-oxazoline) is miscible with poly(vinyl chloride) and poly(vinylidene fluoride) up to 50 wt% poly(2-methyl-2-oxazoline)³⁵. It is not miscible with poly(propylene)³⁵. Poly(2-ethyl-2-oxazoline) was found to be miscible with the polyhydroxyether of bisphenol-A

(phenoxy resins) and styrene/acrylonitrile copolymers having 20 - 40% acrylonitrile by weight, and partially miscible with a vinylidene chloride/vinyl chloride copolymer³⁶. The miscibility between poly(2-ethyl-2-oxazoline) and poly(acrylonitrile-co-methylacrylate)(70/30) was limited to compositions up to 20% of PEOX by weight³⁷. A LCST (lower critical solution temperature) type phase diagram was observed for the blend of poly(2-ethyl-2-oxazoline) ($\langle M_w \rangle = 200,000$) and poly(ether sulfone) ($\langle M_w \rangle = 117,000$)³⁸. The critical point is 210°C with the composition of 70/30 for PES/PEOX (wt./wt.). It is not miscible with poly(methyl methacrylate), poly(carbonate) or polypropylene^{35,36}. Poly(2-propyl-2-oxazoline) is miscible with poly(styrene) up to 25% by weight of the former³⁵.

2.1.4 Copolymerization and Applications

Based on diverse properties of 2-oxazolines with different substituents and their chain transfer and termination free polymerization reactions, copolymers and functional oligomers of these polymers, in addition to their homopolymers, have been explored for various applications.

Poly(2-ethyl-2-oxazoline) was used as a polymeric stabilizer for the preparation of poly(methyl methacrylate) particles with sizes in the micron range³⁹. An ionene polymer has been prepared by termination of a dibromide initiated poly(2-methyl-2-oxazoline) with a tertiary diamine (N,N,N',N'-tetramethylethylene diamine) or an

aromatic diamine(4,4'-dipyridyl). This type of polymer is intended for use as a pharmacological active agent⁴⁰. Termination of poly(2-methyl-2-oxazoline) with a fatty acid generated a nonionic surfactant which was used for the solubilization of oil-soluble Azo dyes in aqueous media⁴¹.

There have been several approaches for preparing copolymers of 2-oxazolines: sequential polymerization of two 2-oxazoline monomers, or one 2-oxazoline monomer with another type of monomer; functionalization of poly(2-oxazoline); functionalization of other polymers resulting in macroinitiators for 2-oxazoline polymerization; and copolymerization via zwitterions.

One-Pot Copolymerization

One-pot two stage copolymerizations were conducted to produce nonionic polymer surfactants composed of amide structures with different substituents. The monomers constituting the hydrophilic blocks were 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline. The hydrophobic block consisted of one of the following: 2-n-butyl, 2-n-octyl, 2-n-dodecyl, 2-phenyl⁴², 2-(4-(t-butyl)phenyl)^{43,44,45}, 2-(1-adamantyl), 2-(1-adamantylmethyl)⁴⁶, and 2-pentafluoroethyl⁴⁷ substituted 2-oxazolines. These copolymers are tabulated in Table 2.1.4. The initiator used for the copolymerization was mostly methyl tosylate. The most important factor in predicting whether or not a block copolymerization by sequential monomer addition will be successful is to analyze the

Table 2.1.4 Copolymers of 2-Oxazolines via Sequential Polymerization*

1st monomer	2nd monomer	DP1:DP2
2-methyl	2-phenyl	(6.3-22):(4.3-31)
	2-ethyl	5.4:5.3
	2-propyl	5.4:5.8
	2-butyl	5.5:(5.3, 12.8)
	2-octyl	(5.5, 11.3):(4.9,4.3)
	2-dodecyl	(6.3, 18.0):4.2
2-ethyl	2-methyl	7.2:6.9
	2-phenyl	11.5:(4.8,10.8)
	2-adamantyl	(14, 20):10
	2-adamantalmethyl	(18-77):(40-75)
2-butyl	2-methyl	6.3:6.8
2-t-butyl-phenyl	2-ethyl	10:(6.9-61.6)
2-pentafluoroethyl	2-methyl	2.7:55

* from references 42,43,44,45,46,47

crossover reaction. In this respect, it is interesting to note that a block copolymer of 2-methyl/2-ethyl or 2-butyl/2-methyl can be obtained by either monomer addition sequence. In addition, triblock copolymers composed of 2-n-butyl-2-oxazoline-2-methyl-2-oxazoline-2-n-butyl-2-oxazoline and 2-n-octyl-oxazoline-2-methyl-2-oxazoline-2-n-octyl-2-oxazoline have been synthesized⁴². Observation of these reactions suggested that the length of the side chains on oxazolines do not affect the crossover reaction.

What becomes more interesting is the so called "one shot" process⁴⁸. In this process, a block copolymer is obtained by feeding the two monomers simultaneously at the beginning of the polymerization. In addition to the requirements for a "living" and a successful crossover reaction, the reactivities of the two monomers are required to be very different. The more reactive monomer selectively polymerizes first and the less reactive monomer polymerizes subsequently. The combination of 2-methyl-2-oxazoline (as the more reactive monomer) and 2-(heptafluoro-n-propyl)-2-oxazoline together with methyl p-nitrobenzenesulfonate initiator was found to satisfy the above requirements. The "one shot" polymerization of these two components was reported to be successful in CH_3NO_2 at 120°C to yield block copolymers⁴⁸.

The sequential monomer addition method has also been successfully applied to monomers from two different families. Tetrahydrofuran (as the hydrophobic block) and 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline (as the hydrophilic block) were

polymerized in that sequence using ethyl triflate as initiator to yield corresponding block copolymers⁴⁹. Block copolymers of vinyl ethers (n-butyl, i-octyl and n-cetyl) and 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline have also been synthesized using this method. However, the resultant block copolymers have unstable linkages between the two blocks which are readily cleaved under acidic conditions⁵⁰.

Functionalization of Poly(2-oxazoline)s

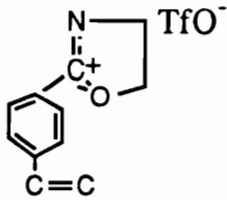
Many functional groups have been incorporated into poly(2-oxazoline)s using either functional or protected functional initiators or using functional terminating agents. A survey of these functional poly(2-oxazoline)s is presented in Table 2.1.5 along with either the functional initiators or terminating agents. These functional poly(2-oxazoline)s are used in the copolymerization with the corresponding second monomer, such as, styrene, methyl acrylate, etc.

Emulsion copolymerization of styryl-functional poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) with styrene monomer generated poly(styrene-g-2-alkyl-2-oxazoline)s which reside on the surface of polystyrene particles. These copolymers acted as steric stabilizers as well as particle surface modifiers⁸⁸.

Macroinitiators

Incorporation of functional groups capable of initiating the polymerization of 2-oxazolines into other polymers comprises another method of make poly(2-oxazoline) containing copolymers.

Table 2.1.5 Functional Groups Incorporated into Poly(2-oxazoline)s via Initiator or Terminator

monomer (2-oxazoline)	Initiator	Terminator
2-methyl ⁵³		
2-methyl ⁵⁴	allyl tosylate	(3-aminopropyl) trimethoxy silane
2-methyl and 2-ethyl ⁵⁵		acrylic acid/ 2,6 lutidine dicarboxylic acid/ 2,6 lutidine
2-methyl, 2-ethyl, and 2-n-butyl ^{56,91}		CH ₂ =C(R')CO ₂ M M = Na, K, Ag, NR ₄ , NHR, SiR ₃
2-methyl and 2-ethyl ⁵⁷		HN(CH ₂ CH ₂ OH) ₂
2-methyl and 2-ethyl ⁵¹	CH ₂ =CHO ₂ CH ₂ X X = I, Cl/NaI	
2-methyl and 2-ethyl ⁵⁸	styryl	

As shown in Table 2.1.6, the most frequently used counterion has been tosylate. In addition to those listed in the table, 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline has been grafted onto carbon black surfaces. The carboxyl groups⁹⁰ or benzyl chloride groups⁸⁹ introduced onto the surface of the carbon black acted as initiators for the polymerization of 2-oxazolines. 2-methyl or 2-ethyl-2-oxazoline grafted carbon block formed stable colloidal dispersions in both hydrophilic and hydrophobic solvents^{89,90}.

No Catalyst Copolymerization

Without a initiator, 2-alkyl-2-oxazolines, as nucleophilic monomers, have been copolymerized with electrophilic monomers via zwitterions of the two types of monomers⁶⁸⁻⁷⁸. Various monomer pairs have been investigated some of which are listed in Table 2.1.7. Even though these copolymers are statistical in sequence distributions due to the presence of homopolymerization, their compositions tend to be richer in one of the two components. In terms of the structures of the monomers, 2-methyl-2-oxazoline is more likely to homopolymerize than the ethyl derivative toward the same electrophile, e.g. p-nitrophenylmaleimide. This was attributed to higher reactivity of 2-methyl-2-oxazoline relative to the ethyl derivative due to steric differences⁷². When the same nucleophilic monomer (2-methyl-2-oxazoline) is considered, p-methoxyphenylmaleimide tends to form homopolymers more readily than p-nitrophenylmaleimide.

Poly(2-oxazoline) Containing Networks

In addition to linear copolymers, poly(2-substituted-2-oxazoline)s have been incorporated into crosslinked networks, either with themselves to form "hydrogel", "amphigel", and "lipogel" or with silica to form organic-silica gel hybrids⁷⁹⁻⁸⁶. Poly(2-oxazoline) networks are formed through either copolymerization with a multifunctional monomer, such as 2, 2'-tetramethylenebis (2-oxazoline)^{79,81} or functionalizing poly(2-oxazoline) linear polymers and crosslinking with added crosslinking agents⁸²⁻⁸⁴. Poly(2-oxazoline)s have been functionalized by hydroxy termination to obtain difunctional hydroxyl groups⁸⁶, or hydrolysis of the polymer to yield multiple secondary amine groups^{80,82,83}. Crosslinking agents included di- and multifunctional isocyanates, furan and maleimide functionality used as reversible gelation agents, and (7-coumaryloxy) acetic acid with dicyclohexylcarbodiimide cured photochemically^{80,82,83,86}. Poly(2-methyl-2-oxazoline)-silica gel hybrids have been synthesized using silyl functional end-capped poly(2-methyl-2-oxazoline) and tetraethoxysilane⁸⁴.

Table 2.1.6 Copolymers of 2-Oxazolines via Macroinitiators

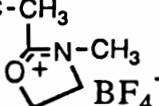
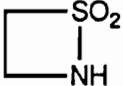
Macroinitiator	Function	2-Oxazoline monomer	Application
Cellulose and Cellulose Diacetate ^{53,60,61}	Tosylate	2-methyl 2-ethyl	Compatibilizer
Cellulose ⁶²	Chlorinated/KI, acetate, halogenacetate, tosylate	2-methyl unsubstituted	
Poly(vinyl alcohol) ⁶³	Bromoacetate, halogenacetate, tosylate	2-methyl unsubstituted	
PMMA and PMA ⁶⁴	$\text{CH}_2=\text{C}-\text{CH}_3$ 	2-methyl 2-t-butyl	
Poly(ethylene oxide) ^{33, 65}	Tosylate, mesylate	2-methyl 2-ethyl	Anti-electrostatic agent
Poly(ethylene oxide) ⁶⁶	chloroformate /silver triflate/KI	2-phenyl 2-methyl	
Poly(ethylene-co-vinyl acetate) ³³	Tosylate	2-methyl 2-ethyl	anti-thrombogenic
Poly(styrene) ⁶⁷	Chloromethylate	2-methyl	

Table 2.1.7 Copolymers of 2-Oxazolines via No Catalyst Copolymerization*

Nucleophilic monomer	Electrophilic monomer	Copolymer composition
2-methyl-2-oxazoline	p-nitrophenyl maleimide	rich in 2-methyl-2-oxazoline
	phthalic anhydride	rich in 2-methyl-2-oxazoline
	N-phenyl maleimide	
	ethanesultam (ESM) 	rich in ESM
2-ethyl-2-oxazoline	p-methoxyphenyl maleimide	rich in p-methoxyphenyl maleimide
	N-phenylmaleimide	rich in N-phenyl maleimide
	o- and p-phenyl maleimide	rich in o and p-phenyl maleimide
	p-methoxyphenyl maleimide	rich in p-methoxyphenyl maleimide

* from references 68-74

2.2 Living Cationic Polymerization of Alkyl Vinyl Ether

2.2.1 Introduction

Alkyl vinyl ethers are nucleophilic monomers and can be induced to polymerize by many cationic initiating systems. Iodine was used as the catalyst in the first polymerization of a vinyl ether in 1878⁹². Since then many other initiating systems have been found gradually, boron trifluoride etherate, aluminum trichloride, stannic chloride, to name a few. In contrast to the "ancient" history of cationic polymerization, living cationic polymerization of vinyl ethers was not discovered until 1984⁹³ with the polymerization of isobutyl vinyl ether initiated by the HI/I₂ system. As the art of obtaining living cationic systems were mastered, more initiation systems were discovered to produce living poly(alkyl vinyl ether)s. The key factor in achieving living polymerization involves the stabilization of carbocations and has been very well summarized in review articles^{94,95}. This principle will be demonstrated through the review of each specific initiation system.

2.2.2 HI/I₂ System

HI/I₂ was the first initiation system discovered to produce living poly(alkyl vinyl ethers)⁹³. The idea of a combined initiating system originated from the observation that an iodine initiator produced a long-lived propagating species of isobutyl vinyl ether⁹⁶ and n-butyl vinyl ether⁹⁷ and that hydrogen iodide has a greater dissociation constant than iodine. HI in combination with iodine was

believed to lead to faster initiation as compared to iodine alone. Thus the slow initiation problem of iodine alone was overcome and a living polymerization system resulted. The living characteristics of the polymerization of isobutyl vinyl ether (IBVE) initiated by HI/I₂ were evaluated using an $\langle M_n \rangle$ -conversion plot. $\langle M_n \rangle$ was determined by VPO, conversion was obtained by GC, and molecular weight distribution was determined by GPC in chloroform using a polystyrene calibration. A narrow molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle \leq 1.1$) and increase number average molecular weight with conversion of IBVE indicated that this polymerization system was living.

The individual and combined effects of HI and I₂ on the polymerization were evaluated. In hexane at -15°C, it was found that polymerization initiated with HI/I₂ (equal molar mixture) proceeded very fast without an induction period. By contrast, the polymerization initiated with I₂ alone proceeded slower with an induction period. HI alone induced very slow polymerization and yielded virtually no polymer in the time frame that polymerization using the HI/I₂ initiating system was complete. Polymers initiated with HI/I₂ exhibited narrow molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle < 1.1$) while those initiated with I₂ displayed broader molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle = 1.45-1.60$).

The effects of initiator concentration, and solvent on the polymerization of IBVE were also investigated. In n-hexane at -15°C, the initiator concentrations were $[HI]_0 = [I_2]_0 = 1.2, 2.2, 5.0$ and 7.6 mM

with $[M]_0=0.38\text{M}$, with targeted number average molecular weights of 32,000, 19,000, 7600, and 5,000 g/mol. The resultant molecular weight distributions were narrow. Minor deviations from linearity on the $\langle M_n \rangle$ -conversion plot were observed for systems with low initiator concentrations ($[HI]_0 = 1.2$ and 2.0), but no explanation was given. This may be an indication that there is a molecular weight limit beyond which the system is not perfectly living. As for the effects of solvent on the living nature of this polymerization system, it was noted that at -15°C with $[M]_0 = 0.38\text{M}$, $[HI]_0 = 5.0\text{mM}$, using toluene or methylene chloride as solvents, relatively broad molecular weight distributions were obtained with $\langle M_w \rangle / \langle M_n \rangle = 1.37$ in toluene and $\langle M_w \rangle / \langle M_n \rangle = 1.58$ in methylene chloride. When very high initiator concentrations ($[HI]_0 = 10\text{mM}$ with $[M]_0 = 0.38\text{M}$, $M_n = 3800$ g/mol) were used, living PIBVE was obtained⁹⁸. In more polar solvents ($\text{PhNO}_2/\text{CH}_2\text{Cl}_2$, 1/4, V/V), polymers with broad molecular weight distributions were generated⁹⁸. The most probable side reactions which caused the broadening of molecular weight distribution were believed to be β -proton elimination and chain transfer to monomer, both of which would yield a terminal double bond. These double bonds were reported to be present in the nonliving samples and absent in the living polymer samples as determined by ^1H NMR⁹⁸.

The change in concentration of I_2 was determined to only affect the polymerization rate. No effects on molecular weight or polydispersity resulted when $[HI]_0/[I_2]_0$ changed from 10/5 to 10/0.2.

Following the living polymerization of IBVE, living polymers of other vinyl ethers were also synthesized using HI/I₂ initiating systems. These monomers and living conditions are tabulated in Table 2.2.1. The number average degree of polymerization ranged from 32 to 267 depending on the monomer. In the polymerization of 2-chloroethyl vinyl ether, low temperature (-40°C) and an excess of HI over iodine were found to be necessary to obtain polymers with narrow molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle \leq 1.1$)⁹⁹. At -15°C or if equimolar ratios of HI and iodine were used, broader molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle = 1.2-1.3$) were obtained.

The mechanism of living polymerization of vinyl ether using the HI/I₂ initiating system in nonpolar solvents has been elucidated based on investigations of IBVE polymerizations using NMR and UV/visible spectroscopy¹⁰². Adducts of HI/IBVE and I₂/IBVE were observed by NMR and confirmed by UV/visible to form at -70°C and to persist as the temperature was raised to -50°C, as polymerization proceeded. Unreacted iodine (13% of [I₂]₀) also existed and remained constant throughout the reaction. A decrease in the feed concentration of HI yielded polymers with higher molecular weights while changes in feed concentrations of iodine did not affect the molecular weights of the polymers. In addition, the I₂/IBVE adduct was isolated in acetal form at the end of the polymerization by quenching with methanol. Therefore, the propagating species was believed to be covalent, coming from the HI/IBVE adduct. Since propagation did not occur in the mixture of HI/IBVE until after the

Table 2.2.1 Living Poly(alkyl vinyl ethers) Initiated by HI/I₂

Monomer	Solvent	Temp.	[M] ₀ : [HI] ₀ : [I ₂] ₀
MVE ¹⁰⁰	toluene	-35°C	38:1:1 100:1:1
EVE ¹⁰⁰	toluene	-35°C	38:1:1 190:1:1
i-PVE ¹⁰⁰	n-hexane	-15°C	47:1:1 168:1:1
n-BVE ¹⁰⁰	n-hexane	-15°C	134:1:1 267:1:1
i-BVE ¹⁰⁰	n-hexane	-15°C	72:1:1 134:1:1
CVE* ¹⁰⁰	MCH**	-5°C	64:1:1 111:1:1
CIEVE ⁹⁹	toluene	-40°C	50:1.6:1
$ \begin{array}{c} \text{CH}_2=\text{CH}^{101} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{N}-n\text{-C}_3\text{H}_7 \\ \\ \text{SO}_2\text{C}_8\text{F}_{17} \end{array} $	Freon***	-15°C	300:10:2

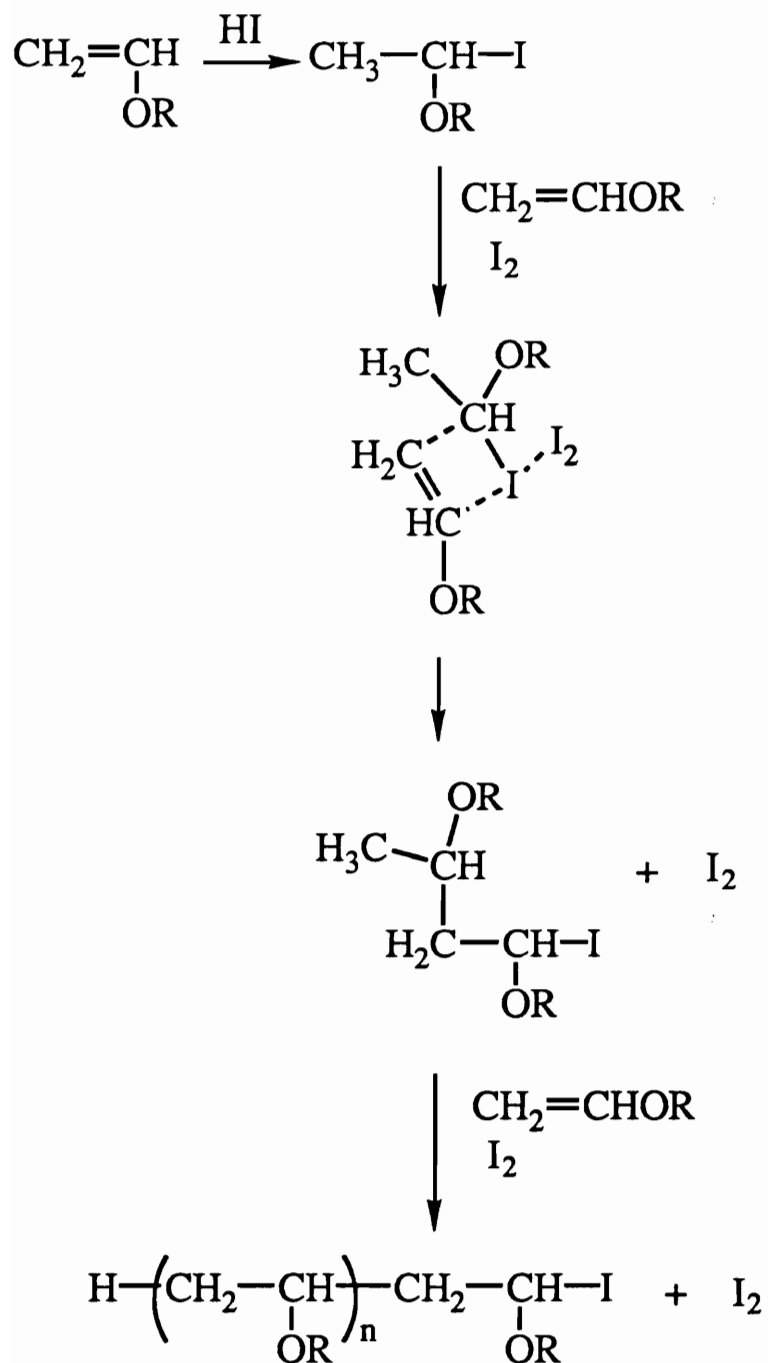
* CVE = n-C₁₆H₃₃ vinyl ether

** MCH = methylcyclohexane

*** Freon = 1,1,2-trichloro-1,2,2-trifluoroethane

addition of iodine, the propagating species was believed to be activated by free iodine. However no spectroscopic evidence was reported for the activated propagating species, for example, a chemical shift change due to the change from -CHI to -CHI--I_2 upon addition of iodine to HI/IBVE adduct. Nevertheless, the propagation mechanism for HI/I₂ initiated living polymerization of IBVE was proposed as shown in Scheme 2.2.1. Direct evidence of activation of the C-I bond by iodine was obtained by Cho and McGrath using ¹³C NMR¹⁰³. A small downfield shift (0.83 ppm) was observed upon addition of 0.5 equivalents of iodine to the HI/n-BVE (n-butyl vinyl ether) adduct. Their study of the polymerization of n-butyl vinyl ether and ethyl vinyl ether using the HI/I₂ catalyst confirmed the living behavior of these polymerization systems. However, the rate of polymerization showed a zeroth order dependence on monomer, and a linear dependence on the initial concentration of HI and I₂. To account for these observations, a charge-transfer complex between monomer and I₂ and two propagation modes were proposed. In one of the propagation modes, the monomer-I₂ complex, instead of monomer, reacts with nonactivated R-I in the propagation steps. In the other mode, a monomer reacts with the activated R-I, i.e., R-I--I₂ to form the propagation steps. The function of the monomer-I₂ complex was believed to tie up some I₂ so that only a small portion of R-I could be activated by I₂. No preference for either of the two modes was given. Further investigation by Sawamoto and his coworkers on the kinetics of polymerizations of ethyl, n-butyl, and

Scheme 2.2.1 Living Polymerization Mechanism of Alkyl Vinyl Ethers by HI/I₂ Initiating System¹⁰²



2-chloroethyl vinyl ethers initiated by HI/I₂ in various solvents⁹⁴ indicated that the dependence of polymerization rates on monomer concentration were affected by both the solvent and monomer structure. The polymerizations of ethyl and n-butyl vinyl ethers showed zeroth order dependence on monomer in n-hexane and first order dependence on monomer in toluene. For polymerization of 2-chloroethyl vinyl ether, the polymerization rate showed zeroth order dependence on monomer when toluene was the solvent but first order on monomer in methylene chloride. The change in kinetics was believed to be due to the competition of complexation between a monomer and iodine and between a solvent and iodine. Thus the detailed polymerization mechanism is far more complicated than discussed above.

Once the polymerization of vinyl ethers using the HI/I₂ initiating system was established, many applications of living systems have been pursued. One goal was to synthesize block copolymers via sequential polymerization of two vinyl ether monomers or one vinyl ether monomer and a second monomer, such as p-methoxystyrene. The copolymers synthesized in this manner are summarized in Table 2.2.2. Sequential polymerizations of protected functional vinyl ether monomers and hydrocarbon substituted vinyl monomers resulted in copolymers with one block containing potential hydroxyl, acid, or amine pendent groups. These copolymers are listed in Table 2.2.3. Alkaline hydrolysis of the pendent ester or alkaline hydrolysis of the malonic ester followed by

Table 2.2.2 Vinyl Ether Copolymers via Sequential Polymerization
Initiated by HI/I₂¹⁰⁰

First PZN monomer, solvent, temp.	Second PZN monomer, solvent, temp.	DP1:DP2	<Mw>/<Mn>
CVE*, MCH**, -5 °C	MVE, toluene, -15 °C	29:86	1.26
	EVE, toluene, -15 °C	40:28	1.07
MVE, toluene, -35 °C	CVE, CCl ₄ , -15 °C	38:20	
	p-MOS***, CCl ₄ , -35 °C	35:35	1.26
EVE, toluene, -35 °C	CVE, CCl ₄ , -15 °C	38:20	
	p-MOS, CCl ₄ , -35 °C	35:35	1.25
IBVE, CCl ₄ , -35 °C	p-MOS, CCl ₄ , -35 °C	38:38	1.25

* CVE = hexadecyl (cetyl) vinyl ether

** MCH = methylcyclohexane

*** p-MOS = p-methoxystyrene

Table 2.2.3 Protected Functional Vinyl Ether Copolymers via
Sequential Polymerization Initiated by HI/I₂¹⁰⁴⁻¹⁰⁶

First PZN monomer, solvent, temp.	Second PZN monomer	DP1:DP2	<Mw>/<Mn>
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{CH}_2\text{CH}_2\text{OCOCH}_3 \end{array}$ toluene, -15 °C	n-BVE	100:10-40:2	1.33-1.51
	i-OVE*	44:8-44:1	1.18-1.26
	CVE**	95:8-40:2	1.29-1.64
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{CH}_2\text{CH}_2\text{OCOC}_6\text{H}_5 \end{array}$ toluene, -15 °C	n-BVE	98:2, 95:5	1.16, 1.15
	i-OVE	92:2, 95:5	1.10, 1.09
	CVE	97:3, 95:5	1.15, 1.08
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{CH}_2\text{CH}_2\text{CH}(\text{COOC}_2\text{H}_5)_2 \end{array}$ toluene, -15 °C	n-BVE	20:16-20:1	1.08-1.06
	i-OVE	18:15-18:1	1.08-1.06
	CVE	19:8-20:1	1.08-1.07
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2-\text{N} \begin{array}{l} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_4 \end{array}$ CH ₂ Cl ₂ , -15 °C	n-BVE	40:10-40:20	1.31-1.23
	CVE	40:34, 40:1.4	1.20, 1.21

* i-OVE = i-C₈H₁₇ Vinyl Ether

** CVE = Hexadecyl (Cetyl) Vinyl Ether

decarboxylation resulted in hydroxyl or carboxylic acid containing blocks. Hydrolysis with hydrazine hydrate of phthalimide functions resulted in pendent amine containing blocks. The addition sequence has been found to be very important to obtain copolymers with well defined structures. If the sequence of addition was reversed, broader molecular weight distributions resulted due to "formation of homopolymers" in these copolymerizations.

Preparation of well defined functional oligomers is another goal using these living polymerization systems. One approach was to use protected functional vinyl ethers together with HI/I₂ as the initiating system to polymerize IBVE, and deprotection of the endgroups to obtain poly(isobutyl vinyl ether) with terminal carboxylic or primary amine endgroups¹²⁸. Terminating a living polymer with aromatic or aliphatic amines also generated amino functional PIBVE^{107,108}. However, the terminal amino ether linkage (-CH(OR)-NHR') is unstable under acidic conditions¹⁰⁶. The esters initiated living polymerization of IBVE quantitatively. The imide initiators generated a small fraction of oligomers probably comprised of homopolymerized imide vinyl ether, since the $\langle M_n \rangle$ of imide containing PIBVE was higher than calculated and their end functionality was close to unity. End-capping living PIBVE with NaC(COCH₃)₂CH₂CH₂CH₂N(CO)₂C₆H₄ also led to amino terminated PIBVE. Termination of living PIBVE and PMVE by malonate anion led to malonic ester functional poly(vinyl ethers)¹⁰⁹. Upon hydrolysis and decarboxylation, carboxylate endgroups were

generated. The combination of functional initiators and termination by malonate anion, or imide containing termination reagents generated bifunctional poly(vinyl ethers) with carboxylic acid or amine at both ends. Bifunctional poly(vinyl ethers) were also synthesized using a difunctional initiator, 1,4-bis(vinyloxy)butane¹¹⁰. Other types of functional groups include methyl acrylate, allylic, and epoxide using initiator methods and vinyl ethers using terminator method ($\text{NaC}(\text{COOEt})_2\text{CH}_2\text{CH}_2\text{OCH}=\text{CH}_2$)^{111,112,113}.

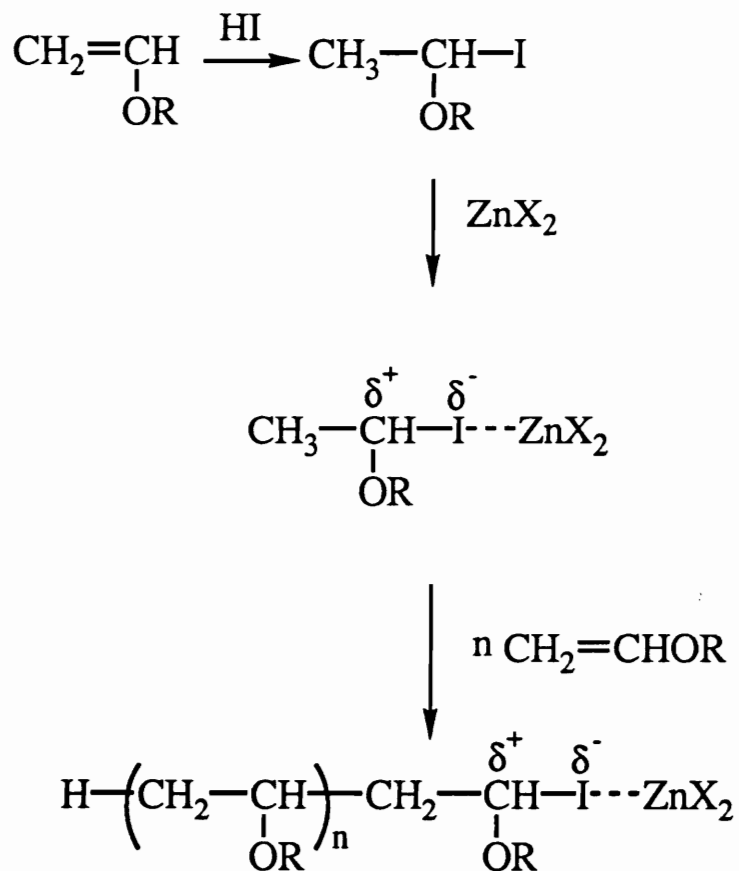
In summary, the HI/I₂ initiating system has induced living polymerizations of a number of alkyl vinyl ether monomers in nonpolar solvents at low temperatures (-40°C to -15°C) with low to moderate Mn's. When temperature is increased or solvent polarity is increased (change from toluene to methylene chloride), molecular weight distribution starts to broaden due to side reactions. In this respect, vinyl ether polymers that are not soluble in nonpolar solvents or at low temperatures cannot be polymerized by HI/I₂ in a living fashion.

2.2.3 HI/ZnX₂ Systems

In HI/I₂ initiated polymerizations of vinyl ethers, the function of I₂ is to activate the terminal CH-I bond to allow propagation. It was then reasoned that replacing I₂ by a weak Lewis acid should serve the same purpose¹¹⁴. Suitable Lewis acids should selectively activate the terminal group without inducing cationic polymerization by itself. ZnI₂ was first selected as such a Lewis acid with the list

later extended to ZnBr_2 and ZnCl_2 . Two advantages of the HI/ZnX_2 system over HI/I_2 were found: (1) only a small amount of zinc salts (1-5 mol% of $[\text{HI}]_0$) were efficient in activating the polymerization as compared with iodine (50-100 % of $[\text{HI}]_0$)¹¹⁵; and (2) HI/ZnX_2 systems permitted living polymerizations at room temperature^{114,116}. The living nature of HI/ZnX_2 initiated systems was established in the same way as in the HI/I_2 case, namely (1) number average molecular weight $\langle \text{Mn} \rangle$ increases in direct proportion to monomer conversion; (2) narrow molecular weight distributions ($\langle \text{Mw} \rangle / \langle \text{Mn} \rangle \leq 1.1$) persist throughout the polymerization. According to monomer addition experiments, however, these systems were perfectly living only at temperatures below 0°C ¹¹⁶. Above 0°C , tailing in molecular weight distributions was observed after the addition of the second monomer feed in the following severity: $\text{ZnCl}_2 > \text{ZnBr}_2 > \text{ZnI}_2$. Living polymers synthesized using HI/ZnI_2 included: PIBVE ($[\text{M}]_0 : [\text{HI}]_0 : [\text{ZnI}_2]_0 = 380 : 10 : 0.2$) in toluene at -40°C to $+25^\circ\text{C}$ or in methylene chloride at -40°C ¹¹⁴, poly(2-acetoxy ethyl vinyl ether) ($[\text{M}]_0 : [\text{HI}]_0 : [\text{ZnI}_2]_0 = 380 : 5.0 : 2$) in methylene chloride at -40°C ¹¹⁴, PMVE ($[\text{M}]_0 : [\text{HI}]_0 : [\text{ZnI}_2]_0 = 380 : 10 : 0.2$) in toluene at -15°C with $\langle \text{Mw} \rangle / \langle \text{Mn} \rangle$ of 1.21¹¹⁷. The proposed living polymerization mechanism is similar to that proposed for HI/I_2 systems, namely HI adds to the vinyl double bond of monomer to form an adduct with a carbon-iodine bond; ZnX_2 activates the "dormant" C-I bond through electrophilic interaction and living propagation starts (Scheme 2.2.2) ^{114,115}. In accordance with the

Scheme 2.2.2 Living Polymerization Mechanism of Alkyl Vinyl Ethers by HI/ZnX₂ Initiating System^{114,115}



proposed mechanism, the concentration of zinc salts were found to only affect the rate of polymerization without affecting molecular weight and polydispersity as $[HI]_0/[ZnI_2]_0$ changed from 12.5:1 to 25:1, while changing $[HI]_0$ changed molecular weight with an inversely proportional relationship¹¹⁴. Kinetic studies of the polymerization of IBVE in toluene at -40°C initiated by HI/ZnX_2 demonstrated that the polymerization rate had a first order dependence on monomer, and a linear dependence on $[HI]_0$ and $[ZnX_2]_0$, consistent with the proposed mechanism under the same polymerization conditions.

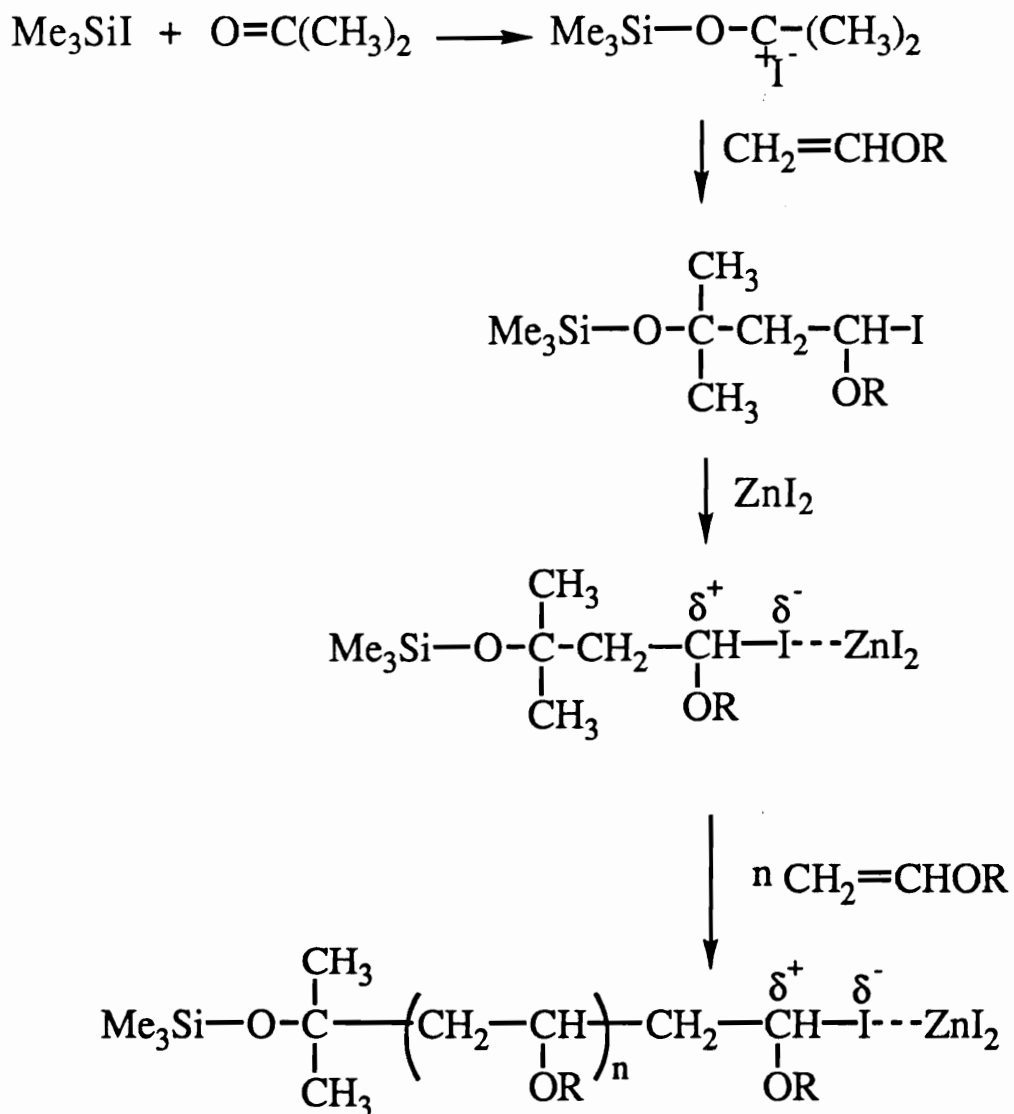
Copolymerization of IBVE, MVE with p-methoxystyrene via sequential polymerization using the HI/ZnI_2 initiating system produced block copolymers with narrower molecular weight distributions than using the HI/I_2 system¹¹⁷. In addition, p-methoxystyrene was found to be much less reactive than either IBVE or MVE and thus had to be polymerized with extra ZnI_2 catalyst after PIBVE or PMVE blocks were formed to achieve quantitative blocking efficiency. Similar to the case of using HI/I_2 initiating systems, the HI/ZnI_2 initiating system was also used to generate block copolymers via sequential polymerization of monomers. Using this method, living block copolymers of ester containing vinyl ether ($CH_2=CHOCH_2CH_2OCOCH_3$) and isobutyl vinyl ether have been obtained¹²⁷. Reaction of these living copolymers with a bifunctional vinyl ether ($CH_2=CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH_2OCH=CH_2$) yielded a star-shaped block copolymer¹²⁷. Alkaline hydrolysis of the

ester functions converted these star polymers into amphiphilic star polymers with the polyalcohol segments forming the outer or inner regions depending upon the addition sequence of the monomers¹²⁷.

2.2.4 Other Initiating Systems

As a substitute for HI, a series of monoacidic phosphate esters ((PhO)₂POOH, (nBuO)₂POOH) were used in combination with zinc iodide to initiate living polymerization of isobutyl vinyl ether in toluene below 0°C¹¹⁸. A similar mechanism was proposed as for the HI/ZnI₂ system, with the difference of having the phosphate counterion. The advantage of this system over HI was that these were easier to handle. When trimethylsilyl iodide was used to replace HI¹¹⁹, a carbonyl compound (aldehyde or ketone in large excess over [Me₃SiI]₀) was necessary to achieve perfectly living polymerization of IBVE^{119,120}. In the absence of, or at lower concentration of a carbonyl compound (less than 10 fold excess), a long lived polymer with a higher than calculated molecular weight resulted. The proposed function of the carbonyl group and subsequent polymerization mechanism is depicted in Scheme 2.2.3. Under these conditions, NMR spectra did show the proposed products¹²⁰. However, the need for huge excesses (50-136 fold over [Me₃SiI]₀) of acetone to obtain quantitative initiation was not explained. The trimethylsilyl endgroups of these polymers lead to alcohol endgroups upon appropriate conversion.

Scheme 2.2.3 Living Polymerization Mechanism of Alkyl Vinyl Ethers by $\text{Me}_3\text{SiI}/\text{Acetone}/\text{ZnI}_2$ Initiating System¹²⁰



More recently, another class of initiators were reported to produce living polymers of vinyl ethers, namely ethylaluminum dichloride (EtAlCl_2) in conjunction with a protogen or cationogen with added bases (ethers, esters, substituted pyridines) ^{94,95,121,122}. Adventitious water or added acetic acid in combination with EtAlCl_2 initiated polymerization of IBVE in n-hexane at 0°C and yielded polymers with broad molecular weight distribution^{95,123}. Upon addition of bases, the molecular weight distribution became narrower, and using optimized amounts of bases, living polymers resulted. The polymerization rate, molecular weight and polydispersity decreased upon the addition of ethyl acetate or ethyl benzoate in the polymerization of IBVE in toluene at -40°C initiated by EtAlCl_2 with adventitious water¹²⁴. When temperature was increased from -40°C to $+25^\circ\text{C}$, similar molecular weight distributions ($\langle\text{Mw}\rangle/\langle\text{Mn}\rangle = 1.12\text{-}1.15$) were observed. Excess amounts of esters over EtAlCl_2 (25 to 250 fold molar excesses) had to be used to achieve narrow molecular weight distributions and control of molecular weight with conversion^{122,124}. Using an IBVE-acetic acid adduct and EtAlCl_2 (1:1 molar ratio) as the initiator, polymerizations of IBVE were found to be living ($\langle\text{Mw}\rangle/\langle\text{Mn}\rangle < 1.1$)¹²² in n-hexane at $+40^\circ\text{C}$ in the presence of 1.0M (250 fold molar excess over EtAlCl_2) ethyl acetate or ethyl benzoate or ethyl carbonate. More polar carbonyl compounds, such as acetic anhydride and N,N-dimethylacetamide, almost completely inhibited the polymerization. Linear increases in $\langle\text{Mn}\rangle$ as the concentration of IBVE-acetic acid

adduct was decreased and invariant $\langle M_n \rangle$'s as the concentration of EtAlCl_2 was increased suggested that the IBVE-acetic acid adduct was the initiator while EtAlCl_2 was the activator. When the concentration of the IBVE-acetic acid adduct was too low (2.0mM), adventitious water (ca. 0.5 mM) began to affect the molecular weight of the resultant polymer. Other initiators, such as CF_3COOH and added water together with EtAlCl_2 polymerized IBVE in a living fashion at 0°C in n-hexane containing excess ethyl acetate. As replacements for esters, ethers (THF, 1,4-dioxane, diethyl ether) were also investigated as the added bases. The polymerization of IBVE initiated by an IBVE-acetic acid adduct and EtAlCl_2 was living at 0°C in n-hexane¹²¹. Added water and CH_3COOH in combination with EtAlCl_2 also polymerized IBVE in the absence of ether base, but the polymerization systems were not perfectly living^{121,123}. The amount of base required to achieve living polymerization depended on the basicity of the ether. Lesser amounts were needed for the most basic ethers; 1-2 vol% for THF, 5-10 vol% for 1,4-dioxane, and 70 vol% for the least basic molecule, diethyl ether. A mechanism for living polymerization of vinyl ethers initiated by protogens or cationogens (water, CF_3COOH , and IBVE-acetic acid adduct) in conjunction with EtAlCl_2 in the presence of added bases was proposed (Scheme 2.2.4). The key in this proposed mechanism is stabilization of the propagating species via interaction of the added base with the carbocationic site to form a living growing end free from chain transfer, termination, and other side reactions^{121,122}. Even though

complexation between IBVE-acetic acid adduct with EtAlCl_2 was determined to be quantitative¹²¹, no direct evidence for the proposed living propagating species was reported. There are several problems that cannot be fully explained by this proposed mechanism: (1) dependence of the polymerization rate on the counteranions derived from different initiators in the order of $\text{CH}_3\text{COOH} < \text{H}_2\text{O} < \text{CF}_3\text{COOH}$ ¹²²; (2) a presumably weaker nucleophilic anion (B^- in the mechanism) as opposed to a neutral ester or ether; (3) the requirement for large excess of base over EtAlCl_2 for achieving living polymerization.

Using the EtAlCl_2 catalyst in combination with 1,4-dioxane, functional groups were incorporated into living poly(isobutyl vinyl ether) via functional initiators ($\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{X} + \text{CF}_3\text{COOH}$, $\text{X} = \text{OOCCH}_3$, $\text{N}(\text{COOC}(\text{CH}_3)_3)_2$, $\text{CH}(\text{COOC}_2\text{H}_5)_2$) or via termination with sodiomalonic ester or phenyllithium. Combination of the two methods afforded homo- or heterotelechelic PIBVE¹²⁵. Using tris(trifluoroacetate)- initiators together with EtAlCl_2 and 1,4-dioxane, tri-armed star polymers of IBVE were prepared¹²⁶.

Living polymerization of isobutyl vinyl ether using other acids in combination with a Lewis acid or a Lewis base (depending on the structure of the acid) as initiating systems have also been investigated. Triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) in combination with a Lewis base (dimethyl sulfide) polymerized isobutyl vinyl ether in a living fashion at -40°C in methylene chloride¹³⁰. Trifluoroacetic acid (CF_3COOH) or trichloroacetic acid (CCl_3COOH) required a Lewis acid

(ZnCl_2) to produce living polymers of isobutyl vinyl ether. Without ZnCl_2 , no polymerization occurred¹³¹. These studies illustrate a wide spectrum of counterions capable of producing living polymers of isobutyl vinyl ether with selected additives.

In summary, two classes of initiators have generated living polymers of vinyl ethers with low to moderate molecular weights. The first type has iodide or phosphate as the counterion, activated by weak Lewis acids (I_2 , ZnX_2). The second class has acetate type (acetate, trifluoroacetate) counteranions, activated by EtAlCl_2 and deactivated by added bases (esters, ethers, and dimethyl derivatives of pyridine) to adjust the balance for living polymerization to occur. The HI/I_2 system was discovered first and thus was studied and utilized most. HI/ZnI_2 systems have major advantages over HI/I_2 systems, namely ZnI_2 alone does not initiate the polymerization of vinyl ethers, allowing higher polymerization temperatures (up to room temperature for IBVE in n-hexane), catalytic amounts of ZnI_2 to be used, and simpler polymerization mechanisms. EtAlCl_2 /acetate type initiators are relatively new systems that produce living PIBVE at up to +40 °C. Due to the sensitive dependence of the propagating species on basicity of the added base, both opportunities and possible problems exist for polymerization of polar monomers using EtAlCl_2 /acetate types of initiators.

2.3 Synthesis of Polyorganosiloxanes

2.3.1 Introduction

Siloxanes are compounds containing silicon and oxygen linkages, Si-O, with substituents on the silicon atom usually being organic groups, such as methyl or phenyl. Those polymers commonly called silicones are actually polyorganosiloxanes^{132,139}. Since their commercial introduction around 1940, polyorganosiloxanes have found wide applications ranging from aircraft, aerospace, automotive, electrical, and construction to medical and consumer goods^{132,133}. Specifically, polyorganosiloxanes have been used as rubbers, electrical molding resins, functional fluids, coatings, printing inks, cellular plastics, textiles finishes, and consumer products^{134,135}. Polyorganosiloxanes possess many unique properties: low glass transition temperature, low surface energy, good biocompatibility, hydrophobicity, high permeability to small molecules, stability of properties over a wide temperature range, thermal and oxidative stability, ultraviolet radiation and atomic oxygen resistance, and low mechanical strength^{132,133,136-138}. In addition, polyorganosiloxane materials can be manipulated by varying substituents on the siloxane backbone, and more importantly, by copolymerization with other polymers to achieve various desired properties¹³².

2.3.2 Chemistry of Siloxanes

In the synthesis of polyorganosiloxanes either as polymers or as reactive oligomers for copolymerization, some basic chemical

properties¹⁴⁰ of silicon-functional groups have been utilized frequently and, thus, are included here in addition to the chemistry of the siloxane bond.

Si-Halogen: SiCl, SiBr and SiI are hydrolyzed easily, while SiF hydrolyzes moderately fast.

Silanols: Depending on substituents and the number of hydroxyl groups, the properties of silanols vary dramatically. For example, Me₂Si(OH)₂ will condense even in the presence of trace amounts of atmospheric acids or residual alkali, while (t-Bu)₂Si(OH)₂ is stable in hot H₂SO₄. In general, the stability of silanols is in the order: R₃SiOH > R₂Si(OH)₂ > RSi(OH)₃, and the bulkier the R, the more stable the silanol.

SiH: The SiH group is a reducing agent; reacts with alkali; undergoes disproportionation in the presence of strong bases or Lewis acids; and, very importantly, undergoes hydrosilylation - the metal catalyzed addition of an organic vinyl group to SiH.

SiOC: SiOC compounds can be hydrolyzed in the presence of acids or bases.

Silyl carboxylates hydrolyze rapidly in the presence of moisture. This is the basis for siloxane RTV sealants.

SiN: SiN compounds react with water to liberate organic nitrogen compounds or ammonia.

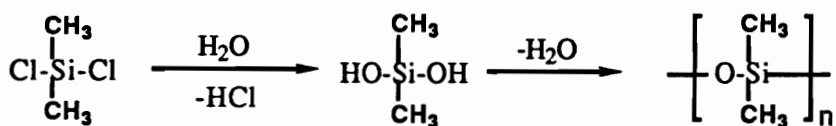
Si-R: Except for β-substituted electronegative groups (SiCH₂CH₂Cl), the chemistry of an organo functional silicon compound is similar to the corresponding silicon-free compound.

Si-O-Si: Due to the low electronegativity and bonding availability of d-orbitals on silicon, the Si-O bond is semi-ionic (40-50%) and may have partial double bond character^{132,137,141}. This contributes to the high stability of the Si-O bond to homocleavage (and, thus, to some of the unique stability characteristics mentioned above) and ease of cleavage heterolytically. Therefore, the siloxane bond is subject to acid or base attack.

2.3.3 Synthesis of Polyorganosiloxanes

A. Condensation (Step-Growth) Polymerization

Polyorganosiloxanes can be synthesized from chlorosilanes, alkoxy silanes or acetoxy silanes via hydrolysis process. In general, the silanes are hydrolyzed to the corresponding silanols. The silanols usually condense rapidly upon hydrolysis of the silanes^{139,143,145}. The hydrolysis of chlorosilanes is commercially important. A general illustration of the process is as follows, using dichlorodimethylsilane as an example¹⁴⁵:



Products of this type of hydrolysis-condensation process usually contain a mixture of cyclic and linear polymers of different sizes. The compositions of the products depend on the conditions of reaction^{139,143,145}. High temperature or basic conditions will favor high molecular weight linear polymers, while low temperature or

acidic conditions have the opposite effect. Use of water-miscible organic solvents will give a high yield of low molecular weight cyclic siloxanes. Hydrolysis of trifunctional silanes will yield random resinous structures^{139,143}.

Reaction of halosilanes with alcohols and carboxylic acids, and that of alkoxy silanes with carboxylic acids also produce polyorganosiloxanes without hydrolysis¹³⁹. Compared with the hydrolysis process, this process is rather unimportant.

B. Ring-Opening Polymerization

There are two important types of ring opening processes: equilibration processes, and living anionic processes^{136,139}.

a. Equilibration (redistribution) processes

This is one of the most important commercial processes for preparing polyorganosiloxanes. Due to the ionic character of the siloxane bond (as reviewed above), linear polyorganosiloxanes can be synthesized by both acid and base catalyzed ring-opening polymerizations of cyclic siloxanes. The cyclic siloxanes are usually the cyclic products of the hydrolysis-condensation process of organochlorosilanes. Molecular weights and end functionality of these polymers are usually controlled by incorporation of specified amounts of difunctional endblockers into the systems^{136,139,143,146}. The polymerization products include linear polymers and cyclics, results of thermodynamic equilibrium. The equilibrium is caused by

similar reactivity of silicon-oxygen bonds in the linear form compared with the cyclic form towards the catalyst (either base or acid)^{136,138,146}. The linear form of polyorganosiloxanes is favored thermodynamically only because of increase in entropy (ΔS) upon polymerization (ΔH is nearly zero)¹⁴⁵. A series of equilibration reactions are depicted in Scheme 2.3.1 using a basic catalyst and D₄ as an example^{137,138}.

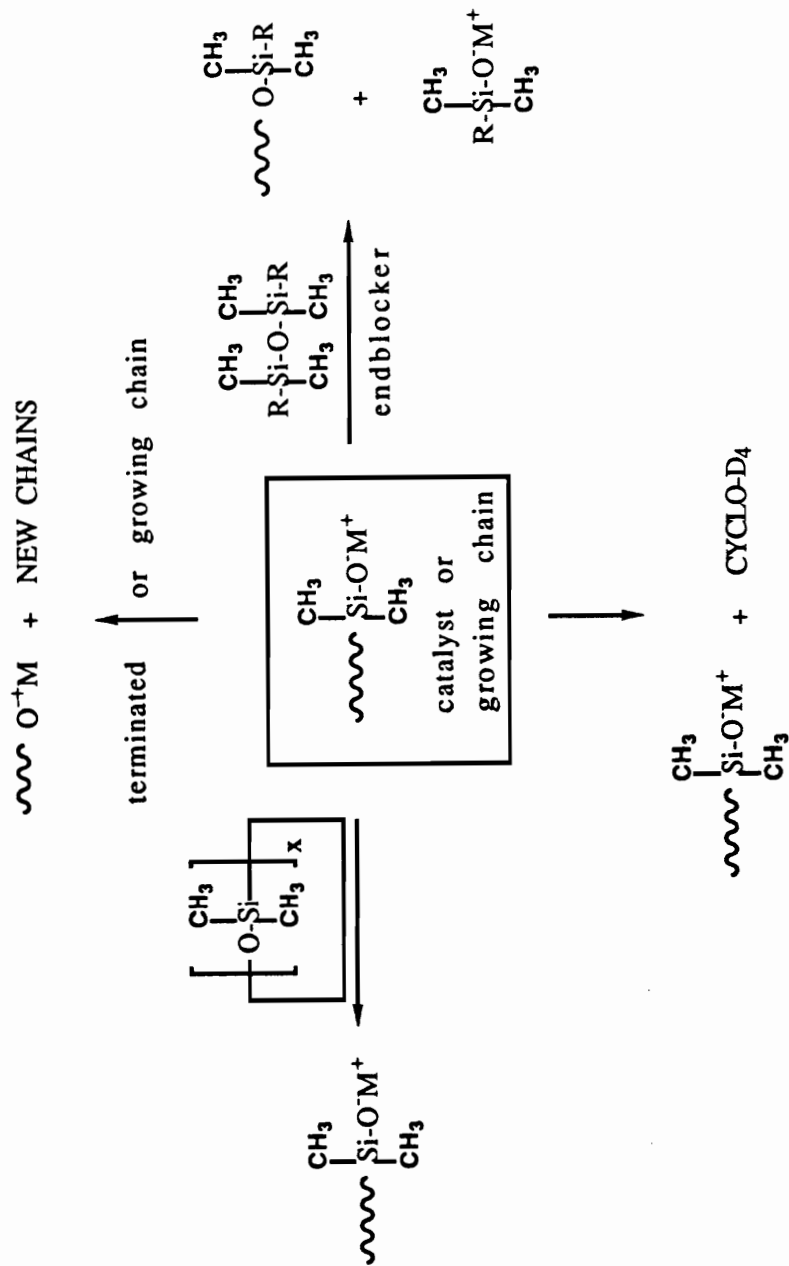
Base-catalyzed-systems

Bases that can be used to catalyze ring-opening polymerization of cyclic siloxanes include: hydroxides, alcoholates, phenolates and siloxanates of alkali metals; bases and siloxanates of quaternary ammonium and phosphonium; and organoalkali metal compounds^{137,146}. The catalytic activities of metallic hydroxides are in the decreasing order¹⁴³: CsOH > RbOH > KOH > NaOH > LiOH. It was found recently that phosphonium and tetramethylammonium siloxanates are more reactive than potassium siloxanolate catalysts¹⁴⁶.

The general activity of siloxanes toward bases is in the decreasing order of¹⁴³: D₃ > D₄ > MD₂M > MDM > MM, where MM stands for an endblocker.

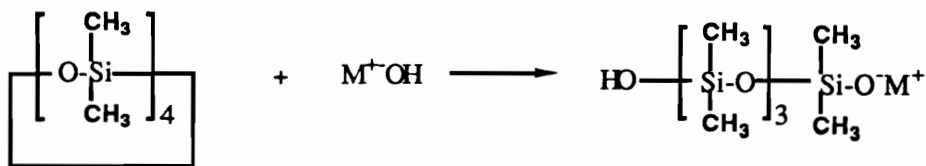
The mechanism involved in base catalyzed ring-opening polymerizations of cyclic siloxanes includes: first, nucleophilic attack on the electropositive silicon atom by catalyst to form siloxanolate

Scheme 2.3.1 Equilibrium Processes in Redistribution
 Ring-Opening Polymerization of D4 Using a Base Catalyst^{137,138}

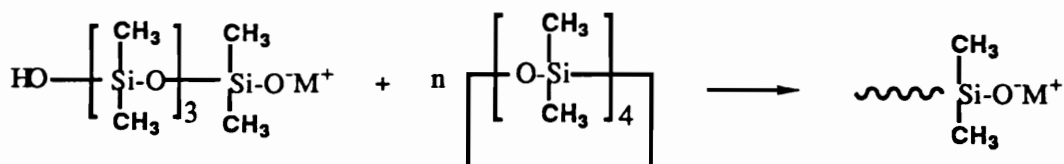


anion, and second, nucleophilic attack upon the electropositive silicon atom by siloxanolate anion^{137,143}, as illustrated in the following:

STEP 1



STEP 2



The active species in this process are siloxanolate anions¹⁴³. The polymerization generally proceeds through a viscosity maximum. Then the viscosity drops and approaches the equilibration value^{137,143}. This phenomenon is due to the fact that D₄ is more reactive than MM toward bases (see above activity order). D₄ becomes incorporated into the polymer chains faster than an endblocker, thus higher molecular weight is achieved at beginning of the polymerization. As the endblocker equilibrates into the polymer chains, molecular weights of these polymers reach its equilibration value gradually.

It is found that at equilibrium, the number average degree of polymerization in this type of equilibration system is dependent only on the molar ratio of the endblocker to the cyclic siloxane, and independent on either type or concentration of the catalyst used. However, the type and the concentrations of catalysts affect the rate of equilibration markedly¹⁴⁶. Therefore, by varying the molar ratio of endblocker to cyclic siloxane, the molecular weight of polyorganosiloxane can be controlled.

Acid-catalyzed systems

Proton and Lewis acids such as sulfuric, selenic, nitric, phosphoric, boric acids and SnCl_4 are useful catalysts for polymerization of cyclic siloxanes¹³⁹. The reactivity of siloxanes toward acids is in the order of¹⁴³: $\text{D}_3 > \text{MM} > \text{MDM} > \text{MD}_2\text{M} > \text{D}_4$.

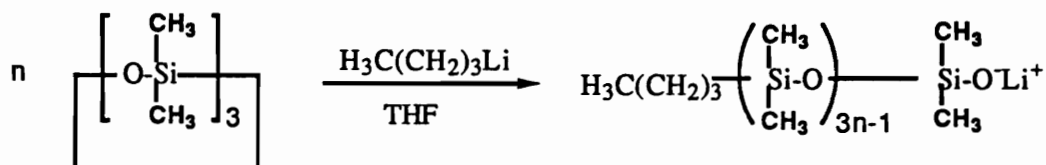
In contrast to the base-catalyzed process, no viscosity maximum is observed in the acid catalyzed polymerization of cyclic siloxanes¹⁴³. This is because MM is more reactive toward an acid than D_4 in the acid-catalyzed system.

The mechanism involved in the acid-catalyzed system is not yet well understood^{137,146}. Although the electrophilic attachment of the proton or Lewis acid to the lone electron pair of the siloxane oxygen atom in the first step seems indisputable, the nature of the active species afterwards is not clear^{137,139,145,146}. The propagating center could be a tertiary oxonium ion or a silicenium ion which is formed via rearrangement of the tertiary oxonium ion, or a covalent

aryl ether, etc. Accordingly, hydroxyl, amine, epoxy and carboxyl functionalities are the most widely used functional endgroups¹³². Selection of catalyst type is generally based on the nature of endgroups, the endblocker, and the type of substituents on the silicon^{138,146}. An endblocker with a basic functional group, such as amine will require a basic catalyst, and an acidic functional endblocker needs an acidic catalyst.

b. Living anionic processes

Under proper conditions, polyorganosiloxanes with narrow molecular weight distributions and well controlled molecular weights can be obtained. Hexamethylcyclotrisiloxane (D₃) polymerizes in a living manner by using lithium compounds, such as butyl lithium or lithium silanolate, as initiators in the presence of small amounts of promoting solvents, such as THF or diglyme¹⁴⁷⁻¹⁴⁹. The overall reaction using butyl lithium as initiator is as follows:



The living end can be terminated by desired functional groups such as styryl, methacryl, vinyl, silanyl, and silane¹⁴⁷.

The reason that the above process produces living polyorganosiloxanes is that: (1) the ring-strain present in D₃ makes

it more reactive than the less strained D₄; (2) the non-terminating nature of the lithium system; (3) the use of promoting solvents (THF, diglyme, or dimethylsulfoxide)^{142,146}. Under these conditions, attack of the propagating species (lithium siloxanolate) on the strained cyclic D₃ structure is allowed and attack on linear backbones is not allowed. Therefore the redistribution process can be precluded. The living polymerization of D₃ allows for preparation of well-defined monofunctional PDMS oligomers suitable for diblock copolymer synthesis.

2.4 Compatibilization of Poly(ϵ -caprolactam)/Poly(propylene) Blends

Polymer blends have been and continue to be a subject for intensive investigation since the late 1970's^{150,151}. Persistent interest in this subject are due to the enormous economic and utility potentials which polymer blends can provide and the complexity in obtaining desired products. Due to entropic reasons, many polymer pairs are not thermodynamically miscible. However, immiscible polymer blends may exhibit synergetic effects under suitable conditions¹⁵². In addition, immiscible blends tend to display their individual characteristics instead of an average. Under suitable conditions, seemingly contradicting properties can be obtained from immiscible blends with little sacrifice of desirable properties. This character is one attractive feature of immiscible blends. There are many aspects involved in defining suitable conditions for bringing out the best of an immiscible blend, ranging from synthesis, polymer physics to rheology. In describing polymer blends, two terms are often encountered, namely, miscibility and compatibility. These two words have been used interchangeably by some authors and distinctively by others^{150,153}. It is useful to distinguish the two and is being adopted by more authors^{150,153}. Polymer blends are miscible if their amorphous regions form thermodynamically stable single phase. Compatible blends, on the other hand, form

multiphases, but the separated phases are stable and resist gross phase separation.

Poly(ϵ -caprolactam) (Nylon 6) and poly(propylene) (PP) are two high-volume commercial polymers with distinct properties. Poly(propylene) is light (low density), nonpolar (hydrophobic), weather resistant, relatively inexpensive and possibly surface active^{154,155}. Nylon 6, on the other hand, is polar, moisture sensitive, moderately to poor weather resistant, relatively expensive but has high strength and a high melting point¹⁵⁵. The blends of these two materials are expected to provide materials with a spectrum of properties. Due to large difference in polarity between these two polymers, the blend of these two is neither miscible nor compatible^{156,157}, resulting in poor mechanical properties.

It is well known that the presence of a block or a graft copolymer of suitable structure can reduce the size of the dispersed phase in an immiscible blend^{150,158}. The ideal location of a block or a graft copolymer in an immiscible blend is at the interface of the two blend components. The presence of a block or a graft copolymer is expected to reduce the interfacial tension between the two immiscible phases and thus reduce the size of the dispersed phase, to prevent gross phase segregation, and to provide interfacial adhesion. This copolymer, often referred to as a compatibilizer, can be generated in situ or independently synthesized. For nylon 6 containing blends, functional groups such as maleic anhydride^{156,157}, methacrylic acid^{156,159,160}, and alkyl chloride¹⁶¹, have been

incorporated in the second blend component to achieve compatibility of blends. The most obvious improvement upon addition of these compatibilizers is the decrease in dispersed phase size.

In the presence of maleic anhydride-grafted poly(propylene) (MAgPP), domain sizes of the dispersed phase in isotactic poly(propylene) and Nylon 6 blends were observed to decrease substantially^{156,157}. For example¹⁵⁷, the dispersed phase in PP/Nylon 6 blends ranged from 5 to 25 μm in diameter depending upon the composition. When MAgPP (5% by wt.) was blended with Nylon 6, the dispersed phase became more uniform in size and the size decreased to about 1 μm in diameter when Nylon 6 was the minor component. The dispersed phase completely disappeared when the amount of Nylon 6 was over 30 wt.%. Surprisingly, ternary blends of PP/Nylon 6 /MAgPP with 5 wt.% of MAgPP and variable compositions of PP and Nylon 6 showed no discrete phases over the whole composition range. No significant differences in Nylon 6 melting point depressions were observed between Nylon 6/PP blends and Nylon 6/PP/MAgPP blends¹⁵⁷. However the glass transition temperatures of these blends were not reported. It is inconclusive whether or not the disappearance of the discrete phase in these blends is due to phase mixing. Addition of 5 wt.% of MAgPP also reduced the size of dispersed phase in Nylon 6/LDPE (low density polyethylene) blends from 12 to 17 μm to 2 to 4 μm in diameters¹⁶². In addition, the presence of MAgPP prevented gross phase segregation in annealed nylon 6/LDPE blends. Mechanical

properties were observed to improve with the addition of MAgPP to Nylon 6/PP blends as compared to without the additive¹⁵⁶. The improvement in compatibility of Nylon 6 and polyolefins was believed due to the formation of graft copolymers (served as compatibilizers) of PP and Nylon 6 via reaction between maleic anhydride groups in PP and amino groups in Nylon 6 ^{156,158}.

Similar effects were observed using ethylene-methacrylic acid-isobutyl acrylate terpolymer (70% neutralized with zinc) as compatibilizer¹⁶⁰. The dispersed phase size decreased from 5 to 10 μm to 1 to 2 μm with 5 wt.% of the compatibilizers for 10 PP/90 Nylon 6 or 10 Nylon 6/90 PP. More pronounced size reduction was observed with Nylon 6 as the dispersed phase. Specific interactions between amine groups of Nylon 6 and the carbonyl groups in the terpolymer were detected by FTIR and believed to be the cause of the observed compatibility¹⁶⁰. Binary blends of Nylon 6 and ethylene-methacrylic acid¹⁵⁹ suggested amidation reactions have taken place during melt mixing of the two. However, the amidation reaction was not found in blends of Nylon 6 and the terpolymer, which was believed to be due to partial neutralization of the terpolymer¹⁶⁰. Thus, the extent of reaction between Nylon 6 and methacrylic acid containing copolymers can be varied by changing the extent of neutralization of the terpolymer.

Reaction of chlorinated poly(ethylene glycol) with Nylon 6 generated graft copolymers of the two components with Nylon 6 as the backbone¹⁶¹. X-ray diffraction revealed the change of the

crystalline structure of Nylon 6 upon grafting. The attempted application of this graft copolymer is to compatibilize Nylon 6 and poly(ethylene glycol) blends.

Blends of Nylon 6 with bisphenol-A polycarbonate at high Nylon 6 contents (>90 % by wt.) exhibited improved impact strength over pure Nylon 6¹⁶⁴, even though at other compositions the two blends were completely immiscible. Chemical reactions between the two components which gave rise to block copolymers were speculated to be responsible for the improved compatibility^{163,164}.

Chapter III

Experimental

3.1 Reagents and Their Purification

3.1.1 Solvents

Chlorobenzene. Chlorobenzene (Fisher, Purified Grade) (800 ml) was washed three times (60 ml each) with concentrated sulfuric acid (Fisher, Reagent A.C.S.) using a separatory funnel (1L) to remove unsaturated impurities. Then it was washed with deionized water once (100 ml) and saturated sodium bicarbonate (Fisher, Certified, A.C.S.) aqueous solution until basic (100 ml x 2), again with deionized water three times (100 ml each). It was dried over magnesium sulfate (Fisher, Certified, ca. 20 g) in a Erlenmeyer flask (1L) with stirring bar stirring, decanted into phosphorous pentoxide (Aldrich, ca. 10 g) in another Erlenmeyer flask, stirred over ground calcium hydride (Fisher, Purified Grade) in a round bottom flask (1L) for ca. 12 h, then distilled under nitrogen. The purified chlorobenzene was transferred via a cannula to a flame dried brown bottle for storage.

Chlorobenzene-d₅. Chlorobenzene-d₅ (Aldrich, 98.5 +% D) was stirred over calcium hydride and distilled under nitrogen.

Acetonitrile. Acetonitrile (Fisher, HPLC Grade) was stirred over ground calcium hydride for ca. 12 h and distilled under nitrogen twice. The solvent was transferred to a flame dried brown bottle via a cannula and stored under nitrogen.

Acetonitrile-d₃. Acetonitrile-d₃ (Aldrich, 99.5% D) was stirred over calcium hydride and distilled under nitrogen and stored in a flame dried brown bottle.

N-methyl-2-pyrrolidinone. N-methyl-2-pyrrolidinone (Fisher, Purified Grade) was stirred over phosphorous pentoxide (Fisher, Certified A.C.S.) for several hours and distilled under vacuum. The solvent was then transferred to a flame dried brown bottle and stored under nitrogen.

Chloroform-d. Deuterated chloroform (Aldrich, 99.8 % D) used in kinetic studies was stirred over phosphorous pentoxide for several hours and distilled under nitrogen. For routine NMR analysis, deuterated chloroform was used as received.

Methanol. Methanol (Fisher, Certified A.C.S.) (700 ml) was added to the refluxing product of 60 ml methanol with 5 g of magnesium turnings (Aldrich, 98%) and 0.5 g of iodine (Aldrich, 99.8% A.C.S. reagent) as the indicator once the color of the latter changed from purple to colorless. It was then distilled under nitrogen and transferred via a cannula to a flamed dried bottle.

Toluene. Toluene (Baker, Analyzed Reagent) was purified in a similar way to that in chlorobenzene except for the last step. Instead of distilling from calcium hydride, toluene was refluxed over several grams of a sodium metal dispersion in paraffin wax (Aldrich, 50% dispersion in paraffin) under nitrogen. Then ca. 0.1-0.3 g of benzophenone (Aldrich, 99%) was added as an indicator. After refluxing for a couple of hours, the color changed from blue to deep

purple indicating a completely dry and oxygen free solvent. The solvent was distilled prior to each reaction. The first ca. 20 mL was removed and the middle fraction was collected in a flame-dried two neck flask fitted with rubber septum. Then the desired amount was transferred either by a syringe to the reaction flask or by a cannula to a flame-dried graduated cylinder then to the reaction flask.

Tetrahydrofuran. Tetrahydrofuran (Baker, Analyzed Reagent) was dried in the same way as toluene discussed above and distilled immediately prior to each reaction.

Cyclohexane. Cyclohexane (Fisher, Reagent Grade) was stirred over concentrated sulfuric acid at room temperature for 7 days, and then decanted, refluxed over sodium metal dispersed in paraffin wax, and distilled under nitrogen prior to usage.

Hexanes. Hexanes (Baker, Analyzed Reagent) was stirred over concentrated sulfuric acid for at least 10 days, and then decanted to a separatory funnel and washed with deionized water, saturate sodium bicarbonate aqueous solution three times, then deionized water three times. The drying procedure is the same as that in toluene.

Diethyl ether. Anhydrous diethyl ether (Baker, Analyzed Reagent) was refluxed over sodium metal in paraffin wax and distilled under nitrogen.

Dichloromethane. Dichloromethane (Baker, Analyzed Reagent) was stirred over calcium hydride for ca. 12 h, distilled under nitrogen, and stored in a flame dried brown bottle.

3.1.2 Monomers

2-ethyl-2-oxazoline and 2-methyl-2-oxazoline. 2-ethyl-2-oxazoline (Aldrich, 99+%) and 2-methyl-2-oxazoline (Aldrich, 98%) were stirred over ground calcium hydride for at least 12 hours, distilled under nitrogen, and stored in flame dried brown bottles under nitrogen in a refrigerator.

2-oxazoline. Unsubstituted oxazoline monomer was synthesized in three steps. First, to 180 mL of ethylformate (Aldrich, 99%) was added 1 equivalent of ethanolamine (135 mL, Fisher, Purified Grade) at 0°C via a addition funnel. The reaction mixture was refluxed (120°C) for 6 h, then the product, 2-hydroxyethylformamide, was vacuum distilled at 114°C, 0.25 torr. Secondly, 90 mL (1.1 eq.) of thionyl chloride (Aldrich, 97%) was added via a addition funnel to 100 g of 2-hydroxyethylformamide and 100 mL of dichloromethane and stirred at room temperature for 2 h. Bubbling nitrogen and aspirator were used to remove the side products, HCl and SO₂ gases, and solvent. The product, 2-chloroethylformamide was isolated via vacuum distillation at 70°C, 0.4 torr. In the final step, 16.37 grams of sodium hydride/mineral oil (Aldrich, 60% w/w) was rinsed with dry diethyl ether three times (80 mL each) in a dry round bottom flask using a cannula to transfer diethyl ether. Then 60 mL of dry NMP was added and the reaction flask cooled to -20°C. The mixture of 60 mL NMP and 40 g of 2-chloroethylformamide in another dried flask was slowly cannulaed

into the reaction flask. The product, 2-oxazoline, was obtained by distilling the reaction mixture under nitrogen. It was further dried by distilling over CaH_2 .

Butyl vinyl ether. Butyl vinyl ether (BVE) (Aldrich, 98%) was washed with deionized water to remove residual alcohols, stirred over KOH pellets (Fisher, certified A.C.S.) for ca. 6 h, passed over neutral alumina, distilled from sodium metal/paraffin wax under nitrogen, and stored in a flame dried brown bottle. Immediately prior to each reaction, the BVE was vacuum distilled over triisobutyl aluminum (Aldrich, 25 wt.% solution in toluene) using the following procedure. The bulb to bulb distillation apparatus, with stirring bar and septum in one side, and a three-way stop-cock in the other was flame dried under vacuum twice. Then ca. 20 mL of the distilled BVE was cannulaed into the distillation apparatus under N_2 and subsequently frozen with liquid N_2 . The apparatus was evacuated for ca. 10 minutes, then the vacuum was turned off by the stop-cock, and the BVE allowed to thaw. This freeze-thaw process was repeated three times to remove any gases in the apparatus. Then, the apparatus was filled with N_2 , and ca. 0.5 mL of triisobutyl aluminum/toluene was syringed into BVE which was stirred at room temperature for 45 to 60 minutes to remove trace amounts of water. The mixture was then put through the freeze-thaw cycle twice to reach a vacuum of less than 100 millitorr. The BVE was distilled into the receiver flask by placing the receiver flask in liquid N_2 bath and allowing BVE to warm up slowly.

Methyl vinyl ether. Methyl vinyl ether (Aldrich, 98%) is a gas at room temperature, therefore special care was taken when handling it. Methyl vinyl ether gas was passed through a dry tube filled with ground calcium hydride and passed via a needle and condensed into a flame dried round bottom flask which was fitted with a rubber septum, equipped with stirring bar and sodium metal/paraffin wax chunks, and cooled to -50°C . The liquid methyl vinyl ether was stirred over sodium metal at -50°C for ca. 6 h and distilled to a round bottom flask filled with dry toluene. The receiving flask was weighed before and after the addition of toluene and the distillation of the methyl vinyl ether so that the exact concentration of methyl vinyl ether in toluene could be calculated.

ϵ -Caprolactone. ϵ -Caprolactone (Aldrich, 99%) was dried over CaH_2 and distilled under vacuum.

Hexamethylcyclotrisiloxane (D_3). D_3 (Donated by General Electric Corporation) was dried over CaH_2 and sublimed under vacuum.

3.2 Initiators, Terminating Agents, and Catalysts

3.2.1 Initiator and Terminating Agent for the Synthesis of Functional Poly(dimethylsiloxane)s

sec-Butyllithium. sec-Butyllithium in cyclohexane (Lithco Division of FMC) was titrated using 2,5-dimethoxybenzyl alcohol to be 1.4 molar and used as received.

Benzyl chloride containing terminating agent. This terminating agent was prepared by hydrosilation reaction of dimethylchlorosilane (Petrarch Systems) and vinylbenzylchloride (DOW) using chloroplatinic acid (Aldrich, 99.995%) as catalyst. The catalyst and dimethylchlorosilane were used as received. A stock solution of chloroplatinic acid in dry toluene and methanol was prepared. The reaction was carried out in a round bottom flask with a thermo-couple inside the flask to monitor the reaction temperature. Dimethylchlorosilane was added in several aliquots to the mixture of vinylbenzylchloride and the chloroplatinic acid. The reaction was monitored by observing temperature increase after the addition of dimethylchlorosilane and by FTIR. Since disappearance of the peak at 2170 cm^{-1} due to Si-H stretch indicates complete depletion of dimethylchlorosilane, more dimethylchlorosilane was added when it occurred. A slight excess of dimethylchlorosilane was added at the end of the reaction. The completion of the reaction was judged by the disappearance of a peak due to the vinyl double bond. The product was purified by fractional vacuum distillation.

3.2.2 Initiators and Terminating Agents for Poly(2-alkyl-2-oxazoline) and Poly(2-oxazoline) Homopolymer Synthesis

Benzyl chloride. Benzyl chloride (Aldrich, 97%) was stirred over ground calcium hydride for 48 h and fractionally distilled under vacuum of 0.6 torr at 45°C .

Benzyl iodide. Benzyl iodide was synthesized from benzyl chloride and sodium iodide. To a solution of 15.1 mL (0.13 mol) of benzyl chloride in 130 mL of acetone was added 30.2 g (0.20 mol) of sodium iodide and the mixture was refluxed for 1 h. The solids were removed by filtration, and the filtrate was concentrated by rot vap. The residue was diluted with 100 mL of deionized water plus 100 mL of diethyl ether. The ether layer was retained and washed with 5% aqueous sodium thiosulfate, then water, then dried over magnesium sulfate. The solvent was evaporated and the resulting thick syrup was dissolved in 50 mL of hexanes and allowed to crystallize in a freezer. Immediately prior each reaction, benzyl iodide with small amount of hexane was dried under vacuum at 0°C to a constant weight. Then stock solution of benzyl iodide in polymerization solvent was prepared.

1-Iodobutane. 1-Iodobutane (Aldrich, 99%) was fractionally distilled from phosphorous pentoxide under nitrogen. Only the middle portion was used.

1-Chlorobutane. 1-Chlorobutane (Aldrich, HPLC grade, 99.5%) was fractionally distilled from phosphorous pentoxide under nitrogen and the middle portion collected for use.

2-Chloroethyl ethyl ether. 2-Chloroethyl ethyl ether (Aldrich, 99%) was stirred over ground calcium hydride for 20 h and fractionally distilled and the middle portion was retained for use.

Methanesulfonyl chloride. Methanesulfonyl chloride (Aldrich, 98%) was fractionally distilled from phosphorous pentoxide

under vacuum of 5 torr at 45°C, and the middle fraction was retained for use.

n-Butanol. n-Butanol (Aldrich, HPLC grade, 99.9%) was stirred over sodium borohydride at 50°C and then over sodium metal/paraffin wax, and fractionally distilled under nitrogen.

n-Butyl mesylate. n-Butyl mesylate was prepared from n-butanol and methanesulfonyl chloride. In a 500 mL round bottom flask, was charged 135 mL of dry methylene chloride via cannula and flame dried graduated cylinder, 30 mL (3 mole per mole of n-butanol) of dry triethylamine via a syringe, 6.2 mL of n-butanol via a syringe. The reaction flask was placed in a ice bath and 6.3 mL of methanesulfonyl chloride (1.2 equivalent to n-butanol) was added slowly via a syringe. The reaction mixture become cloudy during addition and allowed to react at 0°C for 3 h and then warm up slowly. Then 45 mL of dry hexanes was added and the mixture filtered through a flame dried glass frit. Solvents were removed at room temperature under vacuum. The product was purified by fractional distillation at reduced pressure, the middle fraction was collected at 1.5 torr and 76°C.

Methyl p-toluenesulfonate. Methyl p-toluenesulfonate (Aldrich, 98%) was fractionally distilled under vacuum.

Sodium iodide. Sodium iodide (Aldrich, 98%) was recrystallized from water and small amount of ethanol (20 g of NaI, 10 mL water and 2 mL of ethanol), rinsed with diethyl ether and dried under vacuum at 70°C for 12 h.

Terminating agents. Either methanolic KOH (Fisher, 0.1N or 0.5N) or ammonium (Matheson Air Products) in dry methanol was used as terminating agents for poly(2-alkyl-2-oxazoline)s and poly(2-oxazoline). Both methanolic KOH and ammonium gas were used as received.

3.2.3 Initiators and Terminating Agents for Functional Poly(alkyl vinyl ether) Synthesis

HI/Hexanes solution. The HI/hexanes solution was prepared by removing water from hydriodic acid (Aldrich, 99.99%, HI content 57%) solution using P_2O_5 as dehydrating agent. 20 g of phosphorous pentoxide was placed in a three neck 100 mL flask with one joint connected to a 90 degree connector and another to a 10 mL addition funnel, and the third a septum. To the connector, was attached a tube containing P_2O_5 , which was connected to a trap via a piece of Tygon tubing. The trap was connected to another 90 degree connector whose inner tube was immersed into 40 mL of dry hexanes contained in a two neck 100 mL round bottom flask. The three neck flask was immersed in a ice bath and the two neck flask was cooled in a isopropanol/dry ice bath. About 7 mL of HI/H₂O was added to P_2O_5 dropwise through the addition funnel within 30 minutes. The HI/hexanes solution was cannulaed into a flame dried brown bottle for storage. The molarity of the solution was determined by dissolving 0.5 mL of the solution in 3 mL of deionized

water and titrated with 0.1015 N of NaOH solution in water (Aldrich, volumetric standard).

2-Chloroethyl vinyl ether. 2-Chloroethyl vinyl ether (Aldrich, 99%) was vacuum distilled over sodium/paraffin wax twice using the bulb to bulb distillation apparatus and similar procedure as described earlier in the purification of butyl vinyl ether section. The only difference was that sodium instead of triisobutyl aluminum was used in this case.

LiBH₄/THF. LiBH₄ in THF solution (Aldrich, 2M) in a SureSeal™ bottle was capped with two layers of rubber septum, and used as received.

p-Toluenesulfonyl chloride. p-Toluenesulfonyl chloride (Aldrich, 99+%) (20 g) was dissolved in chloroform (50 mL). Then hexanes (250 mL) was added. The solution was filtered, and the solvents were evaporated to yield white crystals.

3.3 Synthesis of Poly(2-alkyl-2-oxazoline) and Poly(2-oxazoline) Homopolymers

3.3.1 Synthesis

Poly(2-ethyl-2-oxazoline)s. To investigate the effects of initiators on the molecular weight control and molecular weight distributions, poly(2-ethyl-2-oxazoline)s with various molecular weights were synthesized using various initiators; benzyl halides, alkyl halides, and mesylate. Typical procedures were: to a flame dried round bottom flask equipped with stirring bar and sealed with

rubber septum were added chlorobenzene (to make 25% polymer wt./v solution), 2-ethyl-2-oxazoline, and desired amount (based on the molecular weight desired assuming complete initiation) of stock solution of a chosen initiator. The reaction mixture was stirred for ca. 30 minutes and placed in a preheated oil bath of 110°C. Upon depletion of the monomer as monitored by ^1H NMR, the polymers were terminated by KOH/MeOH at room temperature. A GPC sample was taken after most solvents were stripped off at room temperature using aspirator or vacuum. Other treatments were avoided to ensure no fractionation of the sample. In case where the polymers were used for blending studies, the reaction mixtures were diluted with chloroform and washed with saturated aqueous solution of sodium thiosulfate and deionized water. Then the solvents were evaporated and polymers were dried in vacuum oven at 60°C to a constant weight. Poly(2-ethyl-2-oxazoline) was also terminated with NH_3/MeOH to obtain amine functional endgroups. In this case, the polymer solution was syringed into a methanolic ammonium solution prepared by bubbling ammonium gas through ice cold dry methanol. The amount of methanol used are based on the solubility of ammonium in alcohol and 100 times equivalents per mole of initiator. The dried polymers are light yellowish glassy material.

Poly(2-methyl-2-oxazoline). Poly(2-methyl-2-oxazoline)s were synthesized by using either benzyl iodide or methyl iodide as initiators and acetonitrile as solvent. The general procedures were the same as in the polymerization of 2-ethyl-2-oxazoline except that

the reaction mixture was heated to 85°C, and the polymers were isolated by precipitating into THF/diethyl ether mixture (ca. 50/50, v/v). The dried polymers are white powdery solids.

Poly(2-oxazoline). Poly(2-oxazoline) was polymerized using methyl p-toluenesulfonate as initiator and NMP as solvent. The basic procedures were the same as in the polymerization of 2-ethyl-2-oxazoline but the heating temperature and work up. The reaction mixture was heated to 85°C and until the polymers precipitated out of the solution. ¹H NMR measurements were conducted using D₂O as the solvent. The polymer was purified by washing with THF, dissolving in water and precipitating into isopropanol/THF mixture (50/50, v/v), resulting in light yellowish fluffy material.

3.3.2 Kinetic Studies

To determine initiation and propagation rate constants of polymerizations of 2-alkyl-2-oxazolines, polymerizations of 2-alkyl-2-oxazolines were carried out in a 5mm screw cap NMR tube fitted with PTFE/silicone septum. The NMR tube was flamed dried under vacuum, filled with nitrogen, and weighed. Then, desired amounts of initiator, monomer, and deuterated solvent were added via syringes. The tube was weighed in between additions so that exact weights can be obtained. The resultant molar ratio of monomer to initiator was ca. 5 and the concentration of monomer was 25% wt./v, resulting in molar concentration of initiator of ca. 0.4 mol/L and monomer of ca. 2.5 mol/L. The NMR tube was then heated inside the NMR

spectrometer probe and NMR spectra were taken every 5 minutes to every two hours depending on the polymerization rates of the polymerization system.

3.4 Synthesis of Functional Oligomers and Copolymers

3.4.1 Synthesis of Poly(dimethylsiloxane-2-ethyl-2-oxazoline) Diblock Copolymers

Functional poly(dimethylsiloxane) oligomers with benzyl chloride functional groups at chain ends were prepared via anionic living polymerization of D₃. Into a flame-dried round bottom flask equipped with Teflon coated stirring bar and a rubber septum secured with copper wire, cyclohexane solutions of D₃, then sec-butyl lithium were added via a syringe. The reaction mixture was stirred for ca. 2 hours at room temperature to allow initiation to take place. Then addition of 10% by volume of THF looses the ion pair and promotes propagation processes. After ca. 48 hours of stirring, the polymerization was terminated by 1.2 equivalent of benzyl chloride containing chlorosilane terminating agent. Washing with methanol and evaporating solvents yielded the functional oligomers.

To make 20 grams of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers with 20% by wt. of poly(dimethylsiloxane)s, 2 molar equivalents of NaI per functional oligomer, 4 grams of functional poly(dimethylsiloxane)s, 16 grams of 2-ethyl-2-oxazoline and 60 mL of chlorobenzene were syringed into a flame-dried 250 mL round bottom flask equipped with a Teflon

coated magnetic stirring bar and a rubber septum secured with copper wire. The reaction mixture was stirred at room temperature for ca. one hour then heated to ca. 110°C until the monomer was depleted as monitored by ¹H NMR. The reaction was then terminated with 1.1 equivalents of methanolic KOH. The copolymers were recovered by adding chloroform, washing with aqueous sodium thiosulfate and then deionized water, and evaporating the solvents. The dry copolymers were soxhlet extracted using hexanes to remove any unreacted poly(dimethylsiloxane) oligomers.

3.4.2 Synthesis of Poly(butyl vinyl ether-2-methyl-2-oxazoline) Graft Copolymers

Poly(butyl vinyl ether) with ethyl chloride functionality incorporated along the polymer backbone was synthesized via cationic copolymerization of butyl vinyl ether with ca. 3% by mole of chloroethyl vinyl ether using an aluminum hydrogen sulfate catalyst. This polymer was provided by my colleague, Mr. J. M. Bronk. The details can be found in his thesis¹⁹⁶.

The synthesis of the graft copolymer was conducted in a Parr reactor at temperature of 110°C which is close to the boiling point of 2-methyl-2-oxazoline monomer (109.5-110.5 °C) in order to complete the polymerization within reasonable period of time (ca. 48 h). To make the graft copolymer with composition of 50/50 by wt., a mixture of 5 g of poly(butyl vinyl ether/2-chloroethyl vinyl ether), 0.48 g of sodium iodide (2 mole eq. NaI to 1 mole of chloroethyl vinyl

ether), 5 mL of 2-methyl-2-oxazoline in 60 mL of chlorobenzene, and 5 mL of N-methyl-2-pyrrolidinone (NMP) was heated to 110°C under N₂ in the Parr reactor equipped with overhead stir, resulting in a pressure of 20 psi. When the polymerization of 2-methyl-2-oxazoline was about 40 % conversion as judged by ¹H NMR, an additional 10 mL of NMP was added. Following completion of the polymerization as determined by ¹H NMR, 19 mL of 0.1 N methanolic KOH (1.2 equivalents per mole of chloroethyl vinyl ether) was added at room temperature to terminate the poly(2-methyl-2-oxazoline) grafts. The graft copolymers were recovered by precipitating the reaction mixture into diethyl ether. When the graft copolymer with higher poly(2-methyl-2-oxazoline) content (75 wt. %) was prepared, additional 10 mL NMP was added at the end of ca. 48 h, and the polymerization took ca. 60 h to complete.

3.4.3 Synthesis of Poly(2-methyl-2-oxazoline- ϵ -caprolactone) Block Copolymers

Monofunctional poly(2-methyl-2-oxazoline)s with hydroxyl endgroups were prepared as described in section 3.3.1. A solution of 6 grams of hydroxyl terminated poly(2-methyl-2-oxazoline) ($\langle M_n \rangle = 10,000$ g/mol) and 19.6 mL of ϵ -caprolactone in 72 mL of dry acetonitrile was heated under reflux in a three-neck flask equipped with a Dean-Stark apparatus and a overhead stir. Almost all of the acetonitrile was removed and the Dean-Stark apparatus was replaced by a condenser. 2000ppm of stannous octoate was added and the

temperature was maintained between 130-140°C until the desired conversion of monomer as judged by ^1H NMR.

3.4.4 Synthesis of Poly(alkyl vinyl ether-2-ethyl-2-oxazoline) Block Copolymers

A. Terminator method

To HI/hexanes solution in a round bottom flask at -20°C was added desired amount of butyl vinyl ether via syringes. The reaction mixture was stirred for 10 min., then ZnI_2 (1/50 eq. of HI) in ether was added. Once the monomer was depleted as judged by ^1H NMR, degassed aqueous K_2CO_3 (15 eq. of HI) solution was cannulaed into the reaction flask to terminate the living chains. The polymers were isolated by washing with saturated aqueous Na_2SO_3 solution twice and deionized water twice and drying over MgSO_4 , filtering, and evaporating the solvents using rot vap, and then vacuum. The endgroups of resultant aldehyde terminated poly(butyl vinyl ether)s were converted into hydroxyl endgroups by reduction using 1 mole eq. of sodium boronhydride (4 mole eq. of H^- per $\text{C}=\text{O}$) in ethanol (10%, wt./v) at room temperature for 1 h. The reduction was followed by FTIR. Presence of 3300 cm^{-1} (hydroxyl) peak and disappearance of 1723 cm^{-1} (aldehyde) peak indicates the completion of the reduction. The polymers were purified by pouring the reaction mixture to HCl/ice mixture slowly, extracting with diethyl ether, washing with saturated NaHCO_3 and then water, dried over MgSO_4 , filtering and evaporating solvents. The hydroxyl

endgroups were further converted into either tosylate or mesylate groups and then to initiate the polymerization of 2-alkyl-2-oxazolines.

B. Initiator method

To HI/hexanes solution at -40°C was added 1 equivalent of chloroethyl vinyl ether/hexanes solution. After about one hour of stirring at that temperature, butyl vinyl ether monomer was added, followed by the addition of cold toluene. In the case of methyl vinyl ether, a cold solution of monomer in toluene was added. Then zinc iodide in diethyl ether (1/50 moles per mole of HI) was added and the reaction temperature raised to -20°C for 1000g/mol PBVE, 2000g/mol PMVE, or -15°C for 10000g/mol PBVE, 5000g/mol PMVE, -10°C for 10000g/mol PMVE, and 0°C for 30000g/mol PBVE. Once the monomer was depleted as monitored by ^1H NMR, the reaction was terminated using 1.2 moles of LiBH_4 in THF relative to one mole of polymer, then deionized water was added to decompose residual LiBH_4 . Subsequently the polymer solution was washed with aqueous Na_2SO_3 and deionized water, dried over MgSO_4 , the solution was filtered and the solvents were evaporated to yield a colorless to light yellowish viscous to semisolid waxy materials.

To make poly(alkyl vinyl ether-2-ethyl-2-oxazoline) block copolymers, a mixture of functional poly(alkyl vinyl ether), sodium iodide (2 mole eq. NaI to 1 mole of chloroethyl vinyl ether), chlorobenzene and a small amount of NMP (1/10 to 1/6 v/v of

chlorobenzene) was heated to 110°C for ca. 8 to 10 h, then the desired amount of 2-ethyl-2-oxazoline was added. When the polymerization was completed as determined by ¹H NMR, the reaction was terminated with 1.2 equivalents of 0.5 N methanolic KOH. The copolymers were isolated by diluting with chloroform, washing with saturated aqueous solution of sodium thiosulfate once and deionized water, precipitating into hexanes and were dried in vacuum oven at 60°C to constant weights.

3.5 Poly(2-alkyl-2-oxazoline)s Containing Blends

Poly(2-ethyl-2-oxazoline), poly(2-methyl-2-oxazoline), as well as poly(butyl vinyl ether-g-2-methyl-2-oxazoline) were melt blended with poly(ε-caprolactam) (Nylon 6, AKZO America) and/or poly(propylene) (AMOCO) in various compositions in a Haake Buchler Rheomix Blender using high shear rotors. All polymers used in the blends were pre-dried in a vacuum oven at 80°C for at least 48 hours. Poly(2-ethyl-2-oxazoline) (30,000g/mol), and poly(2-methyl-2-oxazoline) (30,000g/mol) was blended with Nylon 6 at 240°C for 15 min with the rotor speed of 60 rpm. The blends of poly(propylene), nylon 6 and the blend emulsifier, poly(butyl vinyl ether-g-2-methyl-2-oxazoline) copolymers were prepared in two steps. First a master blend composed of poly(propylene) and poly(butyl vinyl ether-g-2-methyl-2-oxazoline) 90/10 wt./wt. was melt blended at 250°C for 10 minutes at a motor speed of 40 rpm. Then nylon 6 was melt blended with the master blend (at

composition of 70/30 and 90/10, wt./wt. of nylon 6 to master blend at 240°C for 10 minutes at 60 rpm.

3.6 Characterization

3.6.1 Multinuclear Magnetic Resonance Spectroscopy

¹H NMR. ¹H NMR measurements were performed on either a Varian Unity 400 spectrometer or a Bruker WP 270 spectrometer. The Varian Unity 400 spectrometer with a 5mm multinuclear probe was operated at 399.952 MHz with a sweep width of 5000 Hz, and a 22° pulse width of 4.1 μs. The Bruker WP 270 spectrometer was operated at 270.132 MHz with a sweep width of 3000 Hz and a 45° pulse width of 4 μs. A total of 16 transients were accumulated and were Fourier transformed with an acquisition time of 3.744 s each, with no line broadening.

¹³C NMR. ¹³C NMR measurements were conducted on a Varian Unity 400 MHz spectrometer with a 5mm multinuclear probe, operating at 100.577 MHz with a sweep width of 25000.0 Hz, and 90° pulse width of 12.3 μs. Inverse gated Waltz proton decoupling and a relaxation delay of 6 s were used to obtain quantitative spectra. At least 1200 transients were accumulated and Fourier transformed with a line broadening of 1.0 Hz.

¹³C Solid State NMR. ¹³C solid state NMR spectra was recorded on a Bruker MSL300 spectrometer, operating at 75.47 MHz using a 7 mm zirconium oxide rotor. The rotor was spun at the magic angle and at a rate of greater than 2000 Hz. For quantitative

analysis, "HPDEC" program was used which is an inverse gated decoupling program without cross polarization. The relaxation delay was at least 5 times the longest T_1 for the carbon of interest, 106 s. The sweep width was 29411.765, 90 degree pulse of 4.2 μ s, and acquisition time of 50 ms. At least 700 transients were collected and Fourier transformed with a line broadening of 20 Hz.

3.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

NICOLET MX-1 FTIR Spectrometer was used to monitor the hydrosilation reaction, reduction of aldehyde to hydroxyl groups, and to confirm the presence or absence of aldehyde functionality. The liquid samples were placed in between two salt plates and measured immediately.

3.6.3 Gel Permeation Chromatography

The apparent molecular weights and molecular weight distributions of the oligomers and the copolymers were analyzed using a Waters GPC instrument with Waters 490 and R401 detectors. The instrument was operated at a temperature of 30°C and a flow rate of 1 mL/minute. The columns were made of Ultrastyrigel with porosities of 500, 10^3 , 10^4 , 10^5 , and 10^6 Å in THF or 100, 500, and 10^3 Å in CHCl_3 and toluene. A UV detector at 218 nm for THF solvent and 254 nm for CHCl_3 solvent was used. Poly(butyl vinyl ether)s and poly(methyl vinyl ether)s using HI/ZnI_2 initiating system as well as the copolymers of these oligomers with poly(2-ethyl-2-oxazoline)

were analyzed in THF. Poly(butyl vinyl ether)s synthesized using AHS catalyst were analyzed in CHCl_3 . PDMS was analyzed using toluene as the solvent and differential refractive index detector. Apparent molecular weights and molecular weight distributions were calculated based on polystyrene standards. Absolute molecular weights and molecular weight distributions for poly(2-ethyl-2-oxazoline) homopolymers and poly(methyl vinyl ether) oligomers were determined using differential viscosity and refractive index dual detectors and universal calibration on 4 x (300 x 7.8 I.D.)mm steel columns filled with 10 μm Permagel.

3.6.4 Elemental Analysis

Elemental analysis was performed at the Spang Microanalytical Laboratory (Star Route 1, Box 142, Eagle Harbor, Michigan 49951). This analysis was obtained for poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers to verify the compositions. Since micellularization of these copolymers in solvents used to obtain NMR spectra, false compositions have been derived from NMR spectra, which will be discussed in detail in the Results and Discussion section.

3.6.5 Titration

The hydroxy or amino end groups of poly(2-ethyl-2-oxazoline)s were titrated to determine the quantitative functionalization by termination. The titration of hydroxy groups

was based on a modified ASTM D 2849-69 (Method B)²⁰¹, which used imidazole to catalyze the esterification reactions between phthalic anhydride and hydroxy-terminated polymers. Phenolphthalein was used as an indicator. The products of the reaction and blank samples were titrated with 0.1N methanolic KOH. The amino groups were titrated with 0.1N hydrochloric acid (Fisher, Certified, volumetric standard solution) using a Accumet pH Meter Model 825 MP.

3.6.6 Intrinsic Viscosity

Viscosity measurements were made using a Cannon-Ubbelohde size 50 viscometer in THF at 30°C.

3.6.7 Vapor Phase Osmometry

Vapor phase osmometry experiments were conducted on a Wescan model 233 vapor phase osmometer in toluene at ca. 60°C using a multistandard calibration.

3.6.8 Differential Scanning Calorimetry (DSC)

A dual cell DuPont 912 DSC interfaced with a DuPont Thermal Analyzer 2100 or a Perkin Elmer DSC 7 were used for the DSC measurements. The heating program was normally composed of heating from room temperature to ca. 40°C above expected T_m or highest T_g in the sample at a heating rate of 10 degree/min. Then the sample was either slow cooled at ca. 2 or 10 degree/min when a T_m was the interest or quenched when a T_g was the interest,

followed by second heat at 10 degree/min. The Tg at second heat was reported. Tm at first heat or second was reported depending on the system.

3.6.9 Thermal Gravimetric Analysis (TGA)

As a safety measure, TGA was obtained for each sample used for DSC measurements to ensure the dryness of samples and conclusive determination of their Tg's. The TGA was performed on either a DuPont 951 TGA interfaced to the same data station as DSC or a Perkin Elmer TGA 7. The samples were normally heated from 30°C to 800°C at a heating rate of 10 degree/min. in nitrogen or in air.

3.6.10 Dynamic Contact Angle Analyzer (DCAA)

A CAHN DCA-322 dynamic contact angle analyzer was used to measure the surface tension of aqueous solutions of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers of various concentrations (0.0019% to 5%) allowing the critical micelle concentration of these copolymers in water to be determined. The instrument operates based on the Wilhelmy plate method. The plate was a ferro-type plate with a dimension of 0.46mm x 10.19mm x 25.55mm and was burned prior to the measurements in a Bunsen burner to clean the surface and was handled with tweezers to avoid contamination. The speed of the stage displacement was 94 $\mu\text{m}/\text{sec}$. The measurements were conducted at room temperature.

3.6.11 X-ray Photoelectron Spectroscopy (XPS)

A KRATOS XSAM 800 X-ray photoelectron spectrometer was used to investigate the PDMS enrichment at the surface of films made from poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers. The films were prepared by casting 5% (wt./v) chloroform solutions of the copolymers onto ferro-type metal plates which were covered with glass petri dishes to evaporate the solvent slowly. The films were then dried in vacuum oven at room temperature for ca. 48 h. The instrument uses a Mg Ka X-ray source operated at 13kV and 20 mA and the analyzer was in the fixed retardation ratio (FRR) mode. Angular dependent measurements were performed by rotating the sample probe, thereby changing the angle between the sample surface plane and the analyzer.

3.6.12 Scanning Electron Microscopy (SEM)

A Philips EM420 STEM operated in the SEM mode was used to study the topography of the fracture surfaces of various blends. Samples were frozen in liquid nitrogen and then fractured. A razor blade was used to cut the samples to ca. 1 mm thick. Samples were mounted on a strip of copper with silver paint and sputter-coated with gold before analysis to minimize charging effects.

Chapter IV

Results and Discussion

4.1 Synthesis of Poly(2-alkyl-2-oxazoline)s

2-alkyl-2-oxazolines can be polymerized by using a number of cationic initiators, and the kinetics and mechanisms of polymerization using some of the initiators have been extensively studied (Chapter II). The questions, however, as to whether or not the systems can be designed to be "living" and the identification of reaction conditions under which these polymerizations are "living" have not been clearly defined. If they are not living by the strict definition as discussed in Chapter I, the question becomes whether or not the molecular weight of these systems can be controlled. This important aspect must be investigated in order to synthesize poly(2-alkyl-2-oxazoline) homo and copolymers with controlled structure to fulfill designed applications. These questions and related kinetic studies are the focus of this section.

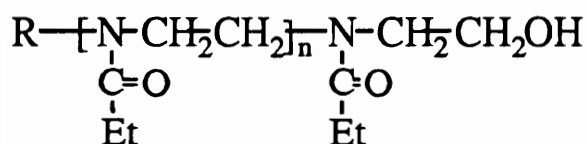
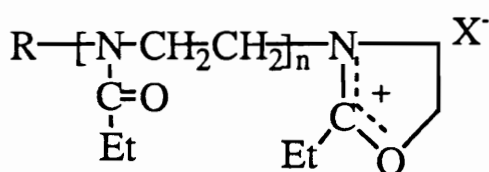
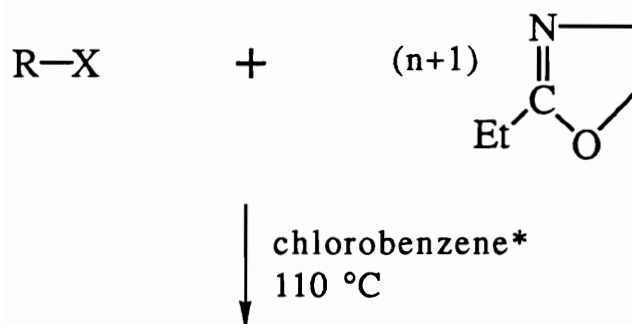
4.1.1 Effects of Initiator Structure on Control of Molecular Weight and Molecular Weight Distribution

In comparison to its methyl counterpart, the polymerization mechanism of 2-ethyl-2-oxazoline has been less studied. In this research, polymerization of this monomer in chlorobenzene was investigated using several initiators. The initiators were selected based on two factors: a) their abilities to initiate the polymerization

of 2-ethyl-2-oxazoline and b) their structural similarity to those which can be incorporated into functional oligomers. The initiator systems studied included butyl mesylate, butyl mesylate in combination with sodium iodide, 1-iodobutane, 1-chlorobutane in combination with sodium iodide, 2-chloroethyl ethyl ether in combination with sodium iodide, and benzyl chloride in combination with sodium iodide. Using these initiators, poly(2-ethyl-2-oxazoline) (PEOX) oligomers with a theoretical molecular weight of 1000 g/mol were synthesized under similar conditions (scheme 4.1.1), and terminated with KOH/MeOH. In order to avoid any fractionation of these materials prior to molecular weight analysis, the normal recovery procedure described for such materials was not followed. Instead, the solvent was simply removed under vacuum. GPC traces for these polymers in THF are shown in Figure 4.1.1. The most significant feature of these GPC chromatograms is the relative breadth of the curves using different initiators. Butyl mesylate initiated polymers exhibited the broadest molecular weight distributions, including some bimodal features. The narrowest curve was generated from polymers prepared using the benzyl chloride/NaI initiator. In addition, the position of the peaks differed as a function of the initiator. Since polystyrene standards were used for the molecular weight calculations on these oligomers, the numbers obtained are not absolute. However, it is assumed that they reflect the relative order in molecular weight of PEOX using the different initiators. As shown in Table 4.1.1, poly(2-ethyl-2-

Scheme 4.1.1

Synthesis of Poly(2-ethyl-2-oxazoline)



R = butyl, ethyl ethyl ether, benzyl

X = Tos⁻, I⁻, Cl⁻/NaI

* In the case of ClEEE/NaI initiated system,
1/3 (V/V) of NMP/chlorobenzene was used.

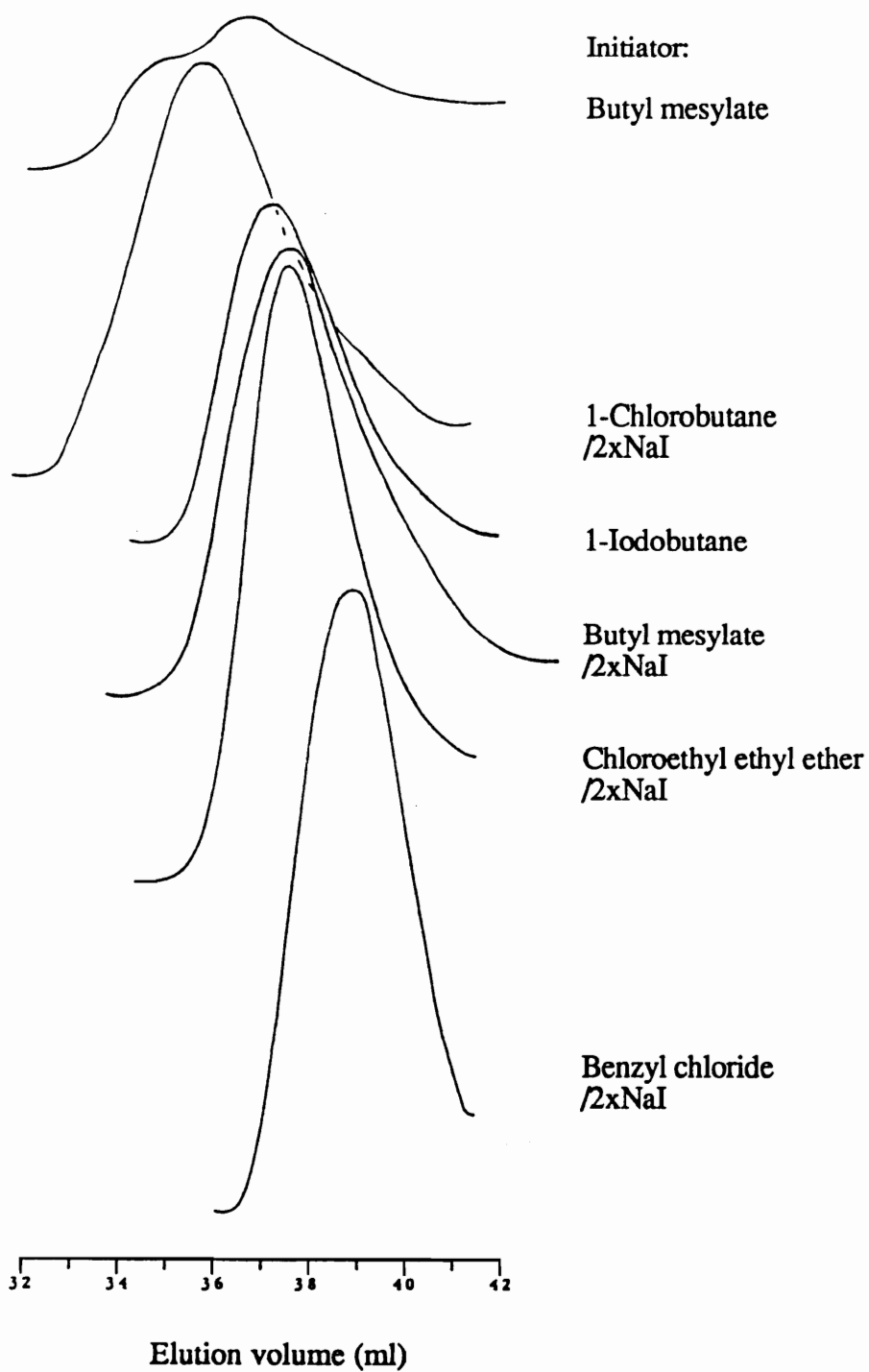


Figure 4.1.1 Gel Permeation Chromatograms of poly(2-ethyl-2-oxazoline) oligomers with a theoretical M_n of 1000 g/mol prepared using different initiators

Table 4.1.1 Molecular weights* of Poly(2-ethyl-2-oxazoline)s via Different Initiators

Theoretical (g/mol)	1-Iodobutane (g/mol)	1-Clbutane /NaI (g/mol)	MeSO ₄ Bu (g/mol)	MeSO ₄ Bu /NaI (g/mol)	Benzyl-Cl /NaI (g/mol)	CIEEE /NaI (g/mol)
1000	2000	2500	2600	1000	900	1600
2000	3200	3600	4700	1900		
5000	5100	6200	9200			

* <Mn> based on GPC using polystyrene standards.

oxazoline) initiated by butyl mesylate showed the highest M_n , followed by 1-chlorobutane/NaI, 1-iodobutane, 2-chloroethyl ethyl ether/NaI, butyl mesylate/NaI, and benzyl chloride/NaI, respectively. Since the molar feed ratio of monomer to initiator is the same in all cases, the difference in apparent molecular weight and molecular weight distribution among these initiators must be due to one or more of the following factors: (1) slow initiation relative to propagation so that propagating species are generated as the polymerization proceeds, and initiator still remains after all the monomer has been consumed, resulting in broader molecular weight and higher molecular weight than theoretical; (2) chain transfer to monomer leading to lower molecular weights and broader molecular weight distributions than theoretical; (3) slow equilibrium between two types of propagating species relative to propagation will broaden molecular weight distribution without affecting number average molecular weight; (4) termination will affect molecular weight distribution but not number average molecular weight. Deactivation of initiator by adventitious impurities would result in higher than expected molecular weight. Since benzyl chloride/NaI initiated polymers exhibit narrow molecular weight distributions, it was reasoned that this system must be relatively free from any of the above-mentioned problems. Sequential monomer addition experiments confirmed this conclusion. As for the other initiating systems, the above-mentioned problems may exist to variable extents depending on the structure of the initiator. Given these

restrictions, it was of interest to determine whether molecular weight could be varied systematically by changing the feed molar ratio of monomer to initiator.

In all cases, when lower concentrations of initiators were used, higher molecular weights were obtained, even for initiators producing rather broad molecular weight distributions, such as 1-chlorobutane/NaI and butyl mesylate (Table 4.1.1). However, the molecular weight obtained using identical concentrations of various initiators was different, indicating that precision in controlling molecular weight varied among these initiators.

4.1.2 Living Characteristics of the Polymerization of 2-Ethyl-2-Oxazoline

The experiments described above demonstrate that poly(2-ethyl-2-oxazoline)s initiated with benzyl chloride/NaI, or with 2-chloroethyl ethyl ether/NaI have rather narrow molecular weight distributions, implying these polymerization systems might be living. In addition these two initiators have similar chemical functional groups to those which can be formed as terminal groups on a variety of oligomeric structures, such as on poly(dimethylsiloxane) and poly(alkyl vinyl ether)s (as will be discussed in the copolymer sections). Therefore it was of importance to investigate the living nature of these systems. One indication of the living nature of these systems would be to demonstrate a linear relationship between number average molecular weight and the extent of conversion.

Additional evidence would be a linear increase in number average molecular weight upon sequential monomer addition following monomer depletion. Thus, a molecular weight-conversion experiment was conducted using benzyl iodide as the initiator, with the final targeted molecular weight being 40,000g/mol. Samples were removed at specified time intervals and their conversion was determined by ^1H NMR. Aliquots of these samples were terminated with KOH/MeOH and dried at room temperature under vacuum as thin films. Their absolute number average molecular weights were determined by GPC using a universal calibration method with on-line dual refractive index and viscosity detectors. However, the molecular weight measurements were not as straightforward as expected. GPC traces in THF as the GPC solvent all exhibited an unusual sharp cut off on the high molecular weight side. Moreover, the number average molecular weights calculated from these chromatograms did not correlate even closely with the expected values based on NMR conversion data. Thus a series of experiments using different solvent compositions of THF/MeOH as well as different sample concentrations were conducted in an effort to obtain realistic data. The THF/MeOH 75/15 (V/V) solvent combination was found to yield such results. Similar results were also obtained using a THF/isopropanol mixture. The polymer conversion, theoretical molecular weight calculated based on the feed ratio of monomer to initiator and conversion, as well as the measured number average molecular weight, and polydispersity are summarized in Table 4.1.2.

Table 4.1.2 Molecular Weights of Poly(2-ethyl-2-oxazoline)s Initiated by Benzyl Iodide

Conversion (%)	$\langle M_n \rangle$ theoretical (g/mol)	$\langle M_n \rangle^*$ measured (g/mol)	$\langle M_w \rangle / \langle M_n \rangle^*$ measured
22.6	9040	12700	1.33
54.2	21680	26100	1.26
66.3	26520	29300	1.32
75.1	30040	32600	1.3
84.7	33880	36800	1.35
91.4	36560	38500	1.37
100	40000	42700	1.52

* by GPC using universal calibration method

Based on these data a plot of molecular weight vs. conversion was constructed as shown in Figure 4.1.2. A straight line can be drawn through these data points, implying the molecular weight increased linearly with conversion. This indicates that polymerization of 2-ethyl-2-oxazoline using benzyl iodide as initiator in chlorobenzene is "living" under the reaction conditions specified. However the molecular weight distributions of these oligomers, with polydispersities of ca. 1.3 (Table 4.1.2), are not as narrow as that of a strict "living polymer", namely a polydispersity of less than 1.1. A number of factors may contribute to the broadening of molecular weight distribution, some of which will be discussed later in the kinetics section.

The living nature of the polymerization of 2-ethyl-2-oxazoline using the benzyl chloride/NaI initiating system was further probed using a sequential monomer addition experiment. Additional monomer/solvent was added after the initial feed of 2-ethyl-2-oxazoline was polymerized to 100 % conversion. The reaction was allowed to continue until the added monomer was depleted. After the same treatment as described above, both oligomers were analyzed by GPC using THF as the solvent. Peak b (Figure 4.1.3) corresponding to the oligomer at complete conversion of the second monomer feed obviously shifted toward higher molecular weight without tailing relative to peak a. Therefore, within the detection limits of GPC, the growing chains formed during the first

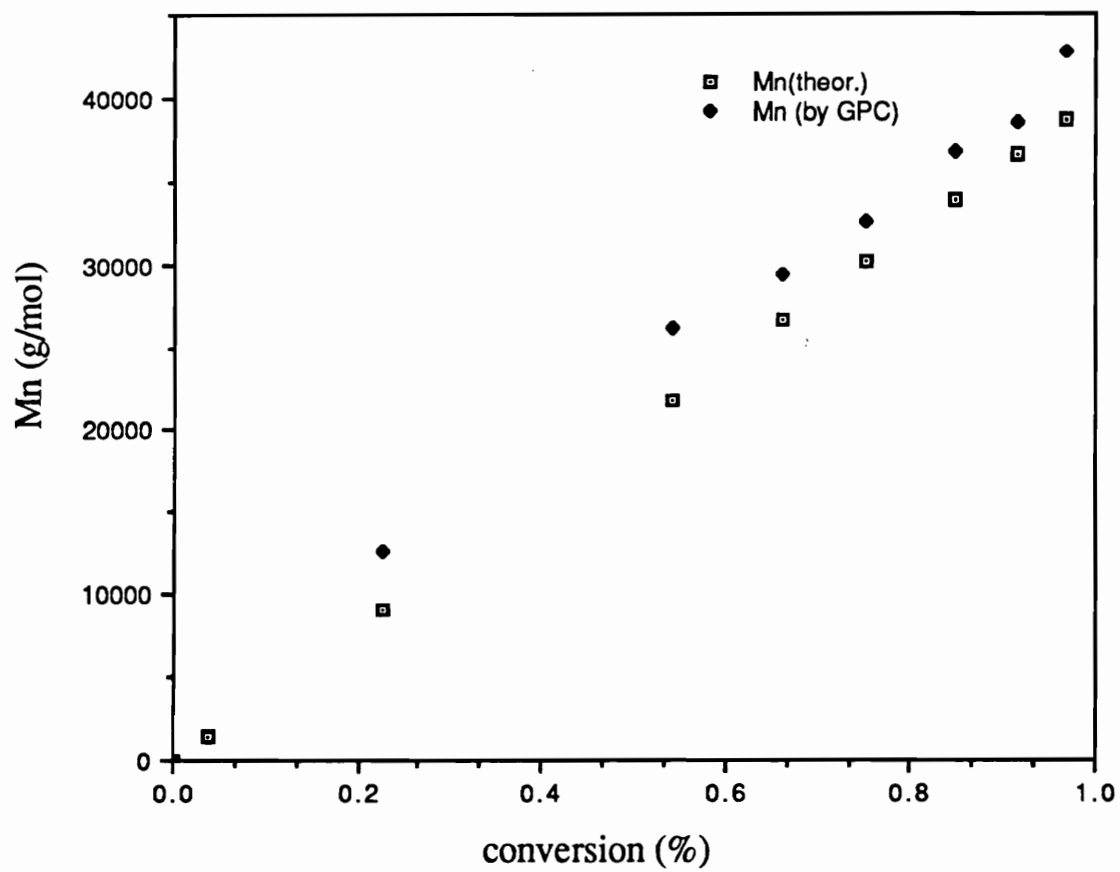


Figure 4.1.2 Mn-Conversion Plot of Poly(2-ethyl-2-oxazoline) with the Final Targeted Mn of 40,000g/mol

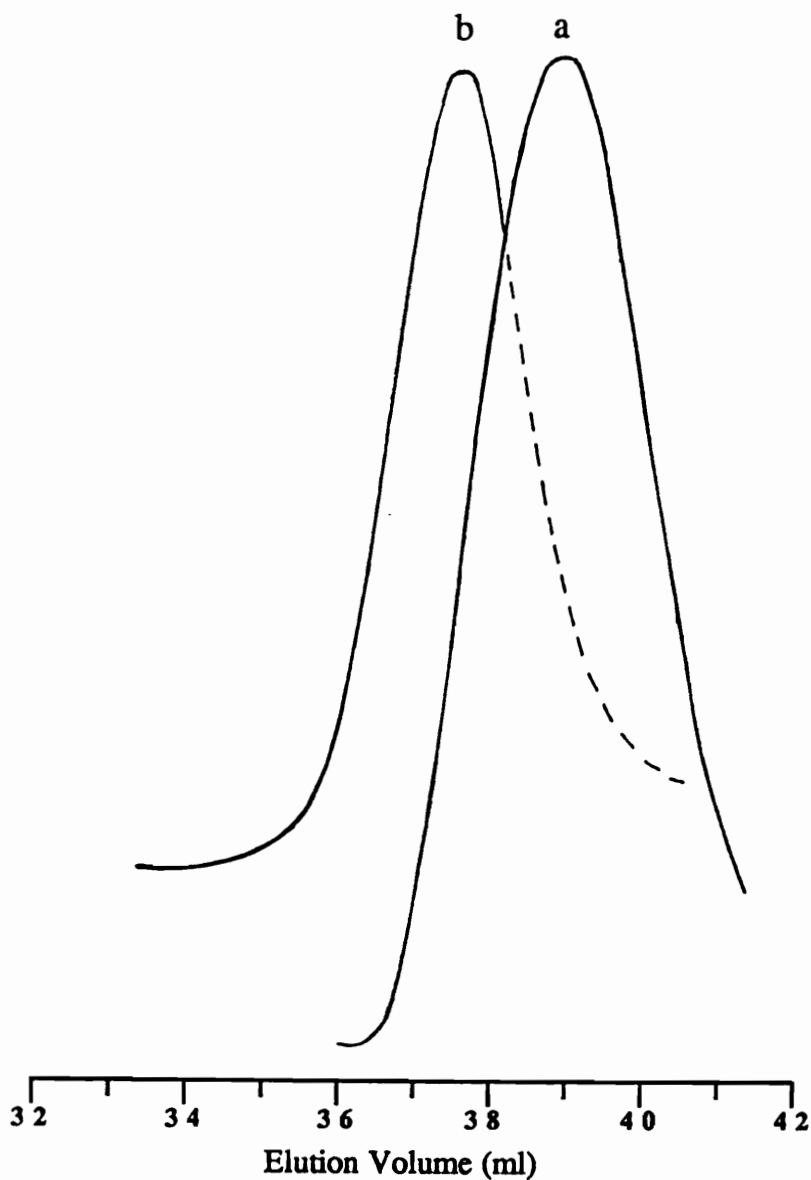


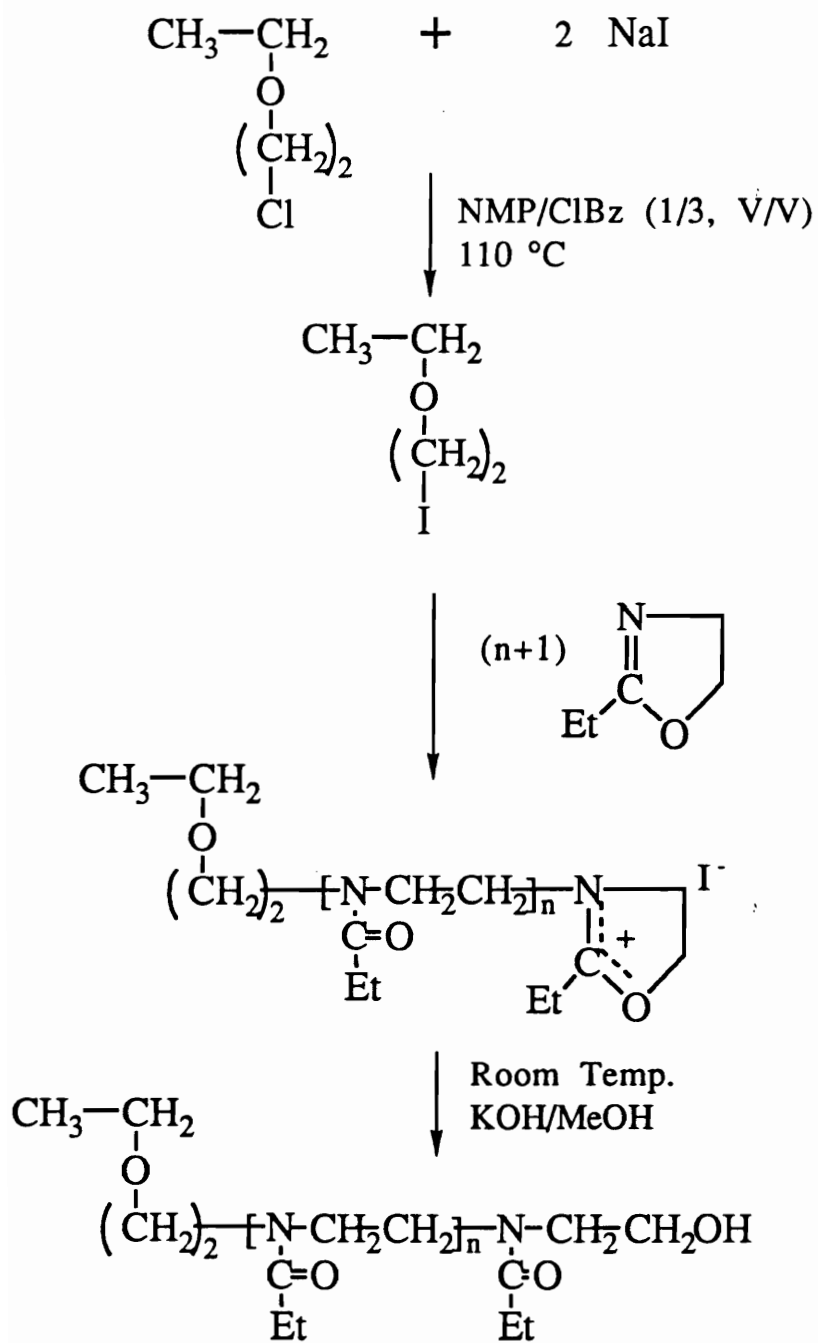
Figure 4.1.3. GPC of PEOX by sequential monomer addition using BzCl/2xNaI initiating system

- a. at 100% conversion of the first monomer feed with theoretical $\langle M_n \rangle$ of 1000g/mol
- b. at complete conversion of the second monomer feed with theoretical $\langle M_n \rangle$ of 2000 g/mol

polymerization process must have remained "alive" and resumed propagation once additional monomer was added.

Similarly, using 2-chloroethyl ethyl ether/NaI as the initiating system, another sequential monomer addition experiment was conducted. In this case (Scheme 4.1.2), 2-ethyl-2-oxazoline monomer was added after 2-chloroethyl ethyl ether was completely converted into the corresponding iodo compound (which will be discussed in more detail in the following section). Sample removal and monomer addition were repeated twice. Theoretical molecular weights were 1000 g/mol at 100% conversion of the first monomer feed, 5000 g/mol at complete conversion of the second monomer feed, and 10,000 g/mol at complete conversion of the third monomer feed, respectively. The molecular weights and molecular weight distributions were again characterized by GPC (Figure 4.1.4). The peaks corresponding to 500% and to 1000% conversion shifted completely to higher molecular weight after each monomer addition. Both the 1K and 5K peaks were rather symmetrical except for a small tailing on the low molecular weight side. By contrast, the 10K peak exhibited a very obvious shoulder on the low molecular weight side, indicating the deactivation of some chains after the second monomer addition. Among many possible reasons, termination by adventitious impurities is very likely and is not related to the polymerization mechanism. In spite of this, the 2-chloroethyl ethyl ether/NaI initiating system did generate long lived poly(2-ethyl-2-oxazoline) chains under the given polymerization conditions.

Scheme 4.1.2
Synthesis of Poly(2-ethyl-2-oxazoline)



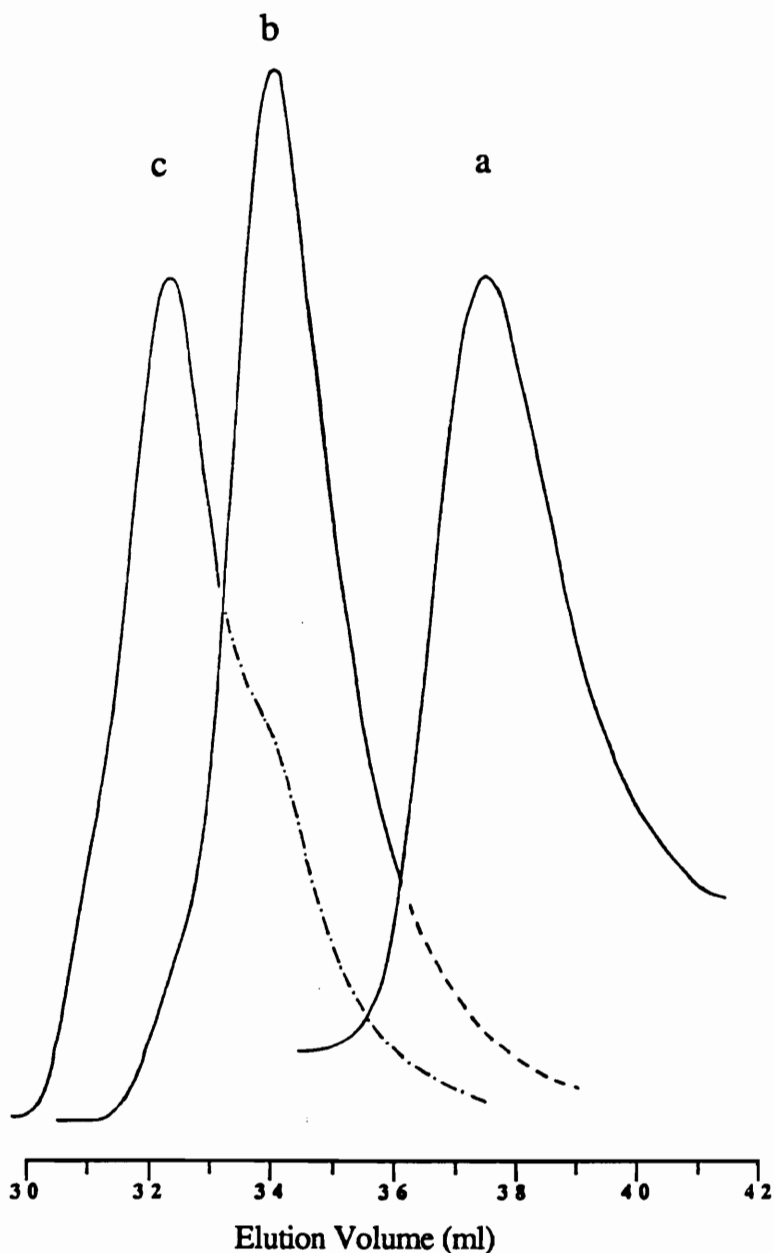


Figure 4.1.4. GPC of PEOX by sequential monomer addition using 2-CIEEE/2xNaI initiating system

- a. at 100% conversion with theoretical $\langle M_n \rangle$ of 1000g/mol
- b. at complete conversion of the second monomer feed with theoretical $\langle M_n \rangle$ of 5000 g/mol
- c. at complete conversion of the third monomer feed with theoretical $\langle M_n \rangle$ of 10,000 g/mol

4.1.3 Kinetics and Mechanisms

As discussed in section 4.1.1, various initiators yielded poly(2-ethyl-2-oxazoline)s with different molecular weight distributions. For example, the molecular weight distribution of polymers initiated by 1-chlorobutane/NaI is much broader than that initiated by benzyl chloride/NaI, even though both systems had the same counteranion. In addition, the molecular weight distributions of "living" poly(2-ethyl-2-oxazoline) are broader than other typical living polymers (section 4.1.2). A mechanistic study was thus undertaken to determine some of the possible causes of these phenomena. In the literature, ^1H NMR has been widely used to study the kinetics of the polymerization of 2-methyl-2-oxazoline and unsubstituted 2-oxazoline (Chapter II). As NMR instrumentation improves, high resolution and accuracy as well as on-line detection are correspondingly improved. In this study, a 400 MHz ^1H NMR with a variable temperature probe was used and NMR spectra were collected as the polymerization proceeded. The general procedure included collecting NMR spectra as the polymerization proceeded, recording the intensity changes of the peaks of interest from the NMR spectra as a function of time, and analyzing these data according to kinetic equations to obtain rate constants. In order to follow the concentration change of initiator, a rather low molar ratio of monomer to initiator was used in most cases, with a typical ratio of ca. 5.

A. 2-Ethyl-2-Oxazoline

Kinetics of the polymerization of 2-ethyl-2-oxazoline have not been previously reported. Compared to its methyl counterpart, a less polar solvent such as chlorobenzene can be used for the polymerization. Since ionic polymerizations are quite sensitive to solvent effects, it was reasoned that this may cause some change in the polymerization mechanism. Since it has been established in section 4.1.2 that the polymerization of 2-ethyl-2-oxazoline in chlorobenzene using benzyl iodide as the initiator is living, the kinetics of this system were investigated first. To probe the effects of initiator structure, the kinetics using 1-iodobutane as initiator were also studied.

Benzyl iodide and 1-iodobutane as initiators at 80°C

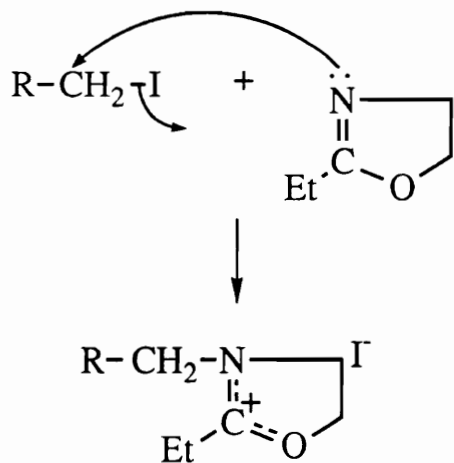
The kinetic studies using benzyl iodide and 1-iodobutane as initiators were first carried out at 80°C in order to obtain accurate data on the conversion of initiator. In previous studies²⁰, the propagating species were found to be oxazolinium ions in the polymerization of 2-methyl-2-oxazoline in CNCD₃ using methyl iodide as the initiator. The indication was that the peaks between δ 4.6 and 5.1ppm in the ¹H NMR spectrum were due to the methylene protons in the 5-position of the oxazolinium ion²¹. An analogous mechanism is assumed in this work to aid in peak assignment for the polymerization of 2-ethyl-2-oxazoline using benzyl iodide and 1-iodobutane as initiators as shown in scheme 4.1.3. The initiation step

involves nucleophilic attack of the nitrogen atom in the oxazoline ring on the initiator, expelling iodide to form the oxazolinium ion with iodide as the counteranion. In the propagation step(s), nucleophilic attack of the monomer on the carbon atom at the 5-position of the newly-formed oxazolinium ion, results in oxygen-carbon bond cleavage and isomerization of the oxazolinium ring to the corresponding chain form. In the ^1H NMR spectrum, the region of interest is between $\delta 0.5\text{ppm}$ to $\delta 5.0\text{ppm}$.

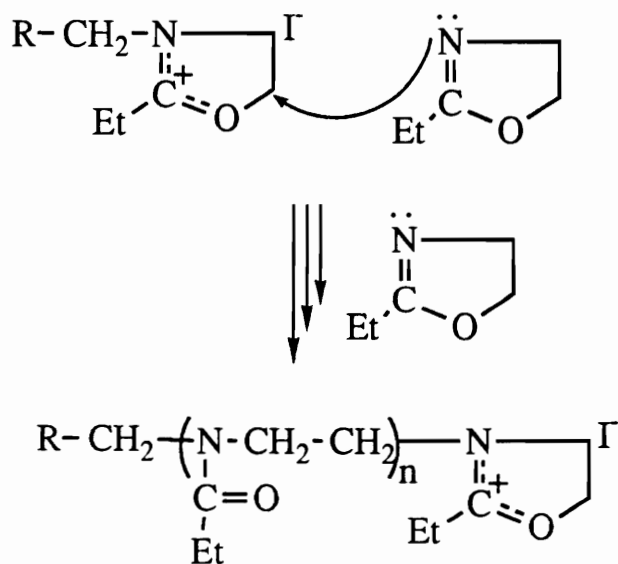
Shown in Figure 4.1.5 is a set of ^1H NMR spectra following the polymerization process when benzyl iodide is used as the initiator. The peaks corresponding to the monomer (Figure 4.1.5 a) are $\delta 1.1$ due to the methyl of the pendent substituents ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NCH}_2\text{CH}_2(\text{O})$), $\delta 2.2$ due to the methylene of the pendent substituents ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NCH}_2\text{CH}_2(\text{O})$), $\delta 3.6\text{ppm}$ due to the methylene in the ring ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NCH}_2\text{CH}_2(\text{O})$), and $\delta 3.95\text{ppm}$ due to the second methylene in the ring ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NCH}_2\text{CH}_2(\text{O})$). These peaks shift and/or broaden once the monomer polymerizes. The peak at $\delta 3.95$ did not overlap with any other peaks during the polymerization, thus its intensity was used to calculate the unreacted monomer concentration. The peak at $\delta 1.1$ only broadened in the polymerization and thus was used as the internal reference. The peak corresponding to the initiator in this region appears at $\delta 4.3$ due to the benzyl methylene ($\text{C}_6\text{H}_5\text{CH}_2\text{I}$). Once the reaction mixture was heated, several new peaks appeared (Figure 4.1.5 b), including $\delta 3.1\text{ppm}$, $\delta 3.55\text{ppm}$, and $\delta 4.45\text{ppm}$. The peak at $\delta 4.45$ is assigned to

Scheme 4.1.3 Preliminary Polymerization Mechanism
of 2-ethyl-2-oxazoline


Initiation



Propagation



$R = CH_3CH_2CH_2$ for 1-iodobutane

$R =$  for benzyl iodide

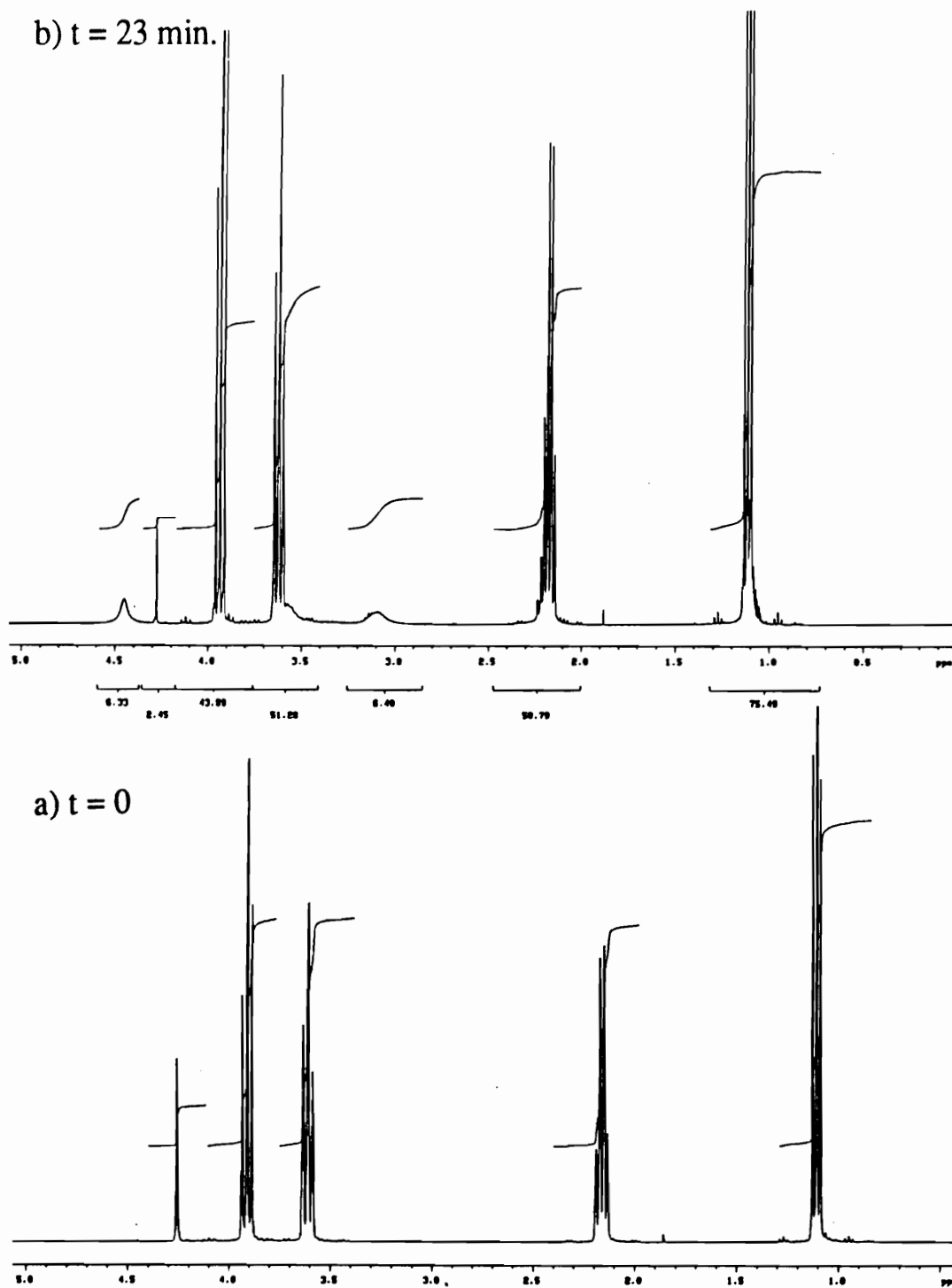
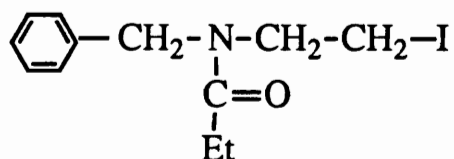


Figure 4.1.5 ^1H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by benzyl iodide, a) $t = 0$; b) $t = 23$ min.

the benzyl methylene of the initiator-monomer reaction product. The peak at $\delta 3.55$ overlapped with that at $\delta 3.6$ (one methylene in the monomer ring). The integration of this peak ($\delta 3.55$) was obtained by subtracting the area under the peak at $\delta 3.95$ from the total area of the peaks at $\delta 3.55$ and $\delta 3.6$. This integration was found to be slightly larger than that of peak at $\delta 4.45$. The difference is less than the amount for one proton. In addition, the area under the peak at $\delta 3.1$ was the same as that of the peak at $\delta 4.45$. Therefore the peaks at $\delta 3.1$ and $\delta 3.55$ must be due to two methylene groups and these two methylene groups must be from the oxazoline portion of the initiation product. However, it is interesting to note that the chemical shifts of these methylene groups are too far upfield compared with the expected chemical shifts ($\delta 4.8\text{ppm}$) due to methylene groups in an oxazolinium ion of the closed ring form as shown in scheme 4.1.3. The peak at $\delta 3.1$ is much more likely to be due to a methylene connected to an iodide. For example, the methylene protons next to the iodide in 1-iodobutane has a chemical shift of 3.2 ppm in CDCl_3 . Also, in view of the appearance of peaks at lower field later in the polymerization, it is concluded that the initiation product is in the opened ring, i.e. a chain form, as follows:



The initiator peak at $\delta 4.3$ is distinguished from the others, thus the disappearance of initiator as a function of time can be determined by monitoring this peak in the NMR spectra. As the reaction proceeded, small peaks around $\delta 5.0$ started to appear when almost all the benzyl iodide had reacted (as evidenced by the disappearance of peak $\delta 4.3$) (Figure 4.1.5 c). At this point there were about 2.3 polymerized repeat monomer units per initiator. Thus some propagation had taken place. At higher conversions, additional peaks at $\delta 2.9$, $\delta 4.15$ and $\delta 4.9$ become more evident and the peak at $\delta 4.45$ splits into two peaks (Figure 4.1.5 d). As expected, the peaks at $\delta 4.15$ and $\delta 4.9$ were due to the methylene protons in the ring of oxazolinium ion. The peak at $\delta 2.9$ can be assigned to the pendent methylene of the oxazolinium ion. Splitting of peak $\delta 4.45$ is probably due to the stereochemistry of poly(2-ethyl-2-oxazoline). Since propagation progresses both before and during the appearance of the oxazolinium signals, it is concluded that two types of propagating species must function in these reactions. At earlier stages in the polymerization, the dominant propagating species is covalently bonded, while later in the process the propagating species are comprised of more of the ionic form. Since the reaction rate of a monomer with a covalently bonded species should be slower than that of the same monomer with the ionic species, the overall rate of propagation should be slower in the earlier stages as compared to the later stage. The plot of $\ln([M]/[M]_0)$ vs. time displays this trend (Figure 4.1.6). The convex curve indicates acceleration of monomer

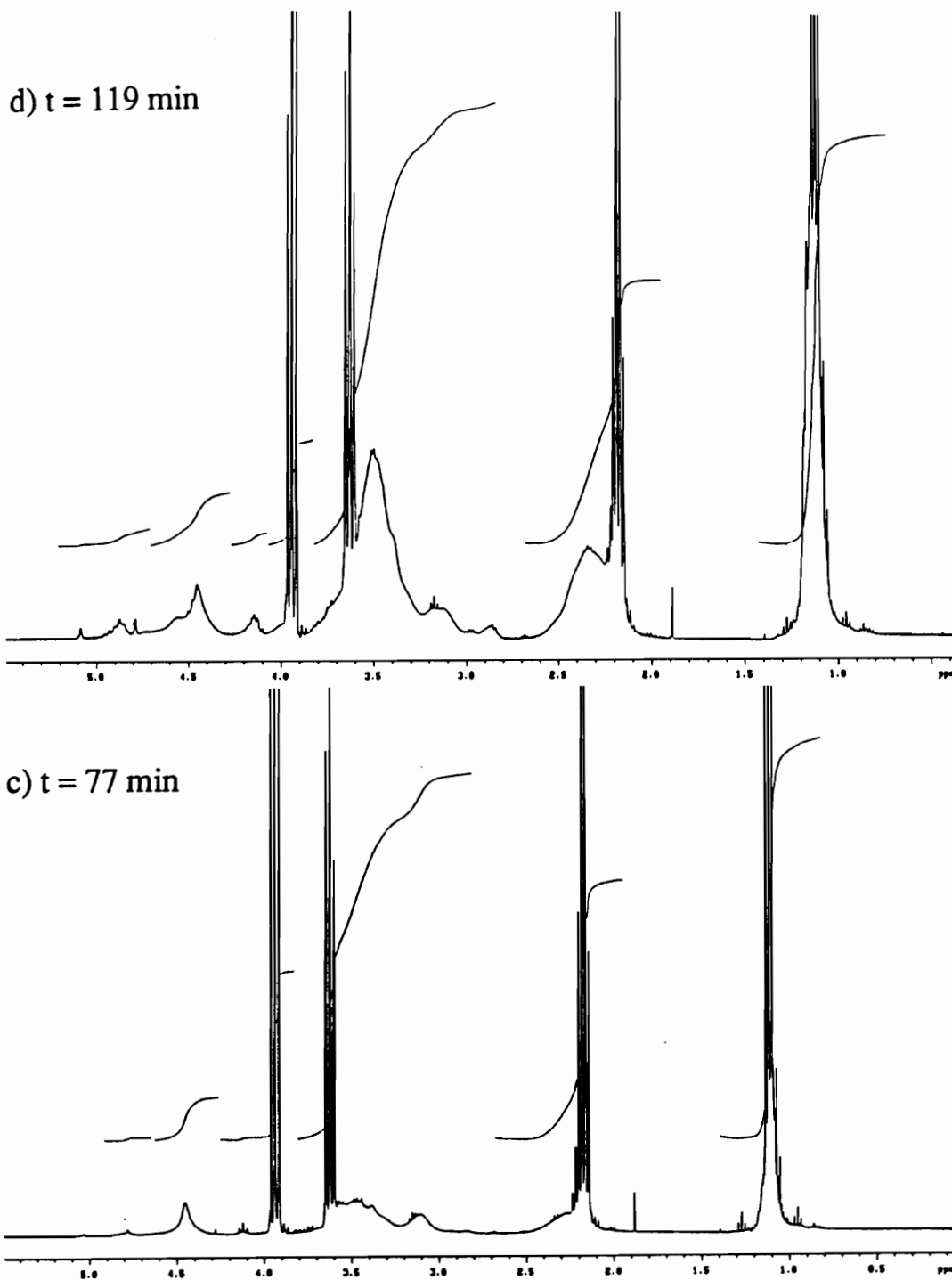


Figure 4.1.5 ^1H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by benzyl iodide, c) $t = 77$ min.; d) $t = 119$ min.

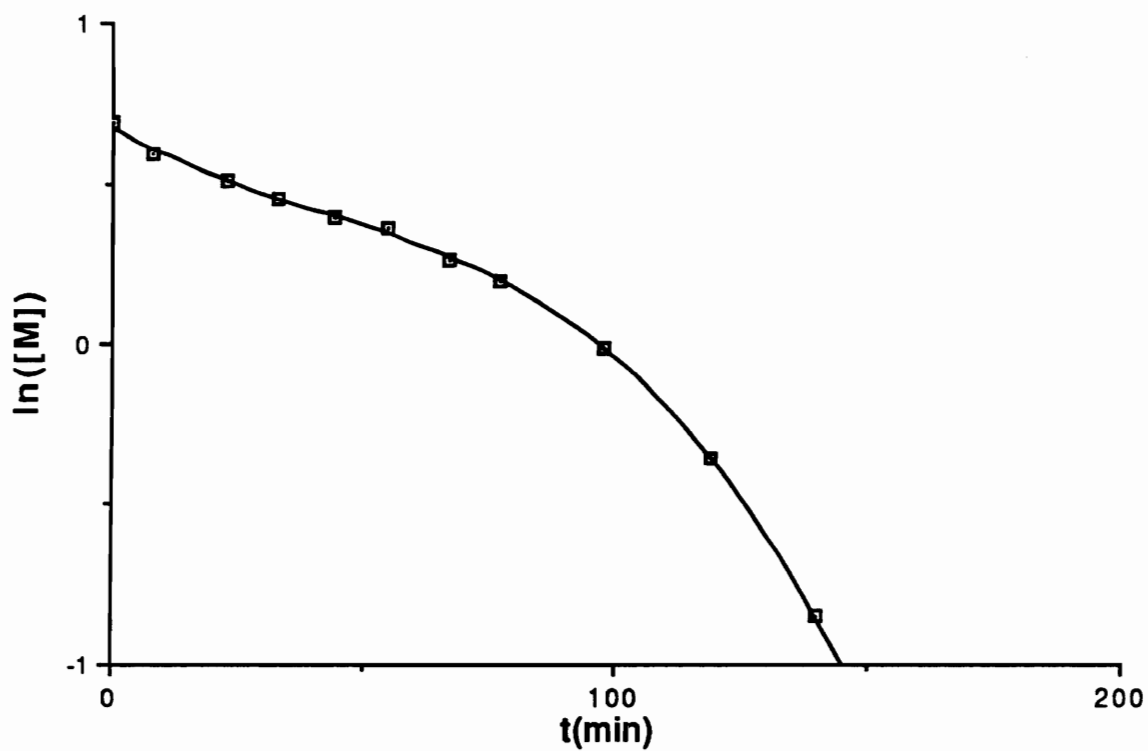


Figure 4.1.6 $\ln[M]$ vs. time plot for polymerization of 2-ethyl-2-oxazoline initiated by benzyl iodide at 80 °C

consumption as time increases. The slight concavity at the beginning of the curve is probably due to a faster reaction between the benzyl iodide initiator and the monomer than that between the initiation product and the monomer. This is reasonable since benzyl iodide should be more reactive than an unactivated alkyl iodide. To quantitatively account for the reaction rate, initiation rate constants and propagation rate constants were derived from data on the initiator and monomer concentration as a function of time. According to scheme 4.1.4, propagation is depicted using both the covalently bonded species as well as the ionic species as active centers. The objective in this simple treatment is to cover both reaction rates with one overall propagation rate constant. The second approach used is to treat the two propagation rates differently by assuming the rate of addition of the second monomer unit to the initiation product is different from the rate of adding the third, fourth, etc. This actually assumes that after addition of the second monomer, the propagation species become ionic. According to the discussion on the kinetics of 2-methyl-2-oxazoline polymerization in Chapter II, only two propagation rate constants could be defined and rationalized. Furthermore complicated equations prevent further breakdown of the constants.

In terms of the overall propagation rate, according to Saegusa et al.^{19,20}, the following equations should be considered:

Rate of Initiation:

$$- d[I]/dt = k_i [I] [M] \quad (4-1)$$

Rate of Monomer Depletion:

$$-d[M]/dt = k_i [I] [M] + k_p [P^*] [M] \quad (4-2)$$

where [I] and [M] are instantaneous initiator and monomer concentrations, respectively, and [P*] is the concentration of propagating species. Since the polymerization is living, $[P^*] = [I]_0 - [I]$ can be substituted into equation (4-2), then the equations can be integrated and rearranged to give:

$$\ln([I]_0/[I]) = k_i \int_0^t [M] dt \quad (4-3)$$

$$\frac{\ln([M]_0/[M])}{\int_0^t [I] dt} = (k_i - k_p) + k_p \frac{[I]_0 t}{\int_0^t [I] dt} \quad (4-4)$$

From eq.(4-3), the slope of the plot of $\ln([I]_0/[I])$ vs. integration of [M] over time gives k_i . From eq.(4-4), the slope of a plot of the left hand side vs. the second term on right hand side will be k_p . The plot according to eq.(4-3) is shown in Figure 4.1.7. Linear curve fitting yielded the slope (k_i) of 5.43×10^{-4} L/mol·s. However, the plot according to eq.(4-4) did not give a straight line. It seems that two straight lines could be drawn with two different slopes (Figure 4.1.8).

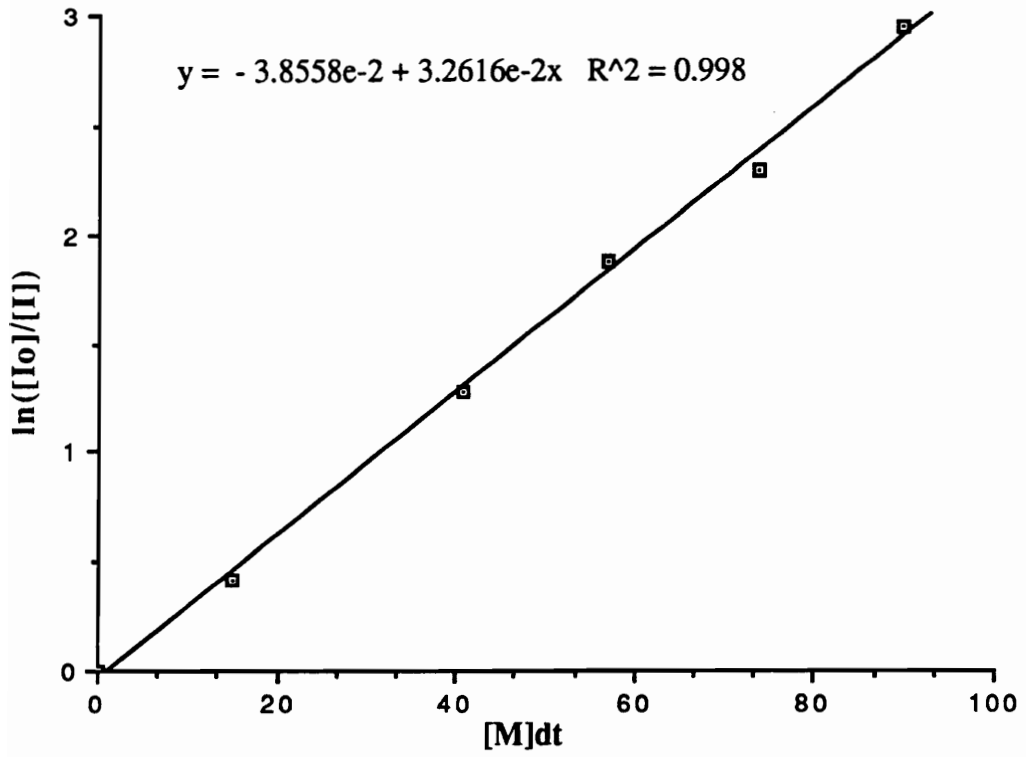


Figure 4.1.7 Determination of k_i According to Eq.4-3

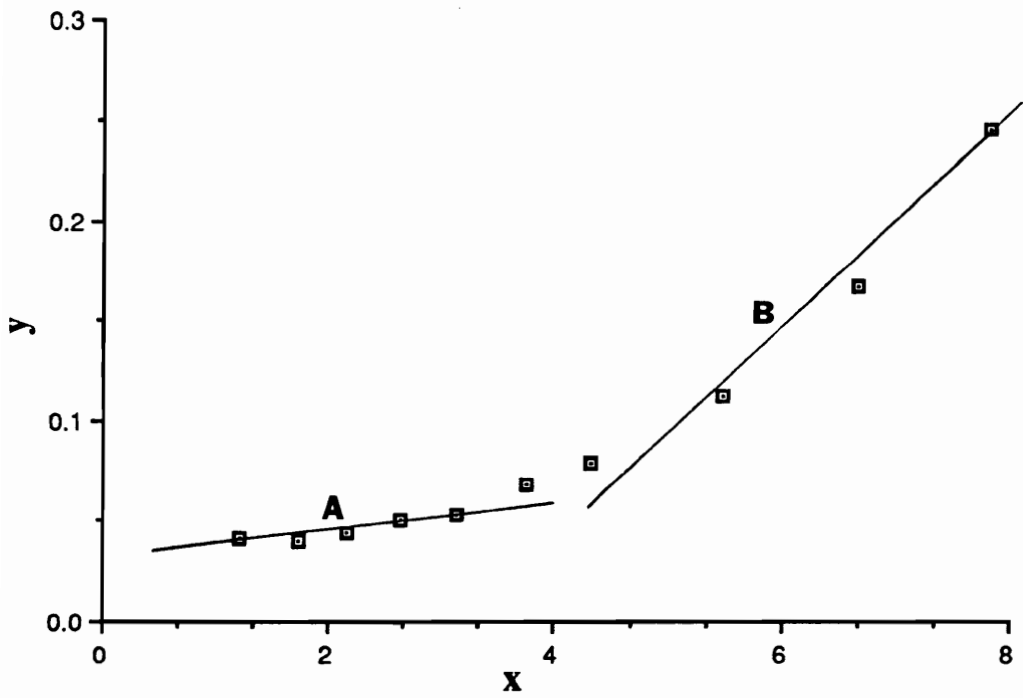
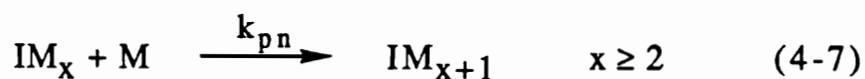
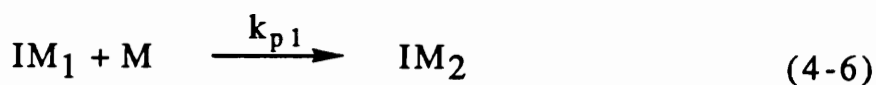
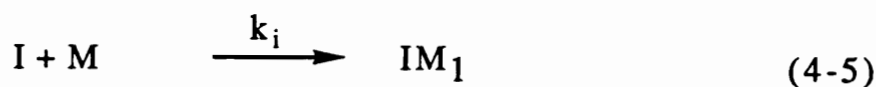


Figure 4.1.8 Determination of k_p According to Eq. 4-4

This behavior further validated the mechanism shown in scheme 4.1.4. Similar observations were reported by Saegusa et al.¹⁹ for the polymerization of 2-methyl-2-oxazoline initiated by methyl tosylate in CD₃CN at 40°C. However, the proposed mechanism is different. The difference in reactivity between two active species, initiation product without the stabilization of oxazoline ring vs. propagation product with the stabilization of at least one oxazoline ring, was believed to be the cause in the case of 2-methyl-2-oxazoline. A transition from covalent to ionic propagating species is proposed for the current system as the cause of slower propagation rate at earlier stage of the polymerization. Using Saegusa's treatment, line A is considered due to k_{p1} and line B due to k_p . The slope of line A yielded $k_{p1}=1.8 \times 10^{-4}$ L/mol·s. From the intercept and k_{p1} according to eq.(4-4), the calculated k_i was 5.65×10^{-4} L/mol·s. which agreed very well with the k_i value obtained independently through eq.(4-3) as discussed above. From slope B, k_p is determined to be 7.88×10^{-4} L/mol·s.

A more strict treatment involves deriving equations using separated relations for k_{p1} and k_{pn} . That is:



Here the propagation rate constant for addition of the second monomer is treated differently from that for addition of the third monomer and the rest, as shown in scheme 4.1.4 assuming $n=1$. Based on these mechanistic relations, kinetic equations have been derived¹⁶⁵. The equation for rate of initiation is the same as eq.(4-1) and,

Rate of consumption of the initiation product:

$$-d[IM_1]/dt = k_{p1} [IM_1] [M] - k_i [I] [M] \quad (4-8)$$

Rate of depletion of monomer:

$$-d[M]/dt = k_i [I] [M] + k_{p1} [IM_1] [M] + k_p \sum [IM_x] [M] \text{ for } x \geq 2 \quad (4-9)$$

After derivation with some effort, the following equations are obtained:

$$\ln([I]_0/[I]) = k_i \int_0^t [M] dt \quad (4-10)$$

$$\frac{\frac{1}{[M]} \cdot \frac{d^2 \ln[M]}{dt^2} - k_i^2 [I]}{\frac{d \ln[M]}{dt} + 2 k_i [I]} = -k_{p1} - k_{p1} k_{pn} \frac{[I]_0 - [I]}{\frac{d \ln[M]}{dt} + 2 k_i [I]} \quad (4-11)$$

Eq.(4-10) is the same as eq.(4-3), therefore $k_i=5.43 \times 10^{-4}$ L/mol·s as found earlier. The values for $d \ln[M]/dt$ and $d^2 \ln[M]/dt^2$ in eq.(4-11) were determined by taking first and second order derivatives on the cubic fit of a $\ln[M]$ vs. time plot. The plot according to eq.(4-11) did not fit a straight line (Figure 4.1.9). After the last four data points were removed, a linear fit on the rest of the data yielded a k_{p1} of 1.32×10^{-4} L/mol·s and k_p of 3.67×10^{-4} L/mol·s. These values are in the same order of magnitude, but smaller than what was obtained by Saegusa's method described earlier. In an attempt to obtain a better fit on the eq.(4-11) plot, a higher order polynomial was used to fit the $\ln[M]$ vs. time plot. Nonlinear behavior was also observed in this effort. Therefore, the rate constants obtained by Saegusa's method are considered more reliable. The rate constants so obtained are $k_i=5.43 \times 10^{-4}$ L/mol·s, $k_{p1}=1.8 \times 10^{-4}$ L/mol·s and $k_p=7.88 \times 10^{-4}$ L/mol·s. Thus, the rate determining step in this polymerization system is the initial propagation step.

In comparison with benzyl iodide as the initiator, several differences in the polymerization are observed when 1-iodobutane is used. Unlike the benzyl iodide initiated system, 1-iodobutane initiated polymerizations displayed a rather long induction period (ca. 5 hours). This is logical in view of the difference in reactivity between the two substrates toward nucleophilic substitution. As the polymerization proceeded, the intensity of methylene protons adjacent to iodide from the initiator decreased very slowly. There was still a substantial amount of the initiator unreacted at the end of

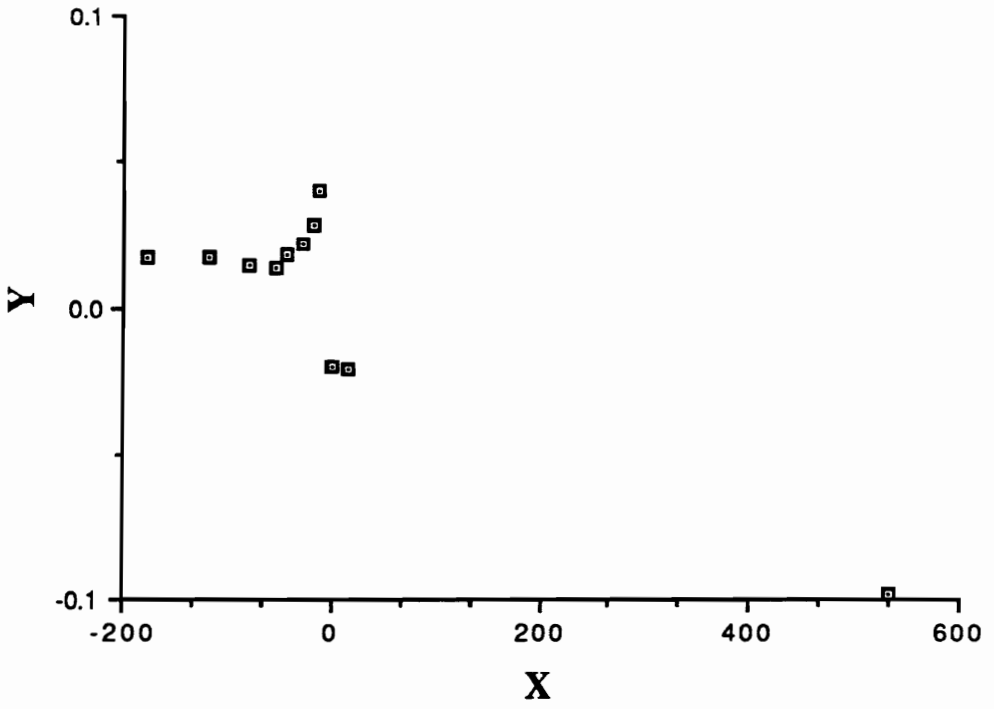


Figure 4.1.9 Plot According to Eq. 4-11

polymerization (Figure 4.1.10 d). Similar to what was observed in benzyl iodide initiated polymerizations, at an early stage of polymerization (Figure 4.1.10 b), new peaks around $\delta 3.2$ and $\delta 3.5$, corresponding to the open chain form of the initiation product, appeared as the intensity of initiator decreased. The expected oxazolinium propagating species did not appear until a later stage in the polymerization (Figure 4.1.10 c), $t = 12$ hours and their intensities were low. These observations again suggested the existence of covalent propagating species at the early stages of polymerization in a rather nonpolar solvent. Since no inflection point during the early stages of polymerization is observed on the $\ln[M]$ vs. time plot (Figure 4.1.11), the initiation rate is at least not greater than that of the initial propagation step. The convex shape of the plot indicates slow initiation and/or slow initial propagation step(s). The initiation rate constant and propagation rate constant need to be derived quantitatively. Since the methylene peak due to the initiator and that of the initiation product are partially overlapped, the change of initiator concentration as a function of time could not be determined accurately from the NMR spectra. The monomer peak can be followed in the same manner as in the benzyl iodide initiator case. Thus, the initiation vs. initial propagation rate constants cannot be separately determined. Since only monomer concentration as a function of time can be obtained, Beste and Halls' method¹⁶⁶ instead of Saegusa's was used to derive some of the rate constants. The trade-off is, however, that these rate constants are not resolved into

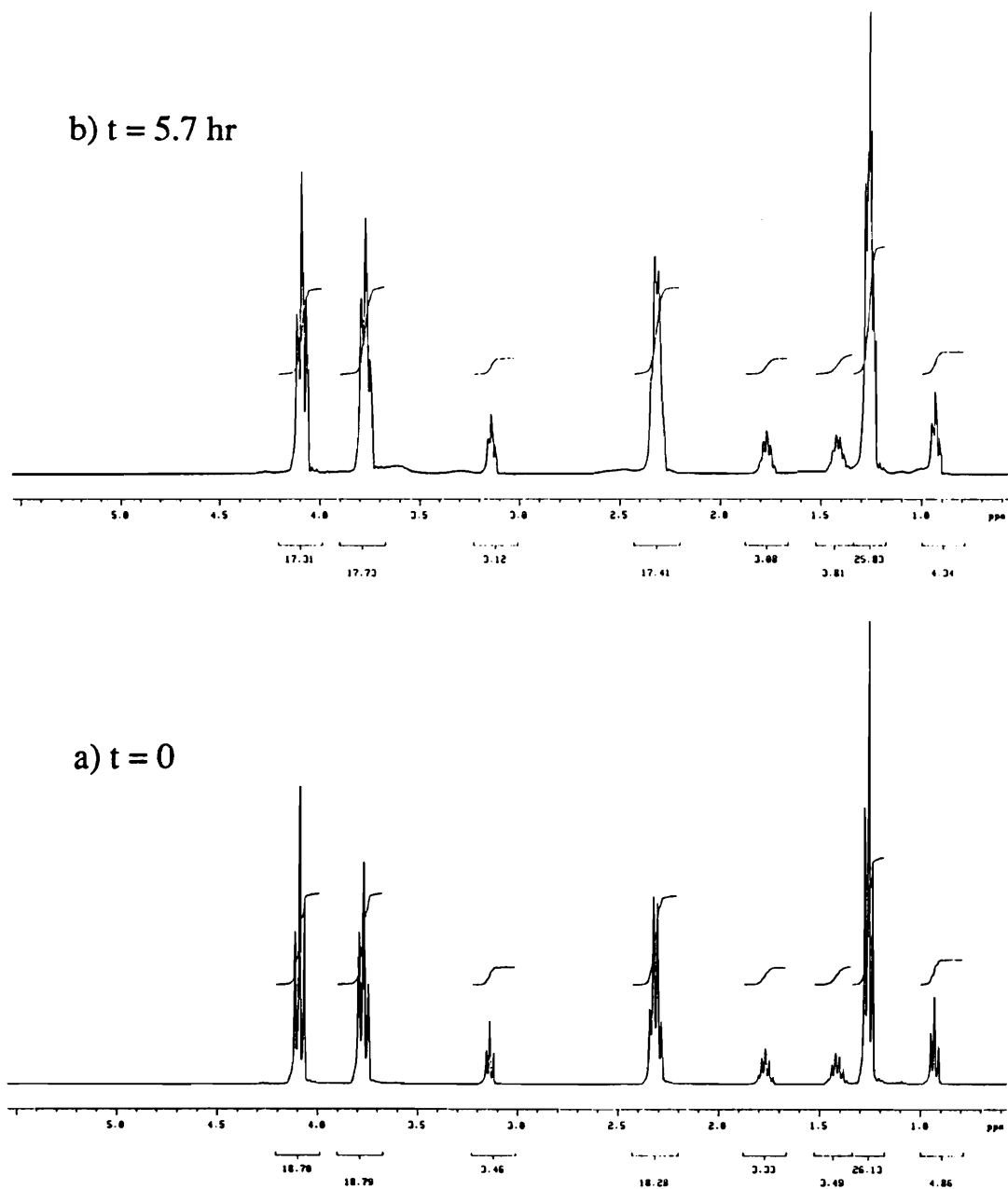
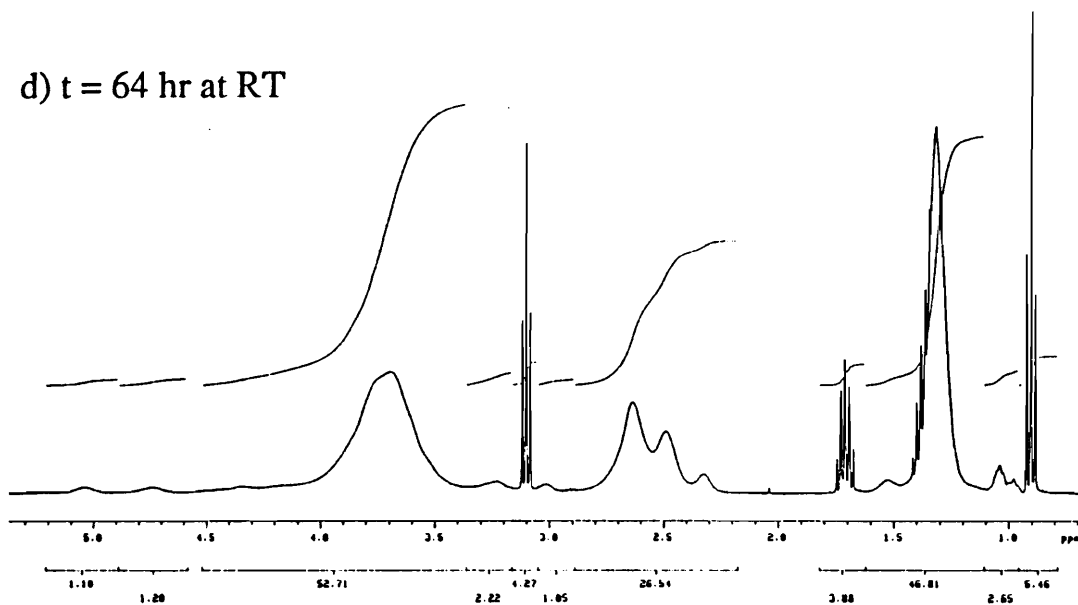


Figure 4.1.10 ^1H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by 1-iodobutane, a) $t=0$; b) $t = 5.7$ hr.

d) t = 64 hr at RT



c) t = 12 hr

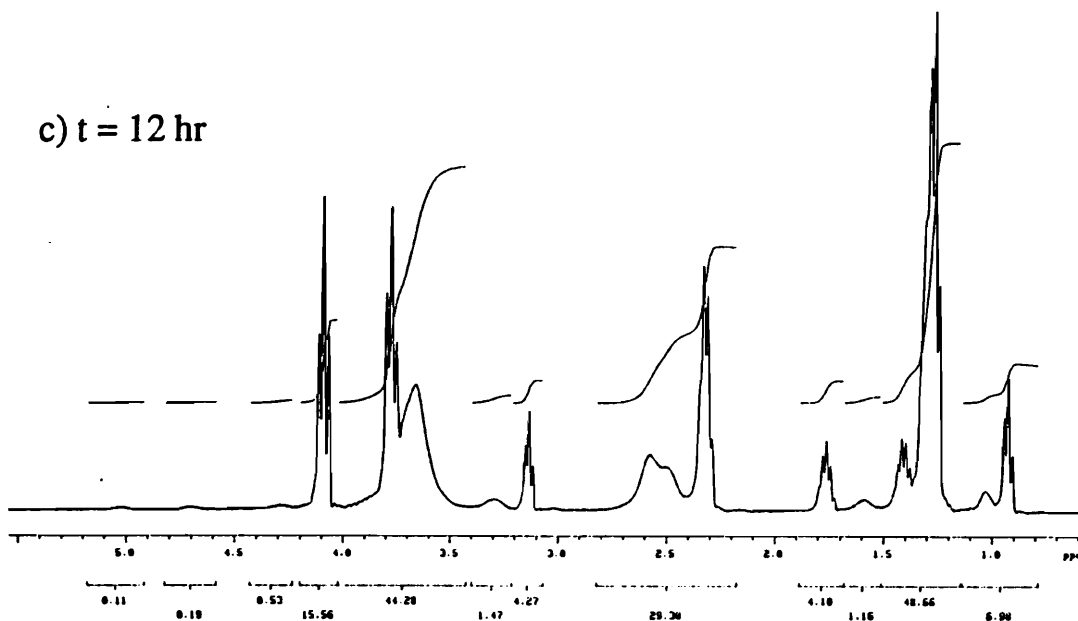


Figure 4.1.10 ¹H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by 1-iodobutane, c) t = 12 hr; d) t = 64 hr at RT.

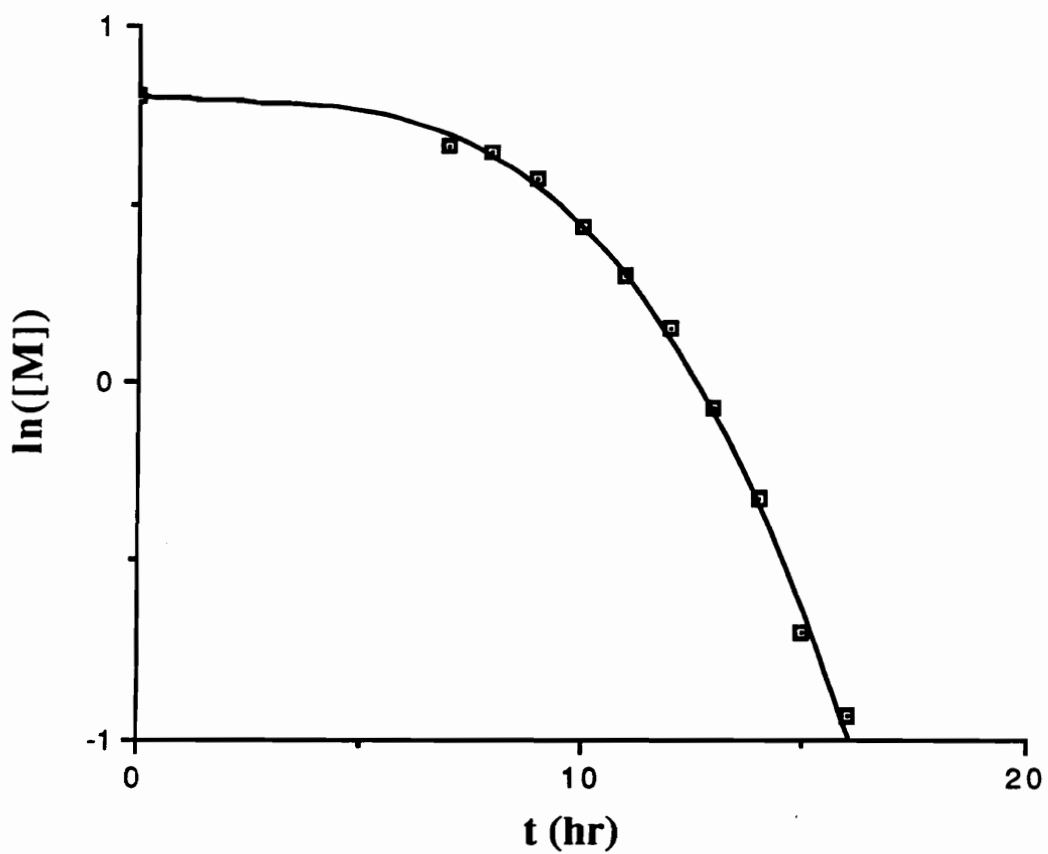


Figure 4.1.11 $\ln[M]$ vs. time plot for polymerization of 2-ethyl-2-oxazoline initiated by iodobutane at 80 °C

k_i , k_{p1} and k_{pn} . Only two reactions are considered using this method, that is, initiation and propagation:



From these two mechanistic equations, the following equation is derived:

$$\frac{1}{[I]_0} \frac{d \ln[M]}{dt} + k_p = (k_p - k_i) e^{-k_i \int_0^t [M] dt} \quad (4-14)$$

where $[I]_0$ is the initial initiator concentration, and $[M]$ is the instantaneous monomer concentration. Beste and Hall's method requires a trial and error type of approach to fit the logarithmic form of eq. (4-14) to determine both k_i and k_p . In using this approach, the logarithm has to be taken twice on the original data and nonlinearity was observed on the plot that presumably should have been linear. This approach was not used. Instead, k_i was estimated by setting $d \ln[M]/dt = 0$, as suggested in Beste and Hall's article¹⁶⁶. Then the value of k_i is substituted into eq. (4-14) and the equation is fitted by iteration to determine k_p . The k_i and k_p values are $k_i = 0.095 \times 10^{-4} \text{ L/mol}\cdot\text{s}$ and $k_p = 2.616 \times 10^{-4} \text{ L/mol}\cdot\text{s}$.

Benzyl iodide as initiator at 110°C

It is desirable to conduct 2-ethyl-2-oxazoline polymerizations at higher temperatures because the reaction rate is increased. Since the actual chosen polymerization temperature is 110 °C for 2-ethyl-2-oxazoline homo and copolymers, kinetic studies were also conducted at 110°C. However, due to the very fast reaction between the benzyl iodide initiator and 2-ethyl-2-oxazoline monomer, fewer data points were obtained relative to the 80 °C case for the change of initiator concentration as a function of time. Thus the following data needs to be viewed with caution in terms of accuracy. Rate constants determined using Saegusa's method are: $k_i=37.4 \times 10^{-4}$ L/mol·s, $k_{p1}=14.3 \times 10^{-4}$ L/mol·s, and $k_p=63.3 \times 10^{-4}$ L/mol·s. These values are obviously greater than those obtained at 80°C. Qualitatively, a similar $\ln[M]$ vs. time plot (Figure 4.1.12) and similar changes in NMR spectra as in the case at 80°C were observed. These observations supported the proposed mechanism in scheme 4.1.4.

To obtain more accurate propagation rate constants, monomer concentrations as a function of time were monitored using a much lower initiator concentration. It was assumed that if very low initiator to monomer concentrations were used, the initiator could be considered used up early in the polymerization. During that period, monomer concentration is considered to be a constant.

Using the k_i value obtained from the higher initiator concentration experiment, and equation (4-3), the time required for the initiator concentration to decrease to 0.01% of the feed value was

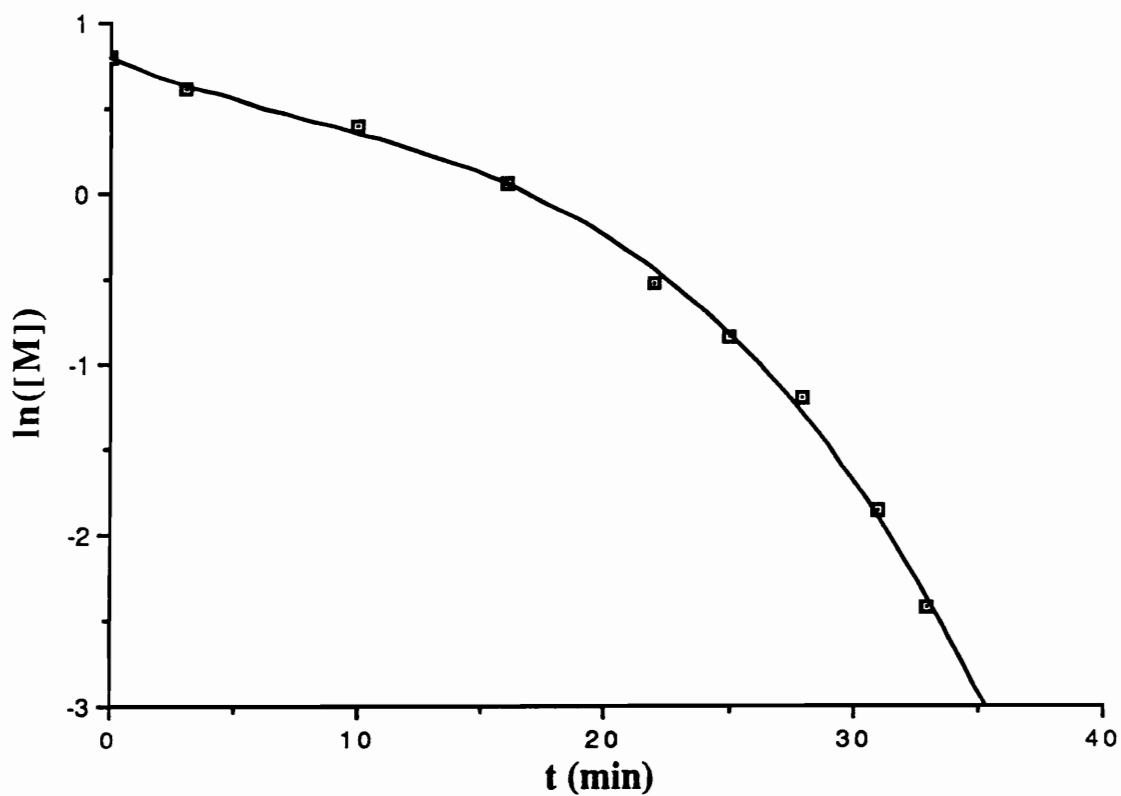
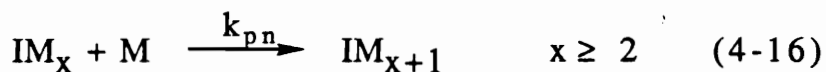
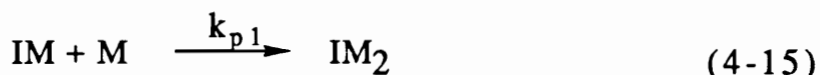


Figure 4.1.12 $\ln[M]$ vs. time plot for polymerization of 2-ethyl-2-oxaoline initiated by benzyl iodide at 110 °C, high $[I]_0$

calculated to be 16.5 minutes. Thus after ca. 20 minutes in the polymerization, the kinetics can be simplified to include only two propagation equations:



Since only the monomer concentration as a function of time could be determined, Hall's method was used to derive these two rate constants by treating the first propagation step as the initiation step. The plot of $\ln[M]$ vs. time (Figure 4.1.13) exhibits the convex feature associated with slow "initiation" and fast propagation.

The details of derivation of the two rate constants using Beste and Halls' method has been described earlier. The determined values are 8.53×10^{-4} L/mol·s for k_{p1} and 62.17×10^{-4} L/mol·s for k_{pn} , respectively. The same data was treated in the following way to obtain only the k_{pn} value. From a plot of $\ln[M]$ vs. time, it was found that a straight line could be drawn through the data points after ca. five hours into the polymerization. This is true when the rate determining step has been completed and the propagation rate constants are the same for all subsequent propagation steps. The following equation then applies:

$$-d[M]/dt = k_p [I]_0 [M] \quad (4-17)$$

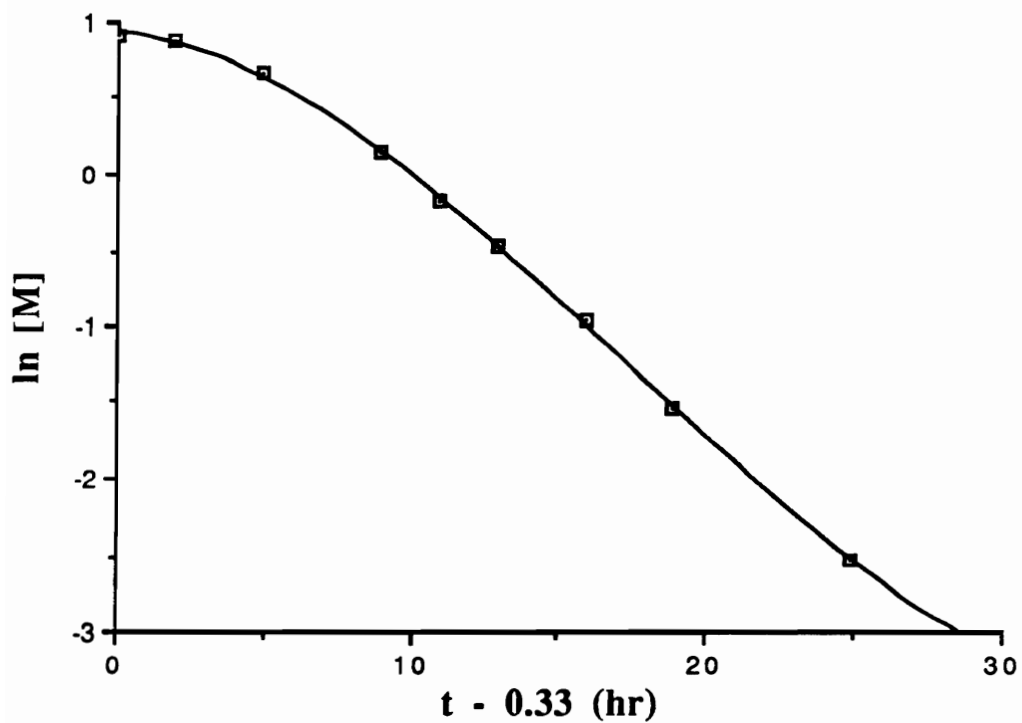


Figure 4.1.13 $\ln[M]$ vs. time plot for polymerization of 2-ethyl-2-oxazoline initiated by benzyl iodide at 110 °C, low $[I]_0$

Integration of this equation results in :

$$\ln([M]/[M]_x) = -k_p [I]_0 (t - t_x) \quad (4-18)$$

where t_x and $[M]_x$ are times when eq.(4-17) holds and the corresponding monomer concentration, respectively.

Upon rearrangement of eq.(4-18), one obtains:

$$\ln[M] = \ln[M]_x + k_p [I]_0 t_x - k_p [I]_0 t \quad (4-19)$$

The first two terms on the right side of eq.(4-19) contained only constants for the system in question. Thus, the slope of $\ln[M]$ vs. time plot results in $-k_p[I]_0$ from which k_p can be determined. The linear fitting on the data after ten hours into the polymerization yields a slope of -0.1679 with a correlation coefficient of 0.9995 (Figure 4.1.14). The calculated value for k_p is 74.6×10^{-4} L/mol·s which agreed with that obtained by the modified Hall's method.

The values at 110°C are about one order magnitude greater than those obtained at 80°C (Table 4.1.3). In all these cases, there is a rate determining step at the beginning of the polymerization, whether it is the initial propagation step(s) in the benzyl iodide initiated system or it is the initiation and/or the initial propagation step(s) in the 1-iodobutane initiated system. As a result, the molecular weight distribution of these polymers becomes broadened, particularly at very low molecular weights.

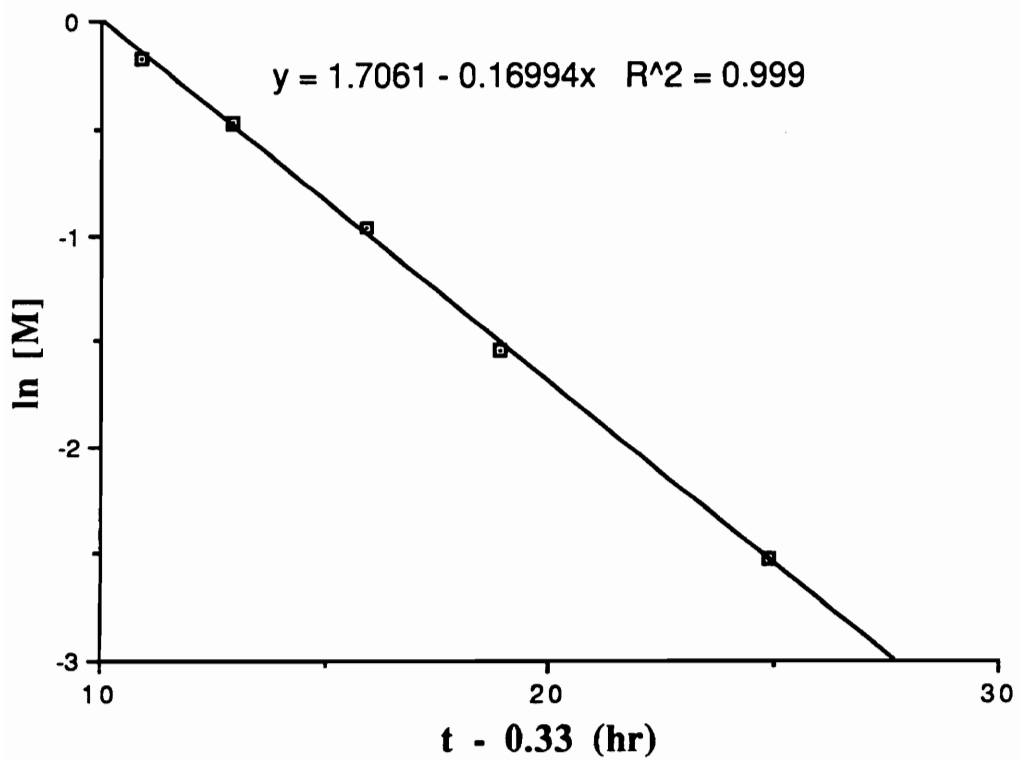


Figure 4.1.14 Determination of k_p According to Eq. 4-19.

Table 4.1.3 Polymerization Rate Constants of 2-ethyl-2-oxazoline

InitiatorTemp. (°C)	$[M]_o/[I]_o$	$k_i 10^4$ (L/mol.s)	$k_{p1} 10^4$ (L/mol.s)	$k_{pn} 10^4$ (L/mol.s)	method		
Benzyl iodide	80	5.65	3.26	1.8	7.88	Saegusa's	
	110	4.28	37.4	14.3	63.3	Saegusa's	
1-Iodo butane	80	5.36	0.095	400	8.53	62.17	Beste & Hall's
						74.6	linear fit
					2.616	Beste & Halls'	

Solvent: chlorobenzene or chlorobenzene-d₅

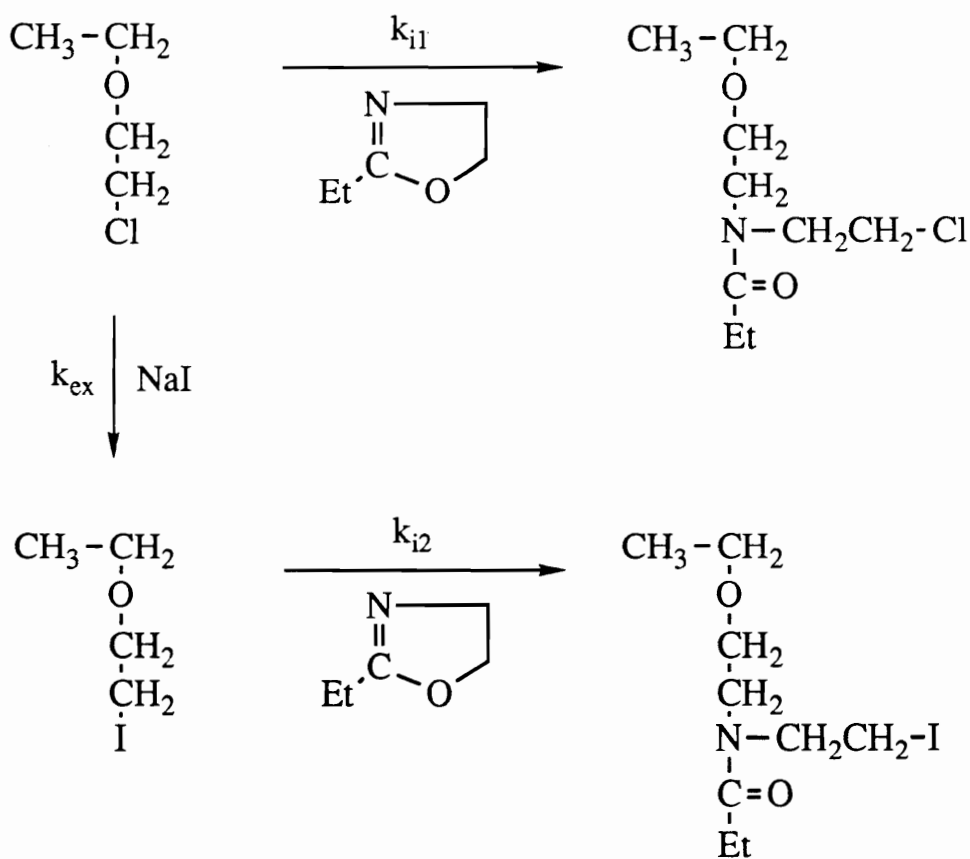
Chloroethyl ethyl ether (CIEEE)/NaI and benzyl chloride (BzCl)/NaI as initiators

From the copolymer synthesis point of view, the kinetics and mechanisms of CIEEE/NaI and BzCl/NaI initiated polymerization are very important. However, the mechanisms are complicated, because of the possibilities of many reactions. For instance, when CIEEE/NaI is heated in the presence of 2-ethyl-2-oxazoline monomer, there are two possible initiation pathways as shown in scheme 4.1.5. If both take place, the relative values of the three rate constants are important in determining the molecular weight distribution of the polymer. A similar scheme can be drawn for the benzyl chloride/NaI initiated system (scheme 4.1.6). Several model experiments were carried out to shed light on the relative importance of each step in the initiation process.

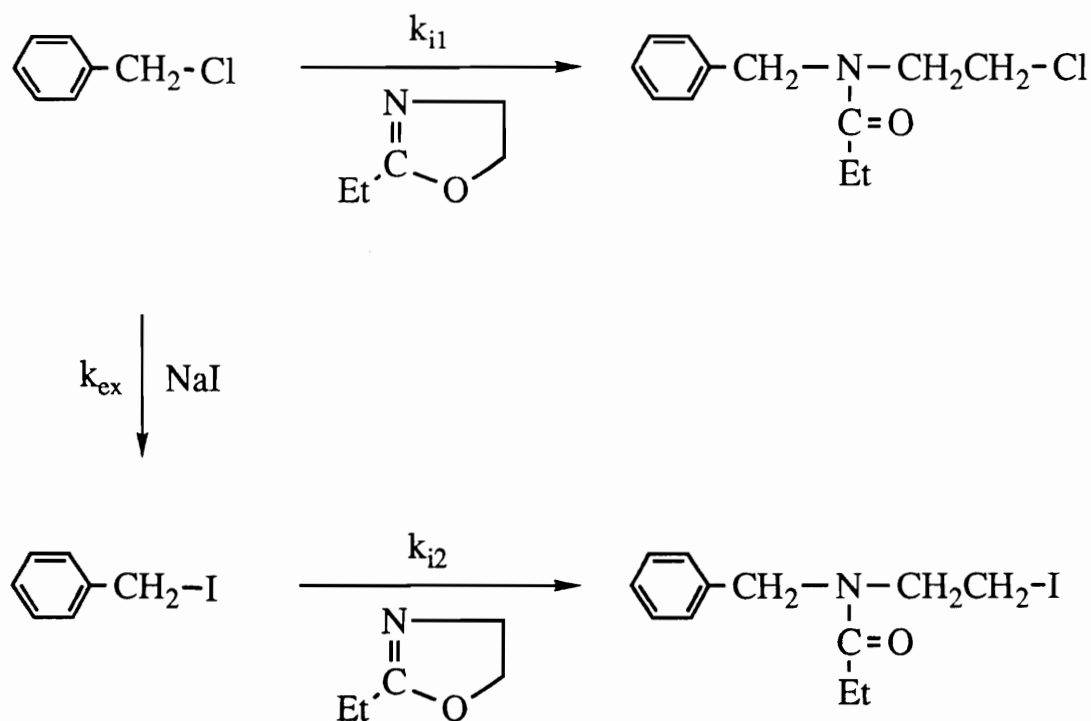
The first set of experiments involves reacting CIEEE or BzCl with 2-ethyl-2-oxazoline under normal polymerization conditions, without the addition of NaI. After 24 hours at 110°C, no polymers were detected for either of the two reactions. After five days there was still no polymer generated using CIEEE as the initiator, while polymer did form in the BzCl initiated system. CIEEE did not initiate the polymerization of 2-ethyl-2-oxazoline. Benzyl chloride did induce the polymerization but not within 24 hours.

The next set of experiments was designed to probe the exchange rate between CIEEE and NaI, or between BzCl and NaI. To avoid interference from polymerization yet maintain the reaction

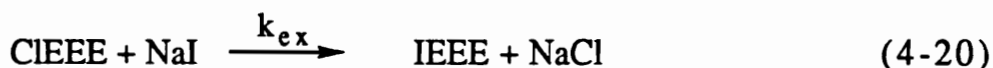
Scheme 4.1.5 Possible Initiation Pathways in Chloroethyl Ethyl Ether/NaI Initiated Polymerization of 2-ethyl-2-oxazoline



Scheme 4.1.6 Possible Initiation Pathways in
Benzyl Chloride/NaI Initiated Polymerization of 2-ethyl-2-oxazoline



media's polarity, NMP was used as a substitute for 2-ethyl-2-oxazoline monomer. In the given solvent mixture (NMP/chlorobenzene = 1/3 by vol.), NaI is soluble. The mixtures were treated following normal polymerization procedures. As detected by ^1H NMR, about 82% benzyl chloride and 0% CIEEE were converted into the corresponding iodo compounds after stirring at room temperature for ca. 1.5 hours (Figure 4.1.15). Thus the exchange rate between benzyl chloride and NaI must be much greater than that between CIEEE and NaI. Within 2 hours at 110°C , both benzyl chloride and CIEEE had "completely" reacted, as judged by NMR (Figure 4.1.16). The exchange rate between CIEEE and NaI at 110°C was determined by following the disappearance of CIEEE as a function of time, and using the following equations:



From eq. (4-20), a kinetic equation can be written:

$$d[\text{CIEEE}]/dt = -k_{ex} [\text{CIEEE}] [\text{NaI}] \quad (4-21)$$

where $[\text{CIEEE}]$ and $[\text{NaI}]$ are the concentrations of CIEEE and NaI, respectively. Since the initial feed molar ratio of NaI to CIEEE is 2, $[\text{NaI}] = [\text{CIEEE}]_0 + [\text{CIEEE}]$, which is substituted into eq. (4-21), and the resulting equation is then integrated, leading to:

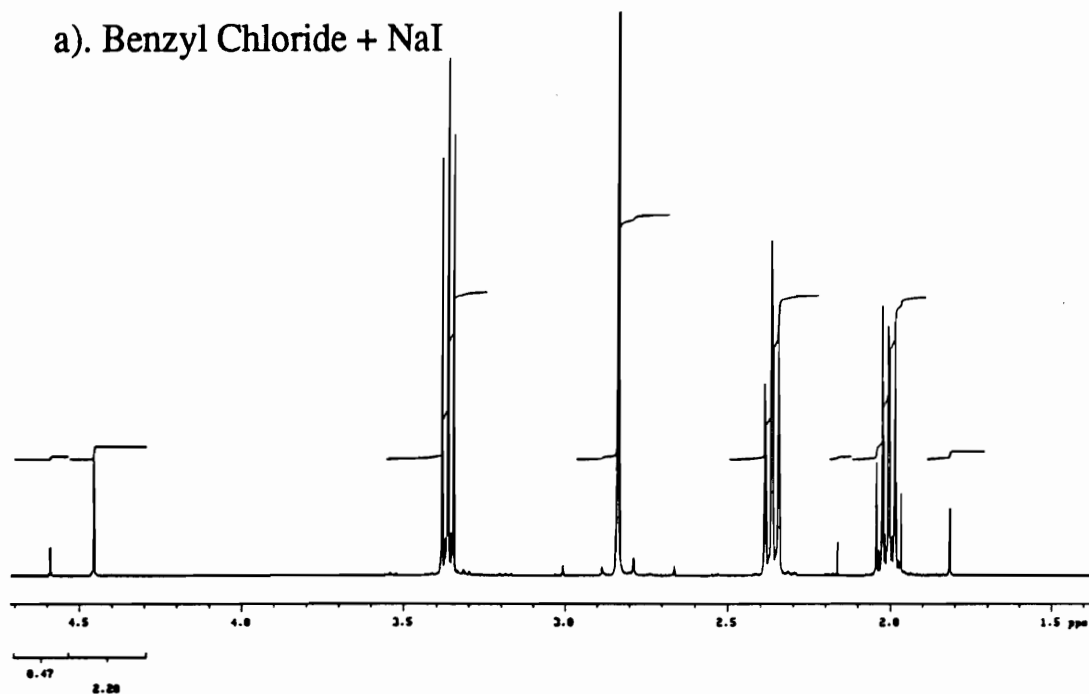
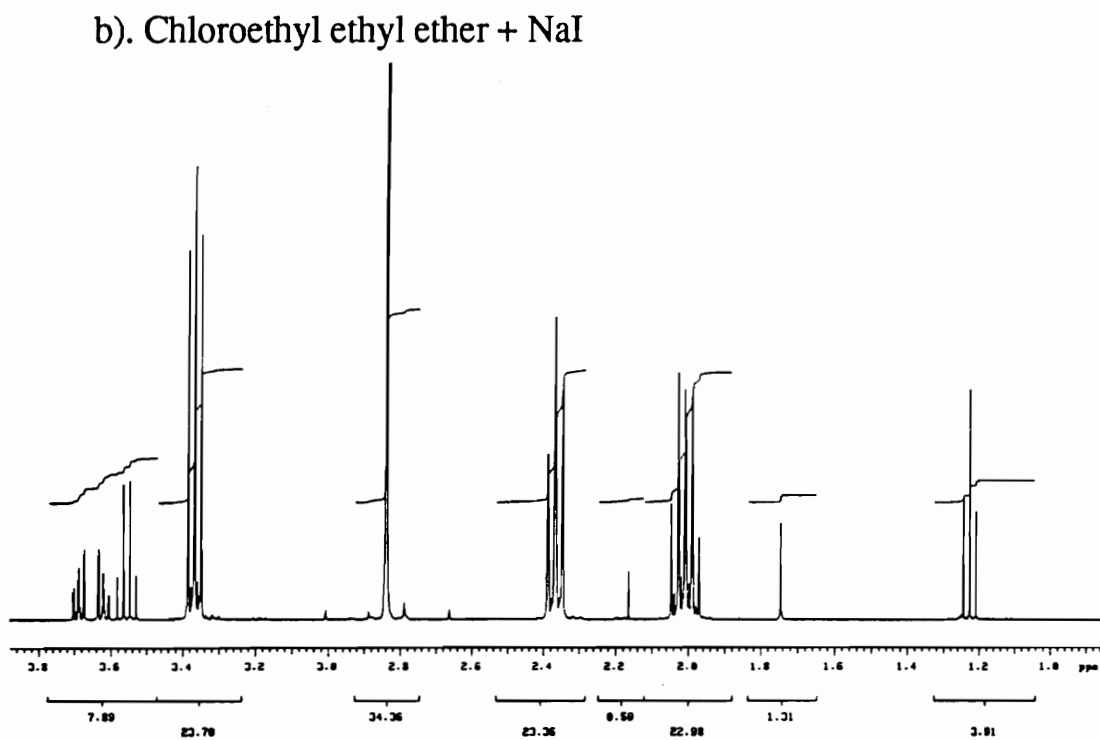


Figure 4.1.15 ^1H NMR of a). Benzyl Chloride + NaI

b). Chloroethyl ethyl ether + NaI

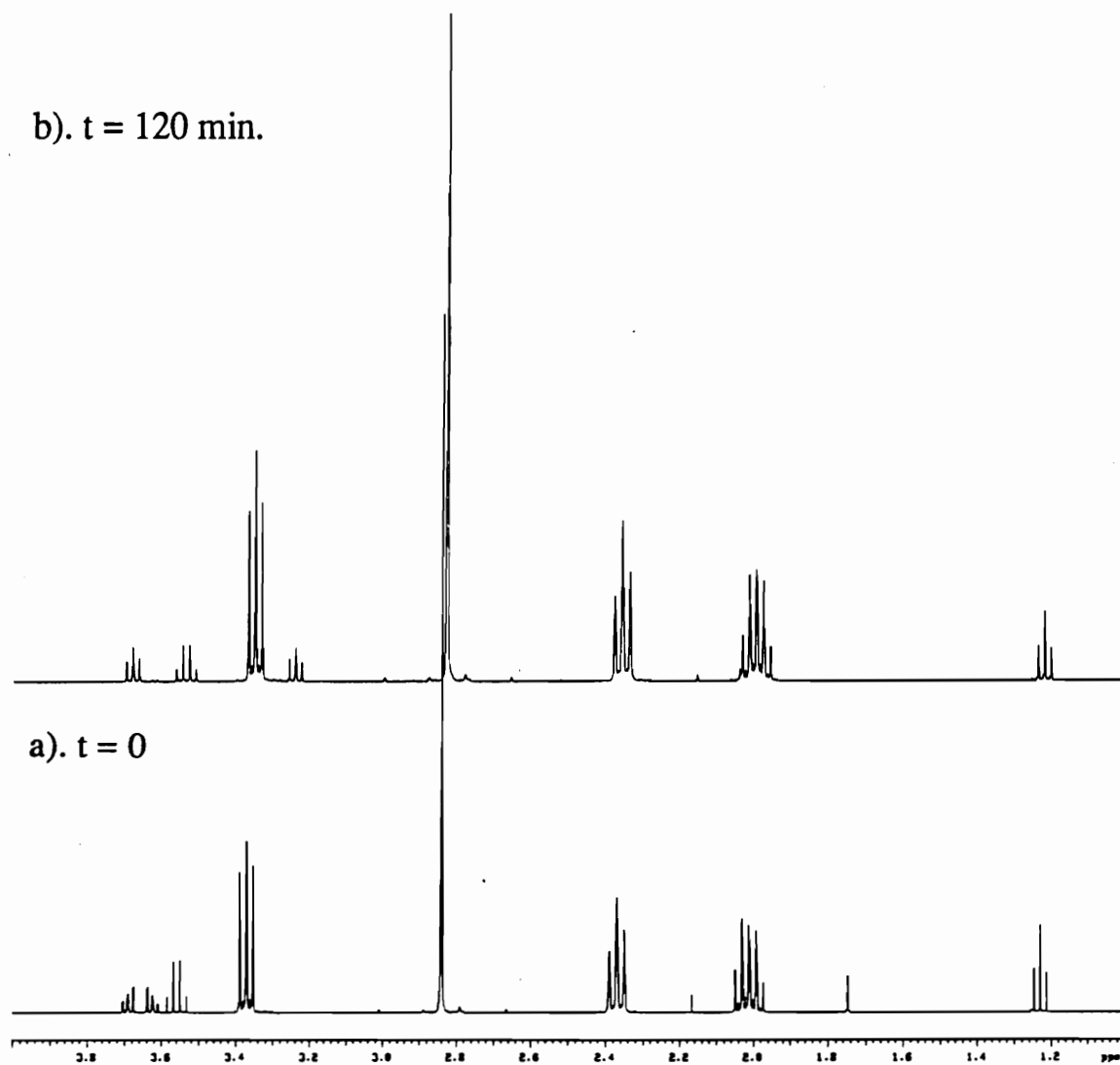


Figure 4.1.16 ^1H NMR of Chloroethyl ethyl ether + NaI
a). t = 0
b). t = 120 min.

$$\ln\{2[\text{CIEEE}]/([\text{CIEEE}] + [\text{CIEEE}]_0)\} = -k_{\text{ex}}[\text{CIEEE}]_0 t \quad (4-22)$$

The slope of a plot according to eq. (4-22) is $-k_{\text{ex}}[\text{CIEEE}]_0$ from which k_{ex} is calculated to be 20.3×10^{-4} L/mol·s. Since the exchange rate between benzyl chloride and NaI is much greater than that between CIEEE and NaI, k_{ex} for BzCl and NaI must be greater than 20.3×10^{-4} L/mol·s. In addition, k_{i1} in Scheme 4.1.6 will be smaller than k_{i2} , since I^- is a much better leaving group than Cl^- . The value of k_{i2} has been determined earlier to be 37.4×10^{-4} L/mol·s (Table 4.1.3). Thus k_{i1} is less than 37.4×10^{-4} L/mol·s. Hence k_{ex} for BzCl and NaI will be greater than k_{i1} , even if BzCl would initiate the polymerization, its rate would be too slow compared with that of path a in scheme 4.1.6. Summarizing the results of the two sets of experiments described above, it has been found that under normal polymerization conditions (1) CIEEE alone does not initiate the polymerization of 2-ethyl-2-oxazoline; (2) CIEEE was converted into IEEE within two hours with an exchange rate constant of 20.3×10^{-4} L/mol·s; (3) benzyl chloride did initiate the polymerization at a very slow pace; (4) benzyl chloride reacted with NaI at room temperature.

Therefore, path a in scheme 4.1.5 is the only one in effect, while in scheme 4.1.6 path a is the only one effective at least within short periods of time. To completely eliminate the effects of path b on initiation, the chloride compounds can be converted into the corresponding iodo compounds before the addition of monomer. This procedure was used in some of the 2-ethyl-2-oxazoline containing

copolymer syntheses. If this approach is taken, the kinetics in the rest of the polymerization process should be similar to that wherein an iodocompound is used as the initiator. However, this is true only if the side product NaCl does not participate in the polymerization. Theoretically, chloride anion can substitute for an iodide anion. However, several observations disfavor this possibility. First, NaCl is less soluble than NaI in the polymerization media. This is demonstrated by the appearance of a precipitate upon heating homogeneous solutions of ClEEE/NaI or BzCl/NaI reaction mixtures. Secondly, a 100% excess of NaI relative to BzCl was used. Both of these factors should drive the exchange equilibrium toward the iodo compound.

B. 2-Methyl-2-Oxazoline

As reviewed in chapter II, the kinetics of polymerization of 2-methyl-2-oxazoline using some initiators have been extensively studied. In this research, attention was focused on initiators which were similar in structure to those which could be attached to "macroinitiators" to be used for copolymerization. The kinetics of butyl mesylate and 1-iodobutane initiated polymerizations of 2-methyl-2-oxazoline in acetonitrile at 80°C were investigated. The plot of $\ln[M]$ vs. time for both initiating systems had a concave shape indicating the initiation rate constants were smaller than those for propagation. Quantitatively, initiation and propagation rate constants were derived from data on initiator and monomer concentrations at

various times using Saegusa's method. The values are listed in Table 4.1.4 along with those from the literature. As expected, initiation rate constants for both initiators investigated were smaller than those for propagation. The k_i value for n-butyl iodide as the initiator is smaller than that reported for methyl iodide, even though the polymerization temperature was lower in the latter²⁰. The reverse is observed for the k_p values. The difference in k_p can be easily accounted for by the change in temperature, since the propagating species in both cases have the same counteranion, iodide. The difference in k_i values cannot be explained by the change in temperature, which would favor the reverse order. The possible explanation is that the steric difference between methyl iodide and n-butyl iodide in an S_N2 reaction is dominating. This observation is also consistent with the report that the formation of a quaternary salt of 2-methyl-2-oxazoline with methyl iodide is exothermic while that with ethyl iodide needs heating at 100°C¹⁶⁷. The rate constants obtained for butyl mesylate initiator are similar to that reported for a dimesylate $((CH_2CH_2O)_3SOMe)_2$ ³³.

C. Is poly(2-alkyl-2-oxazoline) polymerization living?

"Living" polymerizations are often associated with "Poisson" molecular weight distributions. Penczek and Kubisa⁴ identified four possible sources of deviation from Poisson distributions which can apply in cationic ring-opening polymerizations: slow initiation, termination due to interaction between the growing cation and

Table 4.1.4 Polymerization Rate Constants of 2-methyl-2-oxazoline

Initiator	Temp. (°C)	$k_i \cdot 10^4$ (L/mol.s)	$k_{pn} \cdot 10^4$ (L/mol.s)	Source
Butyl mesylate	80	0.1	16.99	author
1-Iodo butane	80	0.53	24.23	author
MeI	40	2.7	1.14	Ref.
Triethylene oxide dimesylate	80	0.25	21	Ref.

Solvent: CNCD₃

counterion, chain transfer to polymer, and reversibility of polymerization. Among these four possible problems, reversibility of polymerization is not applicable to the polymerization of 2-oxazolines. Compared to most heterocyclic monomers, the ring-opening product of 2-oxazolines is much more stable due to isomerization following opening of the ring. Chain transfer to polymer may be a problem in some systems, but not in others. Reports on chain transfer reactions using bulk polymerization and very high initial monomer to initiator ratios (molar ratio in the thousands) have been made²⁶. Even under these conditions, chain transfer constant is 1/300 to 1/800. In addition chain transfer to polymer does not occur until late in the polymerization¹⁶⁸. Therefore for solution polymerizations with moderate to low initial monomer to initiator ratio, as is the case for the present study, no previous data has been reported. Slow initiation may be a problem for some initiating systems and especially when it is coupled with preparation of polymers with low targeted molecular weights. As calculated by Gold¹⁶⁹, when k_p/k_i increases from 0.1 to 10, M_w/M_n increases from 1.008 to 1.019 for DP of 150. As k_p/k_i increases to 100, not all of the initiator is consumed and M_w/M_n becomes 1.242. Therefore slow initiation tends to broaden molecular weight distributions but this becomes complicated by residual initiators in extreme cases. Reviewing Table 4.1.3 and 4.1.4, the highest k_p/k_i ratios occur for 1-iodobutane initiated polymerizations of 2-ethyl-2-oxazoline (ca. 28) and for butyl mesylate initiated polymerizations of 2-methyl-2-

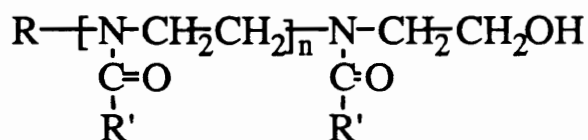
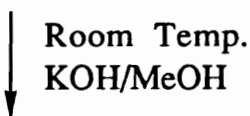
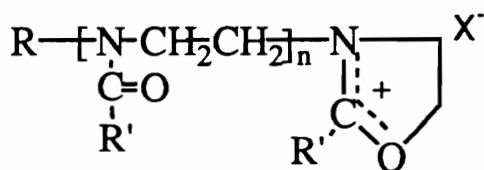
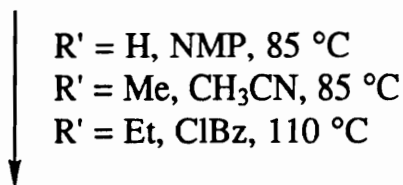
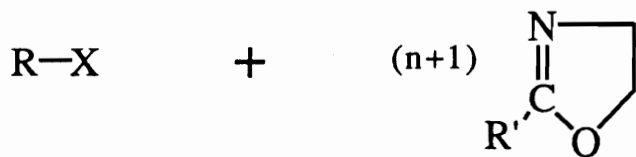
oxazoline (ca. 170). Thus, the molecular weight distributions of these systems are expected to be broadened due to this factor. In addition to broadening molecular weight distributions, slow initiation also affects the number average molecular weight as k_p/k_i increases and targeted molecular weight decreases. Termination by counteranion does not appear to be a problem in polymerization of 2-oxazoline systems, since covalent species also propagate in these systems. However, temporary termination, or an equilibrium between the ionic and covalent propagating species, may broaden the molecular weight distribution. This may have caused the broader than expected molecular weight distribution of "living" poly(2-ethyl-2-oxazoline) initiated by benzyl iodide with a molecular weight of 40,000 g/mol (section 4.1.2). Since the difference between the propagation and initiation, or between propagation and initial propagation step(s) rate constants is not great ($k_{pn}/k_i = \text{ca. } 2$, $k_p/k_{p1} = 4-7$, Table 4.1.3), all the initiators would have been consumed at early stages of the polymerizations. This probably explains the linear relationship between the number average molecular weight with polymer conversion during the sampling region (conversion > 20%), even though the initiation and initial propagation rate constants are smaller than that of propagation. This difference in rate constants cannot, however, account for the polydispersity increase at later stages of the polymerization. This observation becomes reasonable if one assumes that there are covalent propagating species along with the ionic species at later stages of the

polymerization. The concentration of these covalent species may have increased as polymerization proceeded, probably due to the decrease in medium polarity as monomer concentration decreases. The covalent species propagated slower than the ionic species, thus if the equilibrium rate between the covalent and ionic species is slower than the propagation rate of the ionic species, the molecular weight distribution will be broadened.

4.1.4 General Synthesis

For blend studies, poly(2-ethyl-2-oxazoline) and poly(2-methyl-2-oxazoline), each with a theoretical molecular weight of 30,000 g/mol, were synthesized according to Scheme 4.1.7. To ensure solubility through out the polymerization, a more polar solvent, acetonitrile, was used for the poly(2-methyl-2-oxazoline) synthesis. Poly(2-oxazoline) was also prepared (Scheme 4.1.7). In the polymerization of 2-oxazoline, even though a polar aprotic solvent, NMP, was used, poly(2-oxazoline) precipitated out of the solution during the polymerization. DSC thermograms of this polymer exhibited a melting peak at ca. 200°C (Figure 4.1.17). Unsubstituted 2-oxazoline monomer is not commercially available and was synthesized in this lab. The general procedures are included in Scheme 4.1.8 and the details have been discussed in the Experimental chapter. These procedures were adopted from previous studies^{170, 171} with some modification. The major modification is in the last ring closing step, which involved

Scheme 4.1.7
 Polymerization of 2-alkyl, unsubstituted-2-oxazolines



R = benzyl, and X = I⁻ for R' = Me and Et

R = methyl, and X = Tos⁻ for R' = H

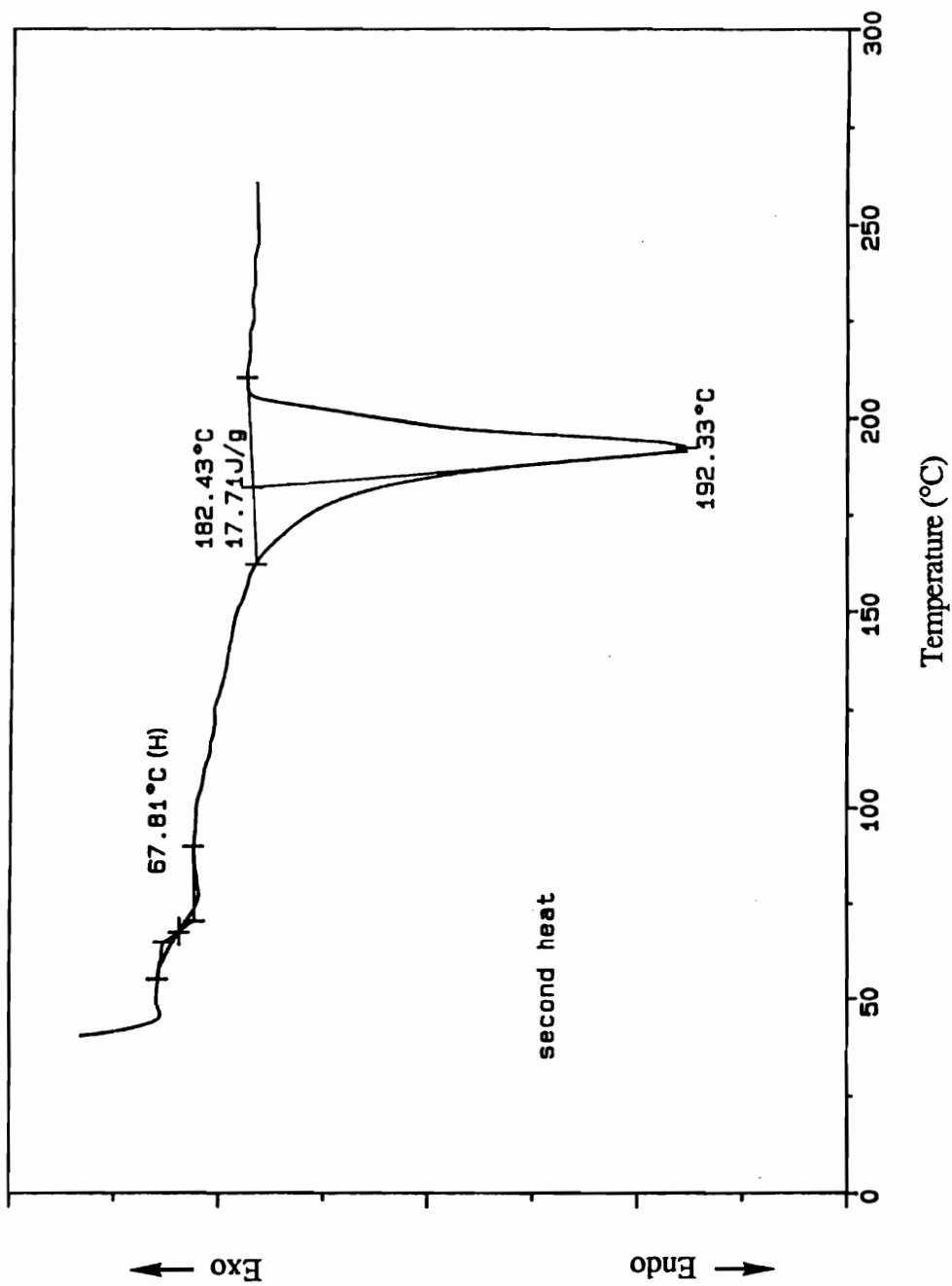
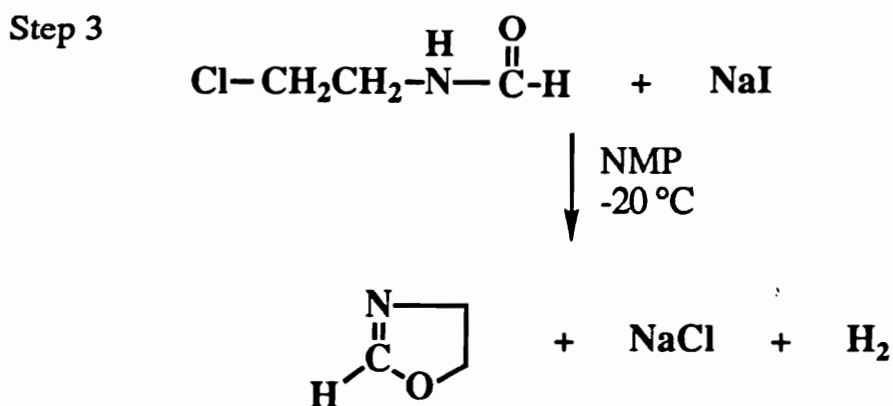
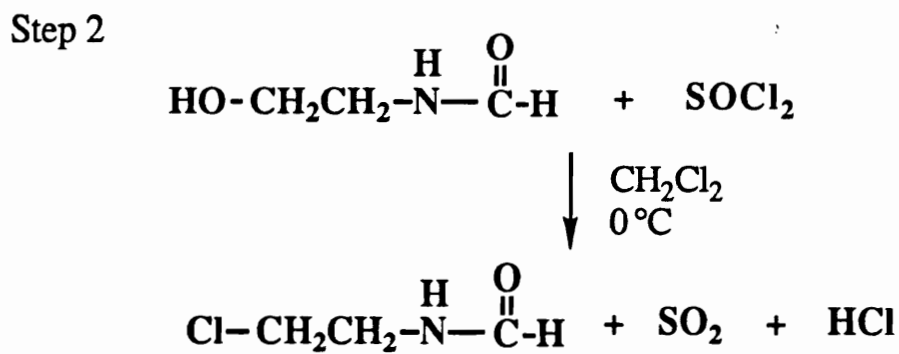
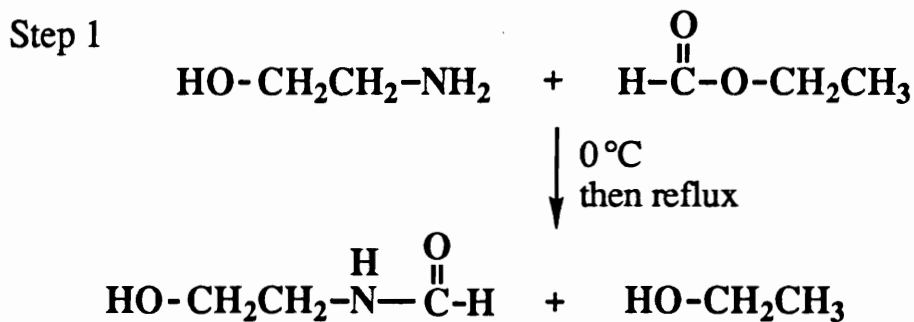


Figure 4.1.17. DSC thermogram of poly(unsubstituted 2-oxazoline)

Scheme 4.1.8
Synthesis of unsubstituted 2-oxazoline



substituting NaH for NaOH as the base and NMP for H₂O as the solvent. This modification provided easier and higher percentage recovery of dry monomer. ¹H NMR confirmed the structure for the product of each step and of the final monomer.

4.2 Synthesis and Characterization of Poly(dimethylsiloxane-2-ethyl-2-oxazoline) Block Copolymers

4.2.1 Synthesis

It is well known that hexamethylcyclotrisiloxane (D₃) can be polymerized in the presence of alkyl lithium initiators and at least a minor amount of polar solvent to produce polymers with narrow molecular weight distributions¹⁴⁷⁻¹⁴⁸. This polymerization system was utilized in this study to obtain poly(dimethylsiloxane) (PDMS) blocks with well controlled molecular weight and narrow molecular weight distributions. A benzyl chloride containing chlorosilane compound was used to terminate the living chains of PDMS to afford functional PDMS oligomers.

The synthesis of this functional termination reagent has been previously established and is described in the Experimental Section. The products of this reaction are two constitutional isomers. Under the particular synthetic conditions employed, the ratio of isomer A to isomer B (Figure 4.2.1) was about 4:1 as determined by ¹H NMR. Although the product distribution is interesting from a purely synthetic standpoint, it was not expected that different isomer ratios would result in property differences in the poly(dimethylsiloxane) oligomers. Thus, no attempt was made to optimize either particular product.

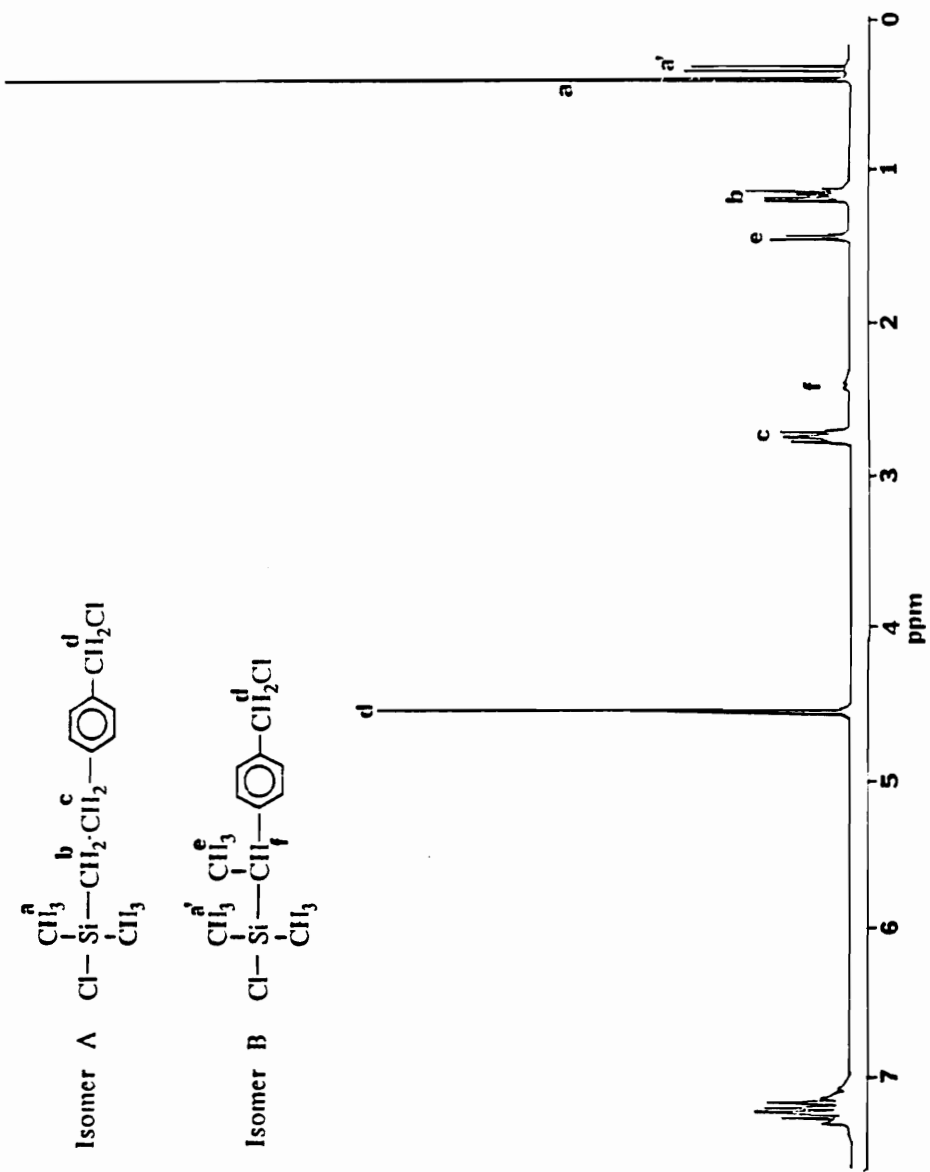
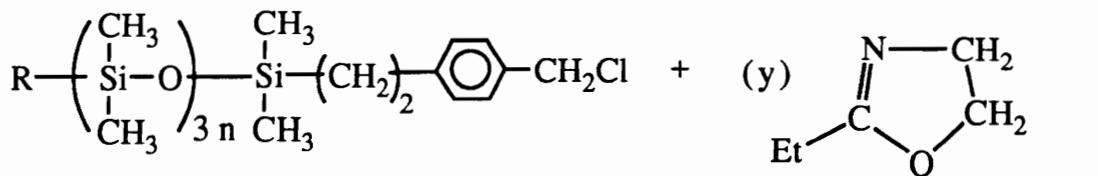


Figure 4.2.1 ^1H NMR of the Termination Reagent

Monofunctional PDMS oligomers were synthesized according to Scheme 4.2.1. Initiation consists of nucleophilic attack on the silicon atom of D_3 by the sec-butyl carbanion to form a lithium siloxanolate ion pair. In cyclohexane, a nonpolar solvent, the ion pair is sufficiently tight so that propagation does not take place. Upon the addition of 10% (V/V) of THF, a polar solvent, the ion pair is loosened and propagation ensues¹⁴⁷⁻¹⁴⁹. This sequence of addition allows separation of initiation from propagation, so that the relative rates of these steps do not affect the molecular weight distributions of the resultant oligomers. It was found that 48 hrs of propagation was sufficient for complete polymerization of PDMS with Mn of 20,000g/mol¹⁴⁸. The living PDMS chains were terminated by addition of the functional terminator as discussed above. Approximately 2 minutes after addition of this termination reagent, a white precipitate of lithium chloride was observed. After the benzyl chloride functional PDMS oligomers were isolated, they were analyzed by GPC and then used for the polymerization of block copolymers. Both ²⁹Si NMR and GPC showed the polymers were free of cyclics and GPC indicated narrow molecular weight distributions.

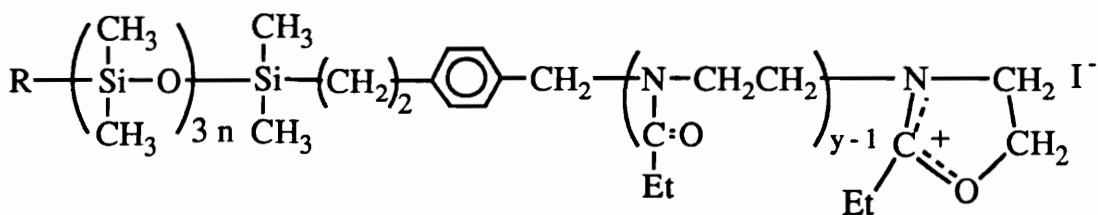
Poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers (PDMS-b-PEOX) were synthesized via cationic ring opening polymerization of 2-ethyl-2-oxazoline using benzyl chloride functional PDMS oligomers as macroinitiators (scheme 4.2.2). The function of the sodium iodide shown in the scheme was to convert the benzyl chloride to the more reactive benzyl iodide in situ.

Scheme 4.2.2 Synthesis of PDMS-PEOX Block Copolymers



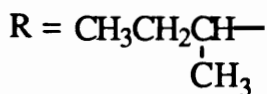
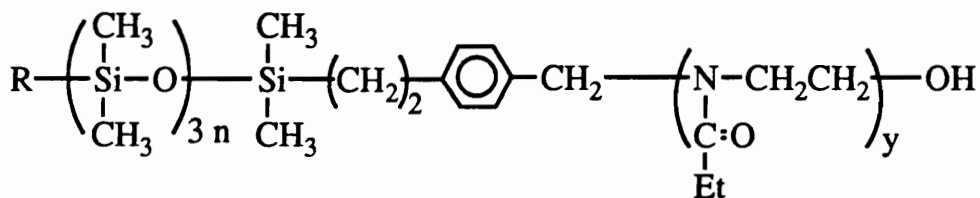
Initiation &
Propagation

25% in Chlorobenzene
NaI
rm. temp. 1hr.
110 °C 10-60 hrs.



Termination

KOH in MeOH
rm. temp.



At room temperature, sodium iodide is soluble in 2-ethyl-2-oxazoline monomer. After addition of the functionalized PDMS at room temperature, sodium chloride precipitated within 5 minutes, indicating the exchange reaction between iodide and chloride had taken place (for further discussion of this particular aspect, see section 4.1). Addition of the polymerization solvent, chlorobenzene, to the reaction mixture made the already cloudy solution milky, probably due to more precipitated sodium chloride. As the reaction mixture was heated to 110°C, a pale yellow color, characteristic of 2-ethyl-2-oxazoline polymerizations, developed. When the 2-ethyl-2-oxazoline monomer was depleted as judged by ^1H NMR, the reaction was terminated using KOH/MeOH at room temperature. Immediately after the addition of KOH/MeOH, the pale yellowish solution became colorless. The block copolymers were isolated as discussed in the Experimental Section. It should be noted that, even though it had been established that these materials were relatively free of homopolymers, they were rigorously soxhlet extracted with hexanes following isolation to insure quantitative removal of any residual PDMS prior to performing structure/property relationship investigations.

4.2.2 Characterization

A. Composition by Elemental analysis

The compositions of these block copolymers were determined by elemental analysis. The wt % PDMS was calculated based on the following formula:

$$\text{wt \% PDMS} = \frac{\frac{\text{wt \% Si}}{28} \times 74}{\text{numerator} + \frac{\text{wt \% N}}{14} \times 99}$$

28 and 14 are the atomic weights for silicon and nitrogen, and 74 and 99 are the molecular weights for the PDMS repeating unit and PEOX repeating unit, respectively.

The results are listed in Table 4.2.1. In all cases, the experimental compositions, after careful extraction with hexane, were very close to the theoretical values. This reflects the quantitative nature of the poly(dimethylsiloxane) functionalization as well as quantitative initiation of 2-ethyl-2-oxazoline. Since the second copolymer block could only have been initiated by the PDMS oligomer, this data also strongly suggests that only diblock copolymer is formed and that the systems are essentially free of homopolymer.

B. Solution Properties

a. ¹H NMR. ¹H NMR is often a convenient method for determining the chemical composition of copolymers. However the calculated weight percentage of PDMS in these block copolymers based on ¹H NMR in CDCl₃, especially for the longer block length (e.g. 20K PDMS-80K PEOX) in the copolymers, suggested much lower PDMS contents than the theoretical values (Table 4.2.2). One possible

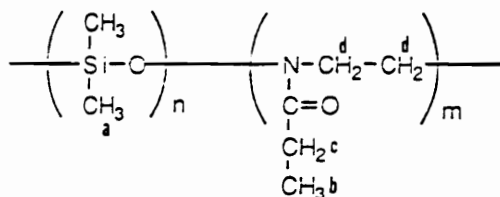
Table 4.2.1 Compositions of PDMS-b-PEOX Copolymers
by Elemental Analysis*

Sample (kg/mol)	Theoretical (wt.% PDMS)	Elemental Analysis (wt.% PDMS)
0.5K PDMS-2K PEOX**	20	17.21
1K PDMS-4K PEOX	20	18.24
2K PDMS-8K PEOX	20	16.95
5K PDMS-20K PEOX	20	19.78
20K PDMS-80K PEOX	20	15.18

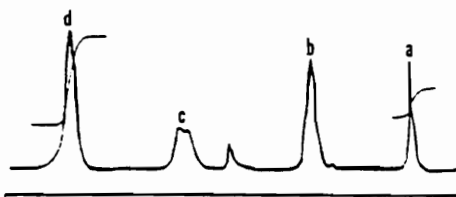
* Performed by SPANG Microanalytical Lab.

** 0.5K PDMS-2K PEOX = 0.5kg/mol PDMS-b-2kg/mol PEOX

explanation for these results is the existence of micelles. Since the core portion of the micelle would behave like a solid which has longer relaxation times than a liquid, the intensity of the peak corresponding to the core would be disproportionally decreased, resulting in apparent low concentrations of that species. Due to the large polarity difference between PDMS and PEOX, the formation of micelle would be expected, especially in selective solvents. Therefore toluene- d_8 , a solvent for the PDMS block but a nonsolvent for PEOX, and D_2O , a solvent for PEOX and a nonsolvent for PDMS were used as NMR solvents and a series of 1H NMR spectra were investigated (Figure 4.2.2). Based on these spectra, the wt % PDMS was calculated for each block copolymer (recorded in Table 4.2.2). Several interesting trends were evident. The wt % PDMS measured using toluene- d_8 as solvent was uniformly greater than that calculated using D_2O . Moreover, in both toluene- d_8 and D_2O , the deviation from the theoretical weight percentages of PDMS (which were in agreement with elemental analysis), consistently increased as block lengths increased. Both of these trends support the hypothesis that micelles are present in these solutions. It is expected that when toluene- d_8 was used as the NMR solvent, the PDMS blocks would be solubilized and form the outskirts of the micelle while PEOX would be insoluble and form the core. Conversely, when D_2O was used as the NMR solvent, the reverse would be true. As the molecular of each block increased, microphase separation in solution



1. IN CDCL₃



2. IN d-TOLUENE



3. IN D₂O

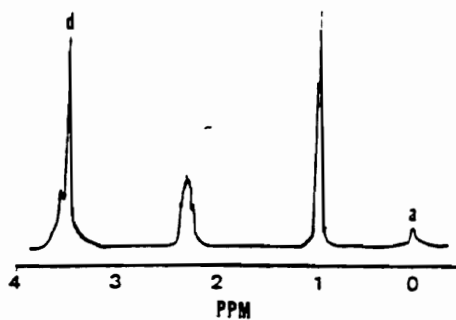


Figure 4.2.2 ¹H NMR of a PDMS-PEOX Block Copolymer in Various Solvents

Table 4.2.2 Compositions of PDMS-b-PEOX Copolymers Determined by ¹H NMR in Various Solvents

Sample (kg/mol)	Theoretical (wt.% PDMS)	CDCl ₃ (wt.% PDMS)	Toluene-d ₈ (wt.% PDMS)	D ₂ O (wt.% PDMS)
0.5K PDMS-2K PEOX*	20	10.7	16.8	13.1
1K PDMS-4K PEOX	20	8.9	18.3	10.7
2K PDMS-8K PEOX	20	9.8	36.1	6.6
5K PDMS-20K PEOX	20	13.4	69.2	4.6
20K PDMS-80K PEOX	20	3.6	71.4	2.2

* 0.5K PDMS-2K PEOX = 0.5kg/mol PDMS-b-2kg/mol PEOX

would be expected to be more complete. Thus, the block length effect also appears reasonable.

b. **CMC Measurements.** In order to confirm the presence of micelles for these PDMS-PEOX block copolymers, the critical micelle concentration (CMC) for the block copolymer having the lowest molecular weight, 0.5K PDMS-2.0K PEOX, was determined in water. Many properties of a solution change dramatically at the CMC, for example, osmotic pressure, turbidity, surface tension and molar conductivity. Measurement of any one of these properties as a function of concentration yields CMC values¹⁷². In this study, surface tension was measured using a dynamic contact angle analyzer, and the measured surface tension was plotted against concentration (Figure 4.2.3). This analysis produced a typical surface tension vs. concentration plot for a surfactant. The CMC value, obtained by the intersection of the two tangents of on the curve, was approximately 0.07 mg/ml (0.028 mmol/L). By contrast, a typical surfactant, sodium dodecyl sulfate has a CMC of 8.1 mmol/L at 25 °C¹⁷³. Therefore it was concluded that these block copolymers were very surface active.

C. Surface Characteristics by XPS

For a block copolymer, the lowest energy component will be energetically driven to concentrate at the polymer/air interface. Since poly(dimethylsiloxane) has a very low surface energy, the air surfaces of poly(dimethylsiloxane) containing copolymers, or blends

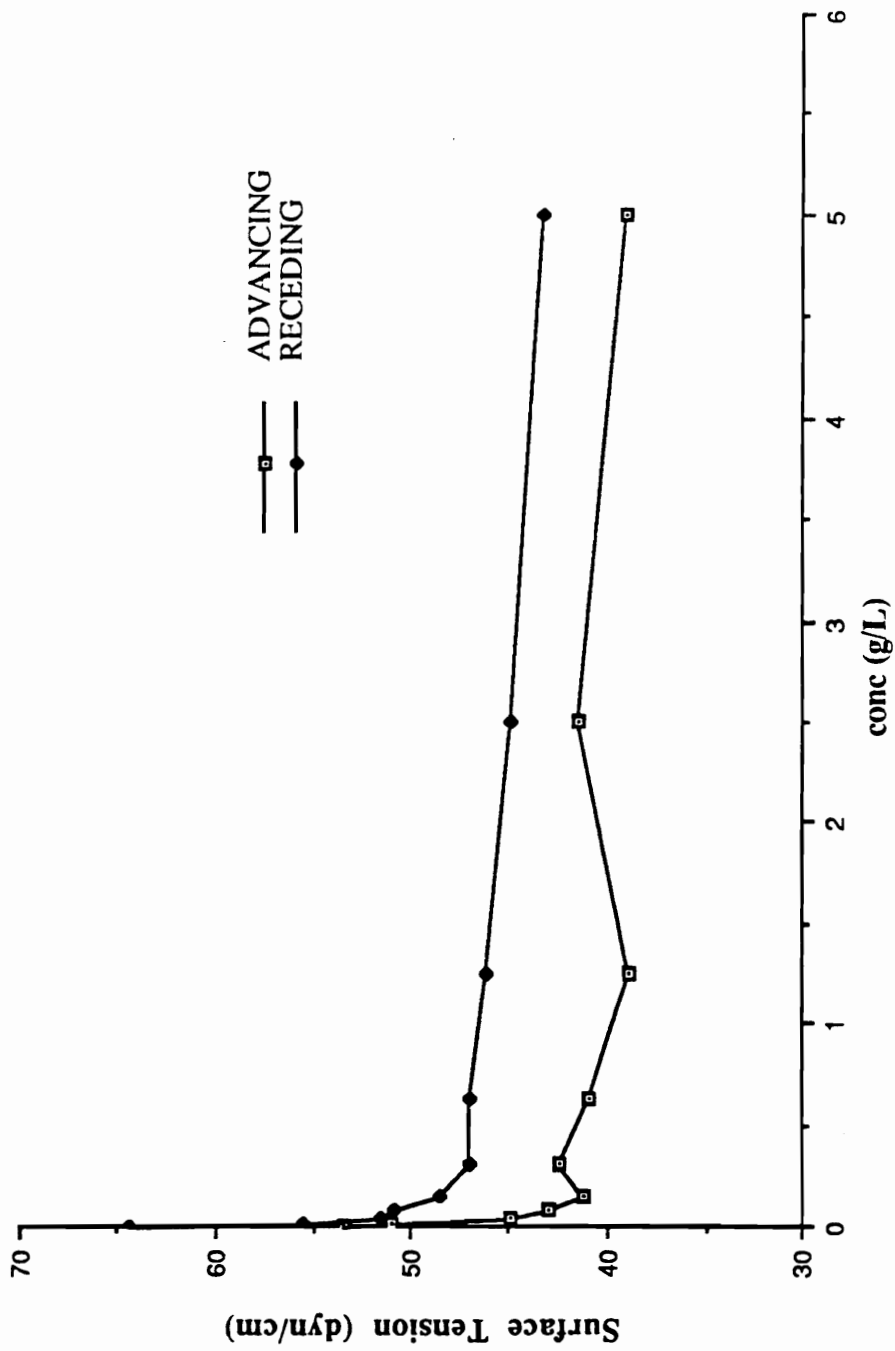


Figure 4.2.3 Surface Tension-Concentration Plot for Determination of CMC

containing these copolymers, are expected to be enriched with poly(dimethylsiloxane). This enrichment has been demonstrated in numerous studies¹⁷⁴⁻¹⁷⁹, through either surface tension and contact angle measurements or via more sophisticated surface chemical composition analysis instruments, such as XPS, SIMS, etc. However, the effects of molecular weight on chemical composition of the surface have not been quantified. Among the surface analysis techniques capable of yielding chemical composition information, such as XPS, SIMS, Auger, and ISS, XPS is the most widely used. The most attractive features of XPS are its ability to differentiate chemical states and its accuracy in quantification. The probing depth of XPS ranges from approximately 10 to 70 Å¹⁸⁰. Since the PDMS-PEOX block copolymers in this study have well defined structures, it was possible to obtain a quantitative correlation between the molecular weight of the copolymers and the surface composition of the copolymers.

The surface chemical compositions of a series of poly(dimethylsiloxane-2-ethyl-2-oxazoline) block copolymers with the number average molecular weight of PDMS varying from 500 g/mol to 20,000 g/mol (all having essentially the same bulk composition of 20 % by wt. PDMS) were determined by XPS measurements. Preparation of samples for the measurements was discussed in Chapter III. Shown in Figure 4.2.4 is a typical XPS wide scan. Since silicon and nitrogen are unique to the poly(dimethylsiloxane) and poly(2-ethyl-2-oxazoline) blocks

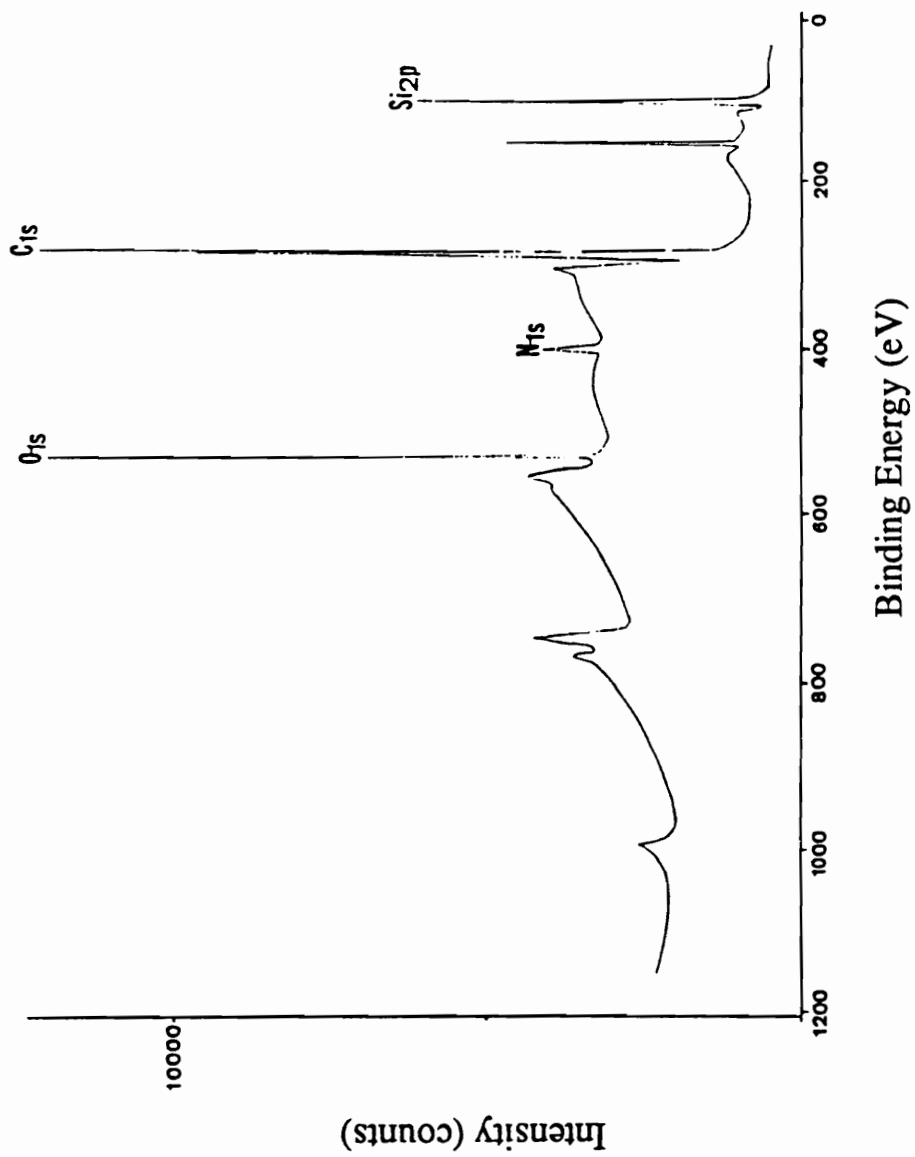


Figure 4.2.4 XPS Wide Scan of a PDMS-PEOX Block Copolymer

respectively, the areas under the XPS Si_{2p} peak and the N_{1s} peak can be directly related to the chemical composition of the sampled depth. The weight percentage of PDMS in the copolymer was calculated by the following equation:

$$\text{wt \% PDMS} = \frac{\frac{\text{area of Si}_{2p}}{\text{sensitivity factor}} \times 74}{\text{numerator} + \frac{\text{area of N}_{1s}}{\text{sensitivity factor}} \times 99}$$

where the sensitivity factor 457.916 for Si_{2p} and 552.978 for N_{1s} determined for this instrument was used, 74 is the molecular weight of PDMS repeating unit, and 99 is the molecular weight of PEOX repeating unit.

The results are summarized in Figure 4.2.5. Two electron take-off angles corresponding to two sampling depths into the surface (15° angle sampling less depth into the surface, ca. 10-20 Å) were investigated. In both cases, as expected, the weight percentage of PDMS on the surface is much higher than that in the bulk, indicating that all surfaces are preferentially enriched by PDMS. Figure 4.2.5 further indicates that weight percentages of PDMS at the 15° take-off angle are greater than those at 90°, implying thin PDMS-rich overlayers on the copolymer films. A second observation was a nonlinear dependence of surface concentration of PDMS on the molecular weight of the block. In the higher molecular weight range (M_n of PDMS > 2000g/mol), the surface concentration of PDMS increased with increasing PDMS block length. This agrees with the

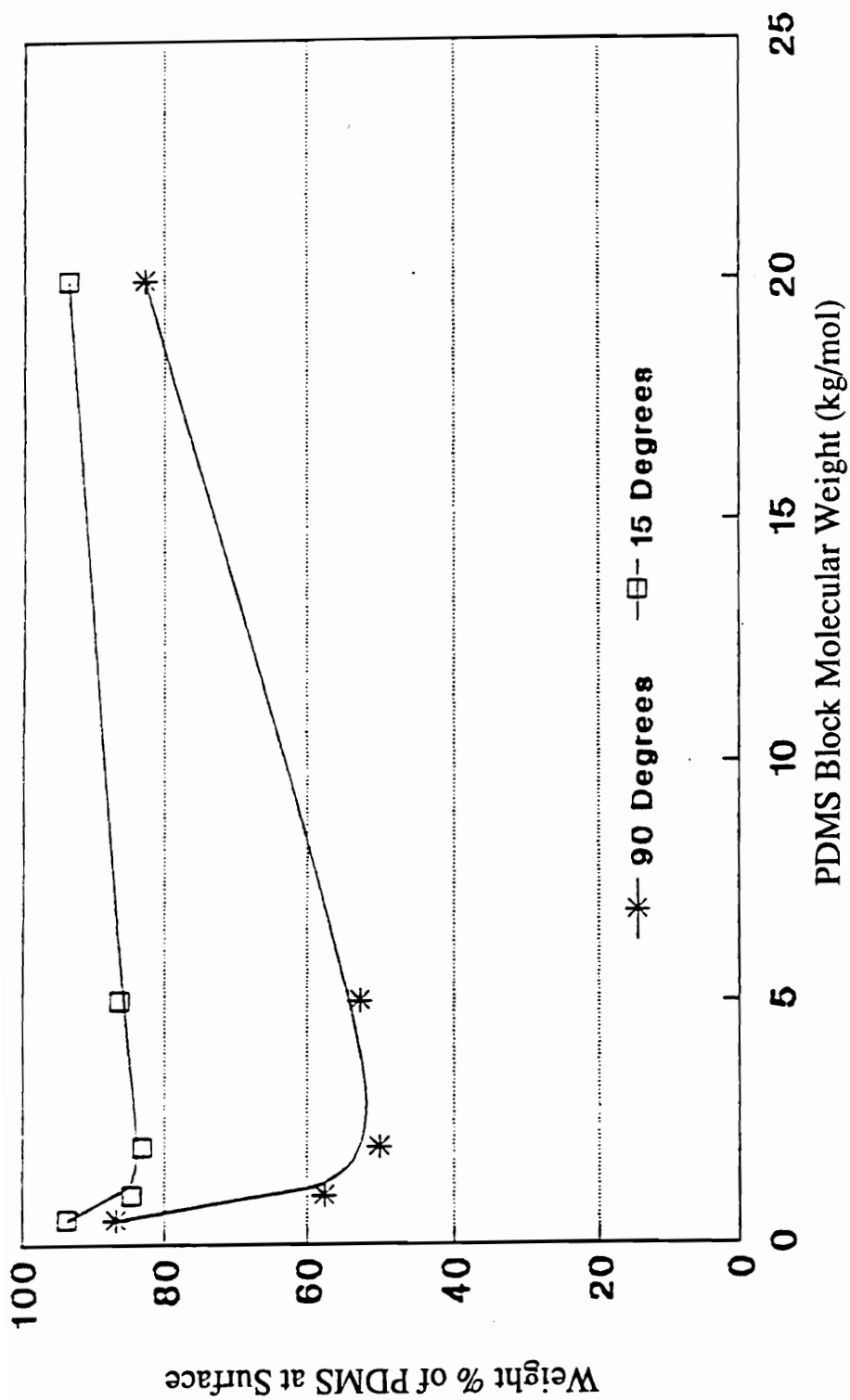


Figure 4.2.5 Surface Composition of PDMS-PEOX Block Copolymers (Bulk Compositions of 20 wt. % PDMS) as a Function of PDMS Block Molecular Weight

observation on polycarbonate-PDMS containing block copolymers¹³⁶, and can be rationalized by the phase separation behavior of block copolymers. Increasing block length of PDMS would lead to better phase separation and increasing PDMS phase thickness. Many studies¹⁷⁹ suggested an overlayer coverage of PDMS on the surface of PDMS containing copolymers. If this is true, then increasing the thickness of PDMS layer should increase the surface concentration of PDMS as probed by XPS, which is a weighted average of the top layer from approximately 10 - 70 Å.

At the lower end of the molecular weight scale (M_n of PDMS < 2000g/mol), the surface concentration of PDMS increased with decreasing PDMS block length. Repeated experiments confirmed this is not experimental error. This cannot be explained by the theory of the phase separation dependence on molecular weight. According to traditional bulk phase separation theory, decreasing molecular weight would lead to less phase separation, and less PDMS at the surface. The observation was to the contrary. One possible explanation is that low molecular weight block copolymers behave differently at a surface. The block length of both PDMS and PEOX were probably too short to behave like a random coil. As a matter of fact, PDMS with M_n of 500 g/mol only contains about 7 repeat units, far below the critical (entanglement) molecular weight of PDMS, i.e. 30,000 g/mol¹⁸¹. In addition, the very low surface tension of PDMS should serve as an extra driving force for phase separation to occur at the surface. They may form a single layer of PDMS as in the case

of monolayer formed by fatty acid on water surface. This speculation need to be confirmed by further experiment.

D. Thermal Properties

The solid state phase separation behavior of these block copolymers were evaluated by investigating glass transition temperatures of the two blocks by DSC. The DSC traces are shown in Figure 4.2.6 with Tg's summarized in Table 4.2.3. The curves in Figure 4.2.6 are arranged in order of increasing molecular weight from top to bottom. By DSC, no transition could be detected around -124°C , the glass transition for PDMS, while there were transitions between 25°C to 75°C corresponds to the Tg of PEOX. The Tg increased with increasing molecular weight. Only one copolymer (20K-80K) had a Tm of PDMS around -48°C . These observations, in general, agreed with those found for another set of PDMS containing copolymers with similar weight percentages and molecular weights of PDMS, namely, PDMS-g-poly(1-butene sulfone)¹⁸². No detectable PDMS Tg was probably due to the low wt % of PDMS in the copolymer. The crystallinity of PDMS would lower the amorphous portion of PDMS, making the amount of amorphous PDMS even smaller in the copolymer which showed a Tm and the detection of PDMS Tg harder. The increasing PEOX Tg with increasing block length is probably caused by the combination of the molecular weight dependence of the PEOX Tg together with the increasing level of phase separation as the block lengths were increased. Comparison

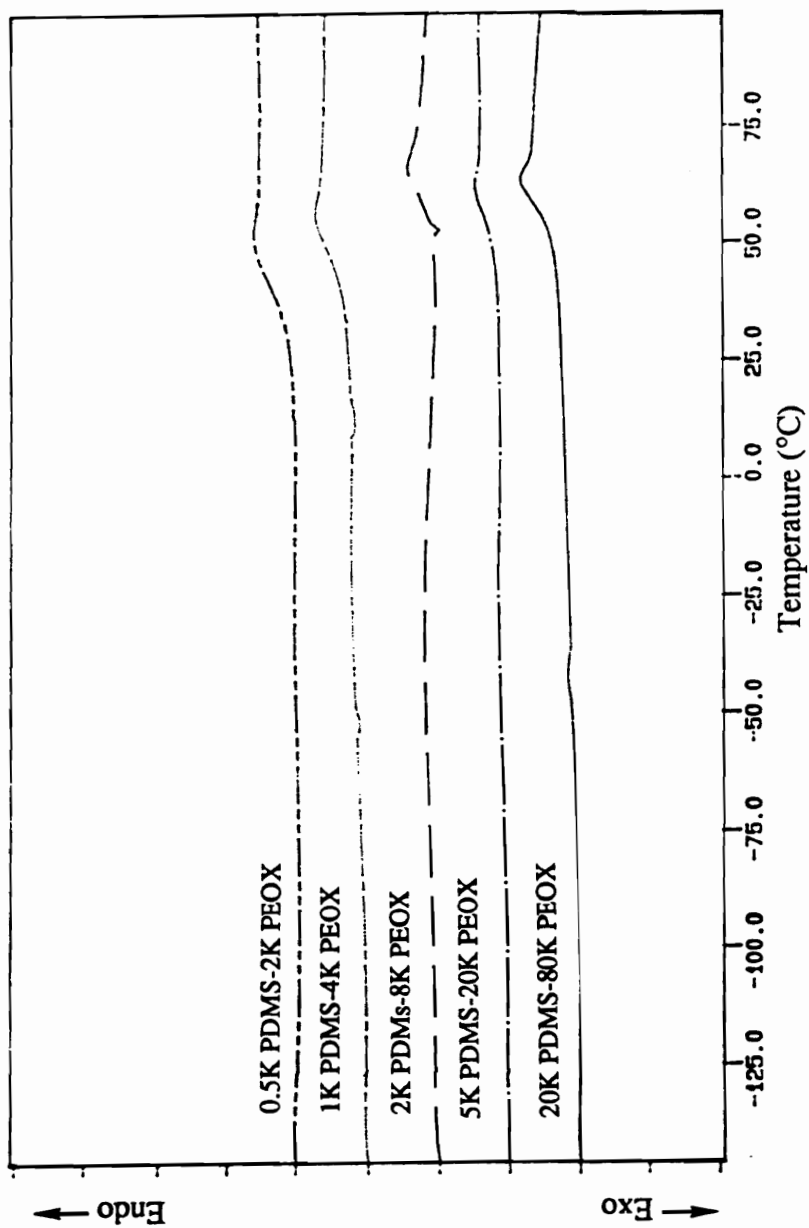


Figure 4.2.6 DSC thermograms of PDMS-PEOX block copolymers

Table 4.2.3 DSC Results on PEOX homopolymers and PDMS-b-PEOX copolymers

Sample (kg/mol)	PEOX T _g (°C)	PDMS T _g (°C)	PDMS T _m (°C)
PEOX 5K	50		
PEOX10K	54		
PEOX 30K	56		
PDMS17K		-124	-48, -37
0.5K PDMS-2K PEOX*	38	NTD	NTD
1K PDMS-4K PEOX	47	NTD	NTD
2K PDMS-8K PEOX	57	NTD	NTD
5K PDMS-20K PEOX	55	NTD	NTD
20K PDMS-80K PEOX	56	NTD	-42

* 0.5K PDMS-2K PEOX = 0.5kg/mol PDMS-b-2kg/mol PEOX

** ND = No Transition Detected

of the PEOX block Tg's with those of PEOX homopolymers of similar molecular weights (using identical DSC heating-cooling cycles) suggests that essentially complete phase separation was probably achieved for block copolymers with molecular weights of PDMS larger than 1000g/mol and molecular weights of PEOX larger than 4000g/mol.

4.3 Poly(alkyl vinyl ether-2-ethyl-2-oxazoline) Block Copolymers

4.3.1 Synthesis

Preparation of poly(alkyl vinyl ether-2-ethyl-2-oxazoline) block copolymers with well defined structures in terms of molecular weight control and narrow molecular weight distributions is of great interest from both the fundamental synthetic and applied points of view. Chemically well defined structures require that two "living" polymerization systems be joined together to form the block copolymers. In this particular case, it was a great challenge to link the two systems without adversely affecting the "living" characteristics of either system. The ultimate objectives in this work is to use these well defined structures to study factors important for blend emulsification and for steric stabilization of concentrated dispersions. Other groups have established that living poly(alkyl vinyl ether)s can be prepared by using HI/ZnI₂ initiating systems^{114,115}. As discussed in section 4.1, it is also known that polymer chains of 2-alkyl-2-oxazolines are "long lived". In this study, living techniques, characteristic of both system, were utilized to afford well defined poly(alkyl vinyl ether-2-ethyl-2-oxazoline) diblock copolymers.

Perhaps the easiest way to make diblock copolymers out of two "living" cationic polymerization systems is sequential monomer addition providing that the crossover reaction from one polymer system to the second is allowed. This method was actually

demonstrated for these types of copolymers by Saegusa and coworkers⁵⁰, where 2-oxazoline monomers were added directly to living poly(alkyl vinyl ether)s. Unfortunately this procedure leads to an unstable linkage between the two blocks since the terminal carbon atom of the vinyl ether segment is connected to two electronegative elements - oxygen and nitrogen. The alternative addition sequence, i.e. adding alkyl vinyl ether to living poly(2-alkyl-2-oxazoline)s, is probably not feasible, because alkyl vinyl ethers are less reactive than 2-alkyl-2-oxazolines. Therefore, in this work, these block copolymers are synthesized in two steps. Several methods were tried. Although all were not successful, each illustrate interesting points with respect to the preparation of well defined block copolymers. Thus a discussion of several methods, some successful and some unsuccessful, follows.

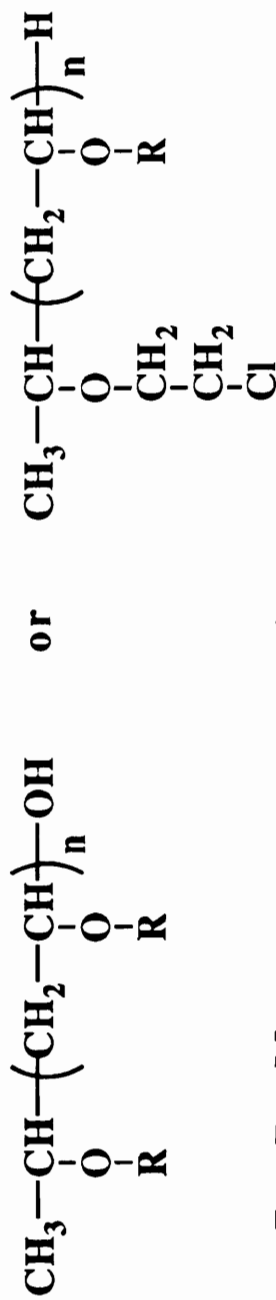
Since 2-alkyl-2-oxazolines can be initiated by methyl tosylates, butyl mesylates, benzyl halides, and alkyl halides, potential methods for preparation of the block copolymers involved preparing monofunctional poly(alkyl vinyl ether)s with one of these functionalities, then using them as macroinitiators for the polymerization of 2-alkyl-2-oxazolines. It has been established in our lab that poly(alkyl vinyl ether)s can be terminated with K_2CO_3/H_2O to afford aldehyde endgroups, and subsequently these endgroups can be converted into hydroxyl groups¹⁸³. Converting these hydroxyl groups into either tosylates or mesylates affords monofunctional poly(alkyl vinyl ether)s capable of initiating the

polymerization of 2-alkyl-2-oxazolines. This constitutes the first potential method. A second potential method investigated was to incorporate an alkyl halide or benzyl halide into poly(alkyl vinyl ether)s at the head of the polymer. These two general themes of preparing poly(alkyl vinyl ether-b-2-ethyl-2-oxazoline)s are depicted in scheme 4.3.1.

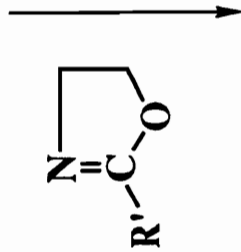
Terminator method

To obtain block copolymers with well defined structures, it is important to make the macroinitiators (monofunctional poly(alkyl vinyl ether)s) 100% or very close to 100% functionalized. The conditions for obtaining such highly functionalized poly(alkyl vinyl ether)s were established through model studies using n-butanol as the substrate. A slight excess of p-toluenesulfonyl chloride was used in converting hydroxyl groups into tosylates to ensure quantitative conversion of n-butanol. The excess amount of p-toluene sulfonyl chloride had to be removed before the addition of 2-alkyl-2-oxazoline, because p-toluenesulfonyl chloride was also shown to be an initiator for 2-methyl-2-oxazoline⁶¹. Unfortunately, the moisture sensitive nature of butyl tosylate together the high boiling point of p-toluenesulfonyl chloride (146°C/15mm) rendered this clean up procedure very difficult. Thus due to the relatively low boiling point of methanesulfonyl chloride (60°C/21mm), it was substituted in this procedure. The reaction procedures discussed in Chapter III were based on that of Crossland's¹⁸⁴ with some modification. Larger

**Scheme 4.3.1 Synthetic Pathways for
Poly(alkyl vinyl ether-b-2-alkyl-2-oxazoline)**



R = Bu, Me



R' = Et, Me

poly(alkyl vinyl ether)-b-poly(2-alkyl-2-oxazoline)

excess of triethylamine and methanesulfonyl chloride were used to ensure quantitative conversion. Addition of hexanes at the end of the reaction facilitated the precipitation of Et_3NHCl salt and its filtration, which was necessary in the preparation of macroinitiators. Under these conditions the conversion of n-butanol to n-butyl mesylate was quantitative as determined by ^1H NMR (Figure 4.3.1). The absence of peaks at $\delta 3.63\text{ppm}$ due to $-\underline{\text{C}}\text{H}_2\text{-OH}$ (Figure 4.3.1 a) and the presence of peaks at $\delta 4.23\text{ppm}$ corresponding to $-\underline{\text{C}}\text{H}_2\text{-OS(O}_2\text{)CH}_3$ in Figure 4.3.1 b indicated quantitative conversion. Using the same procedures, hydroxy-terminated poly(butyl vinyl ether)s were converted into the corresponding mesylate-terminated oligomers. Addition of 2-methyl-2-oxazoline monomer to these oligomers yielded poly(butyl vinyl ether-b-2-methyl-2-oxazoline) (scheme 4.3.2). Low molecular weight PBVE, such as 1000 g/mol, was soluble in NMP, allowing for the use of a single solvent in the copolymer synthesis. The copolymers were isolated via precipitation into diethyl ether. A portion of the materials remained soluble in the precipitation mixture and was recovered by simple solvent evaporation. Both portions were soluble in chloroform. ^1H NMR of these two portions in CDCl_3 (Figure 4.3.2) revealed that their compositions were different. In one case where the theoretical weight percentage of poly(2-methyl-2-oxazoline) in the copolymer was 50%, the ether soluble portion was analyzed as being 20% oxazoline while the ether insoluble portion was 90% oxazoline. Clearly the copolymer was badly fractionated in terms of

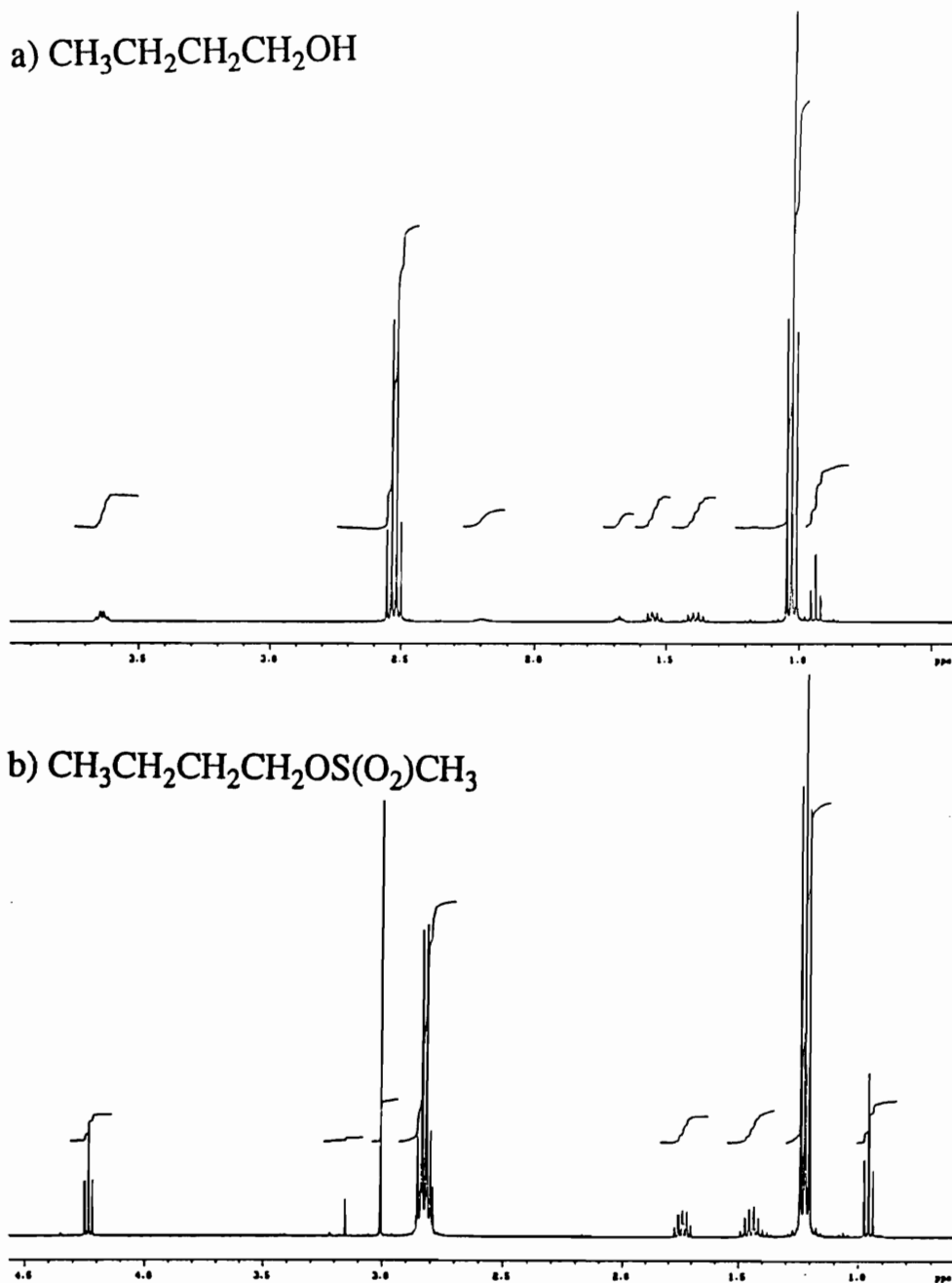
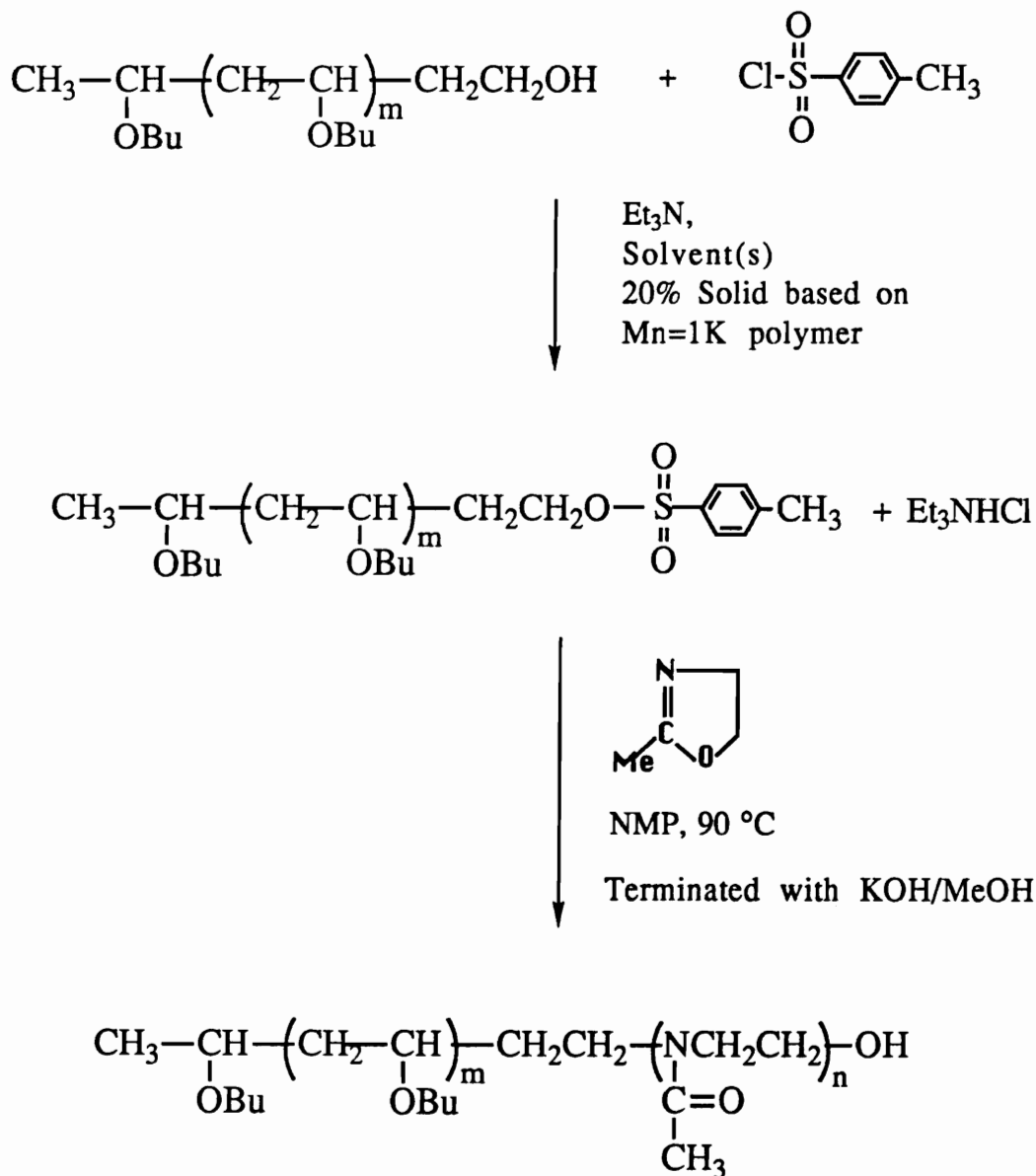


Figure 4.3.1 ^1H NMR of a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + (\text{CH}_3\text{CH}_2)_3\text{N}$
 b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OS}(\text{O}_2)\text{CH}_3 + (\text{CH}_3\text{CH}_2)_3\text{NHCl} + (\text{CH}_3\text{CH}_2)_3\text{N}$

**Scheme 4.3.2 Synthesis of
Poly(butyl vinyl ether-b-2-methyl-2-oxazoline)**



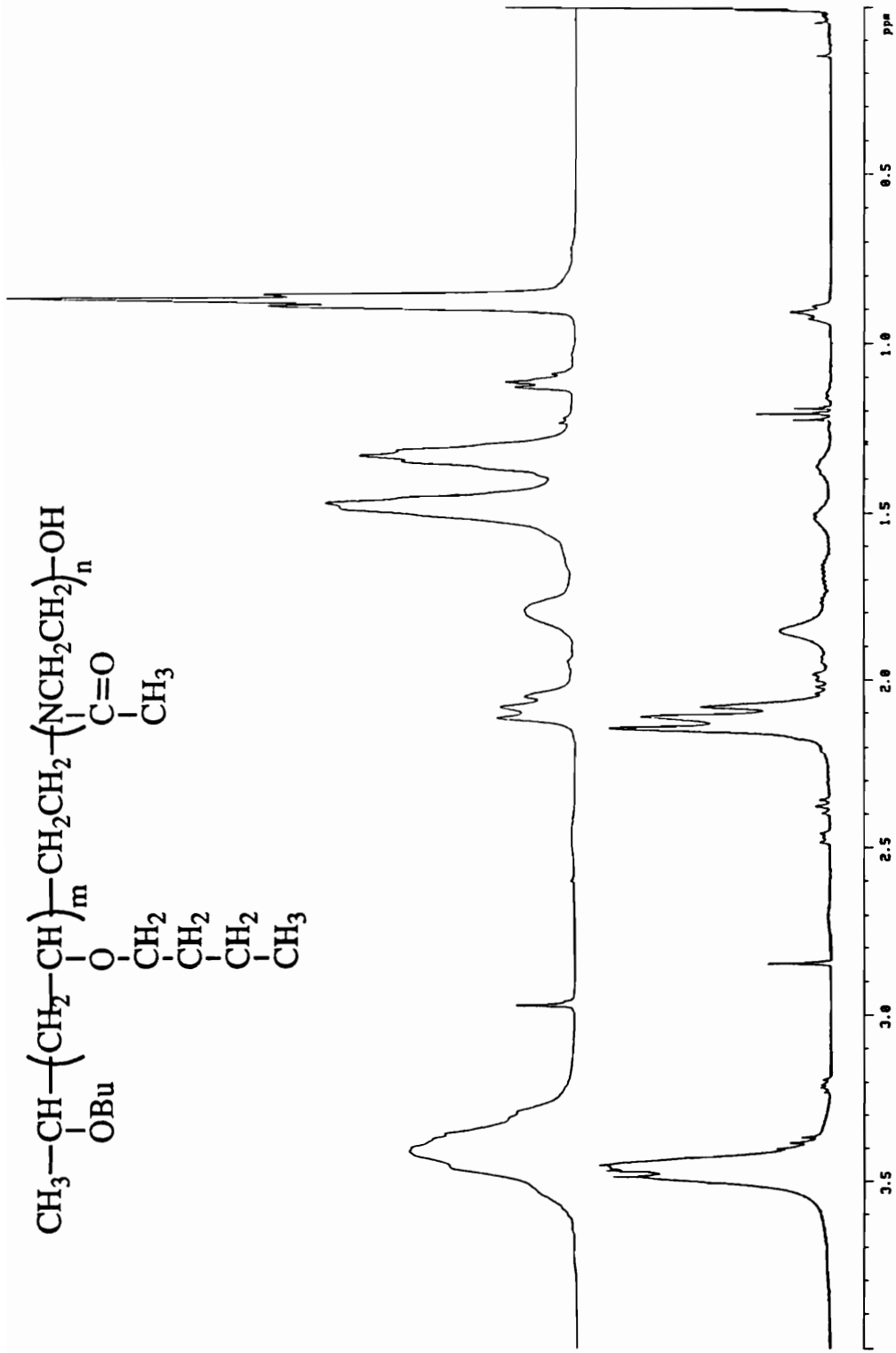


Figure 4.3.2 ¹H NMR of PBVE-b-PMOX copolymer

a) diethyl ether precipitant, b) diethyl ether soluble portion

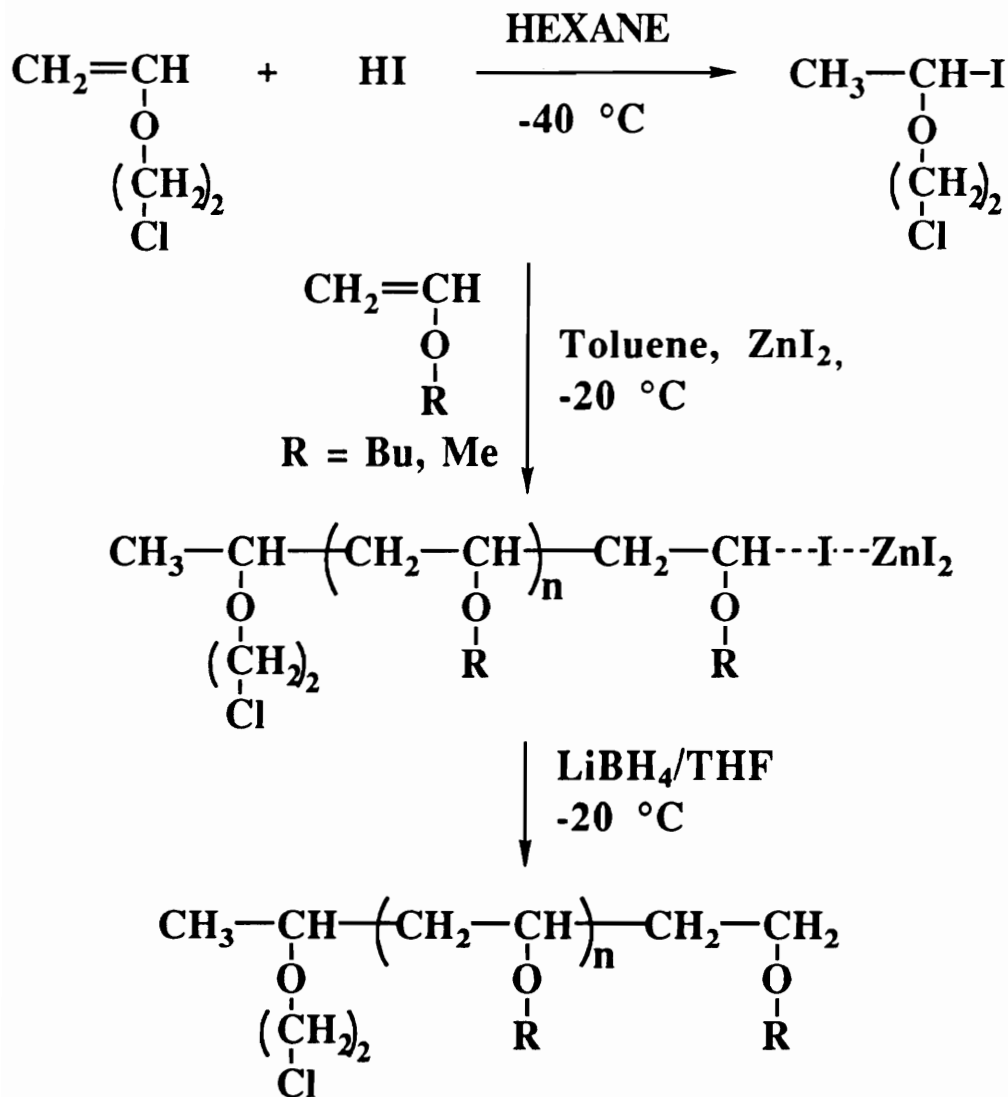
composition. It was speculated that this inhomogeneity in composition was caused by very slow initiation rates compared to propagation rates using mesylates as initiators (section 4.1). Therefore no further investigations using this method was pursued.

Initiator Method

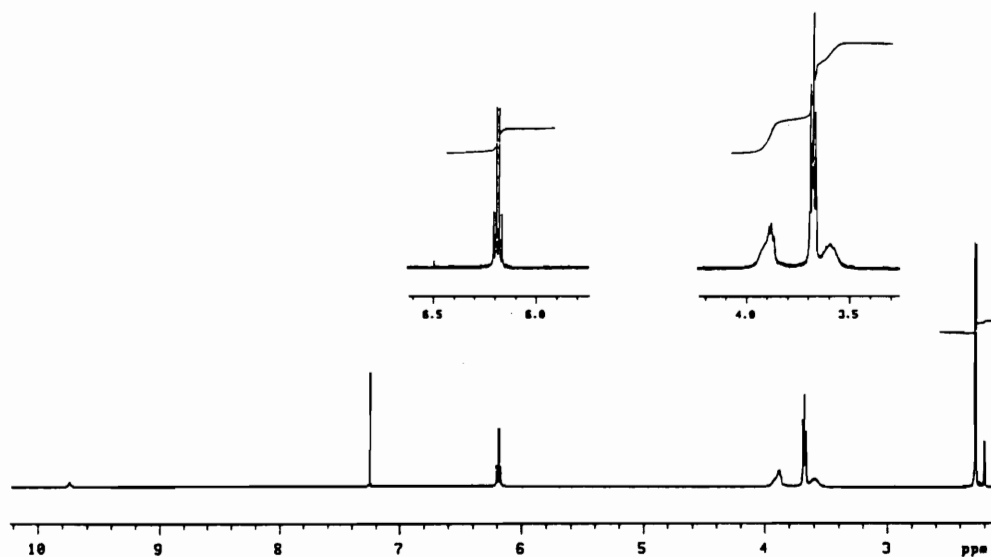
In this method, an alkyl halide functional group was incorporated into the poly(alkyl vinyl ether) chains at their head. Chloroethyl vinyl ether (CIEVE) together with HI/ZnI₂ was used as the initiating system for the polymerization of butyl and methyl vinyl ethers (BVE, MVE) as depicted in scheme 4.3.3. In the first step, HI was added across the double bond of chloroethyl vinyl ether. Figure 4.3.3 illustrates the ¹H NMR spectrum of the resultant vinyl ether initiator. The quartet at δ6.2ppm is due to the only methine proton in the product. The unusual downfield shift is caused by both oxygen and iodide. This product was very unstable. Hence a rather low temperature(-40°C) was used in this first step to avoid any decomposition of the adduct.

In the second step, prechilled BVE monomer or MVE monomer in toluene was added to the preformed HI/CIEVE adduct. Addition of ZnI₂ promoted the crossover reaction between BVE or MVE to the HI/CIEVE adduct and propagation ensured. After stirring for one hour, the temperature was raised to -20°C or higher to speed up the propagation process. The reactivities of both the monomer and the substrate (the adduct) favored the crossover reaction. First, in terms

**Scheme 4.3.3 Monofunctional
Poly(alkyl vinyl ether) Oligomers**



b) Chloroethyl vinyl ether/HI adduct



a) Chloroethyl vinyl ether

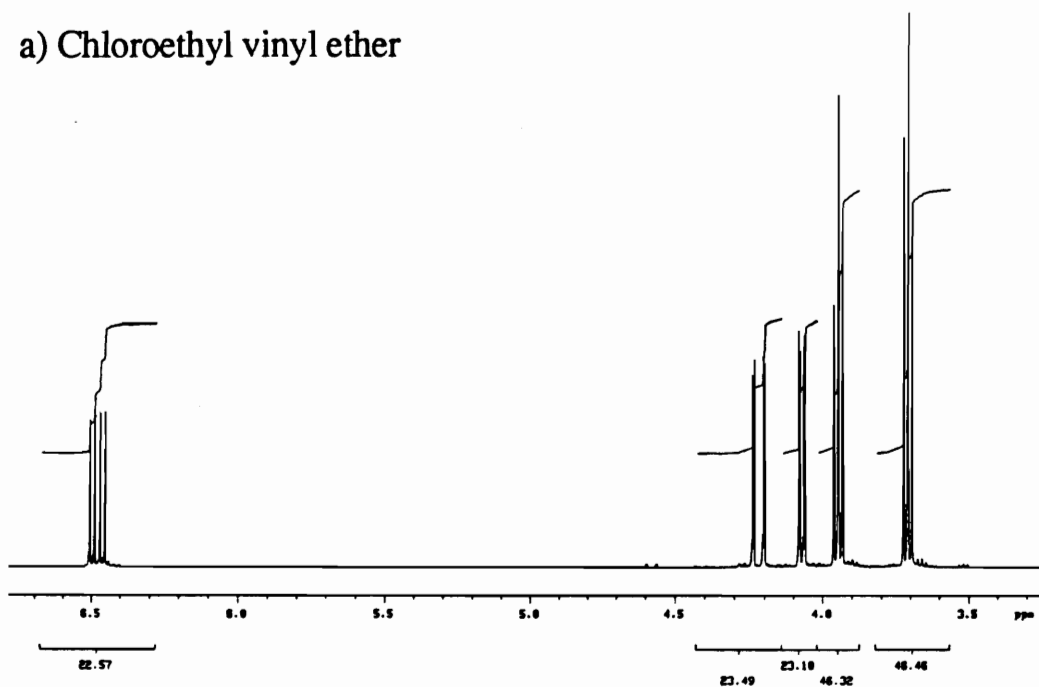


Figure 4.3.3 ^1H NMR of a) Chloroethyl vinyl ether
b) Chloroethyl vinyl ether/HI adduct

of the reactivity of the monomer, both BVE and MVE are more electron rich than ClVE (which has an electron withdrawing chlorine group). Thus it would be expected that BVE or MVE would be more reactive toward an electrophilic substrate than ClVE. Secondly, in terms of reactivity of the substrate, the electron withdrawing effect of the chloride in ClVE would cause the HI/ClVE adduct to be less stable and thus more reactive than an adduct of HI/BVE or HI/MVE would be. The importance of this matching in reactivity to effect a successful crossover reaction between an adduct and a second monomer was further demonstrated by the unsuccessful crossover reaction between a HI/vinyl benzyl chloride adduct and MVE, and also between a HI/MVE adduct and vinyl benzyl chloride as will be discussed later in this section.

Following completion of propagation, the living chain ends of monofunctional poly(alkyl vinyl ether) oligomers were terminated by lithium borohydride in THF at low temperatures (-20°C), affording monofunctional oligomers. Termination of living poly(alkyl vinyl ether)s has been the subject in many studies^{107,109,125,183}. There are two major aspects concerning termination: (1) stability of the endgroup; and (2) elimination as a side reaction. Since the living chain ends contain the C-O linkage, termination with heteroatom containing nucleophiles such as hydroxy and amines generate unstable hemiacetal or aminal linkages. Strong bases as nucleophiles may cause side reactions such as elimination. Among those are alkyl anions. Less basic carbanions, such as the enolate ion generated from

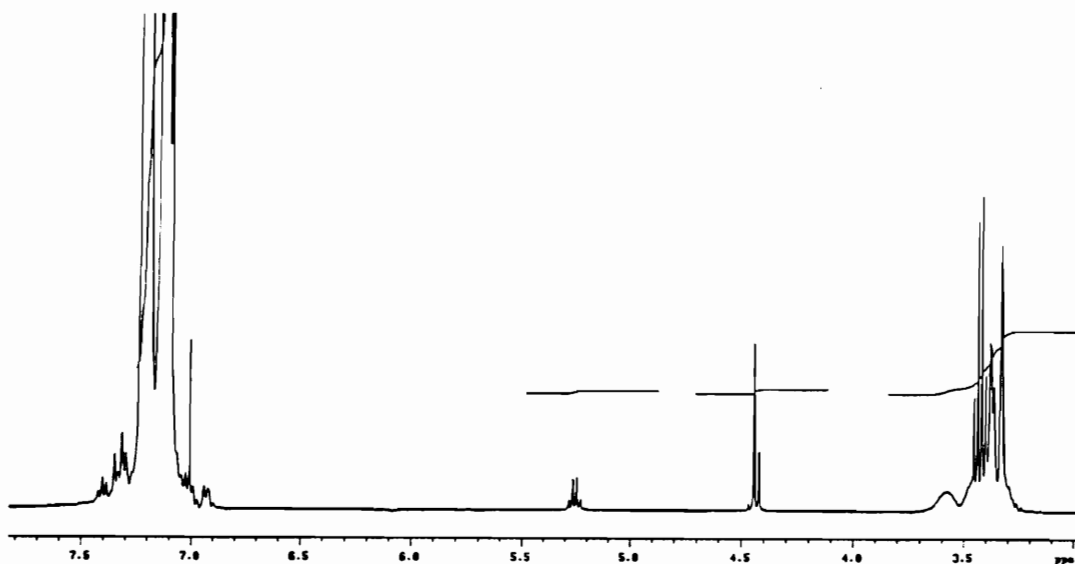
β -dicarbonyl compounds (1,3-keto esters), have been used successfully to terminate poly(alkyl vinyl ether)s¹⁰⁹. Based on these considerations, lithium borohydride was used as terminating agent to afford nonfunctional endgroups. Caution was taken to avoid any side reactions by doing the termination at low temperature -20°C . The last step in the termination procedures was to decompose the excess lithium boron hydride by water before the temperature was raised. One of the decomposition products was hydrogen which was observed immediately upon addition of several drops of water. The temperature of the solution was maintained to be less than -19°C by adjusting the addition speed. These precautions were taken to avoid any substitution reactions between hydride and the ethyl chloride on the chains. Any substitution reaction would yield oligomers with less than 100% functionality which is undesirable for the preparation of well defined block copolymers.

As described in section 4.1, it would be much more desirable to have a benzyl halide functional macroinitiator than an alkyl halide initiator due to the relative initiation rates of these two types of molecules toward 2-alkyl-2-oxazolines. Attempts were made to incorporate such a functionality into poly(methyl vinyl ether)s by using vinyl benzyl chloride. The double bond of vinyl benzyl chloride is less electron rich than MVE, thus less reactive toward a given substrate. This suggests that vinyl benzyl chloride should be used to form the HI/VBC adduct first so that MVE could add to the substrate quantitatively. On the other hand, the vinyl benzyl

chloride/HI adduct is more stable and thus less reactive than a HI/MVE adduct due to the resonance effect of the phenyl ring, suggesting that the HI/MVE adduct should be formed first. These conflicting reactivities rendered the crossover reaction between the two set of monomers, substrates unsuccessful. In fact Cho has found that electron donating groups on the phenyl ring of styrene type monomers were required for successful crossover from the reactive polymer chain end of vinyl ethers¹⁸⁵. The reversed addition sequence i.e. add MVE to HI/VBC was not successful either. Shown in Figure 4.3.4 are the ¹H NMR spectrum of HI/VBC adduct, (a), and that after addition of MVE, (b), in which no evidence of the reaction between MVE and the HI/VBC adduct was observed, even though MVE may have been polymerized by residual HI.

Quantitative functionalization and termination of these oligomers was established by quantitative ¹³C NMR. Peak assignments were based on two types of NMR experiments: heteronuclear correlated spectroscopy (2D), and DEPT (Distortionless Enhancement by Polarization Transfer), performed on both PBVE and PMVE oligomers. Figure 4.3.5 depicts the 2D spectrum of 1K PBVE oligomer. Also shown are the 1D proton (horizontal axis) and carbon-13 (vertical axis) spectra. The cross points on the 2D plane indicate that the corresponding proton on the ¹H axis and the corresponding carbon on the ¹³C axis are connected. Several peaks are present on the ¹³C axis connected to protons in the δ 3.0 - δ 3.5 ppm region, (which is the possible chemical shift region for methylene protons on

b) VBC/HI Adduct + Methyl Vinyl Ether (t = 2 hrs.)



a) Vinyl Benzyl Chloride

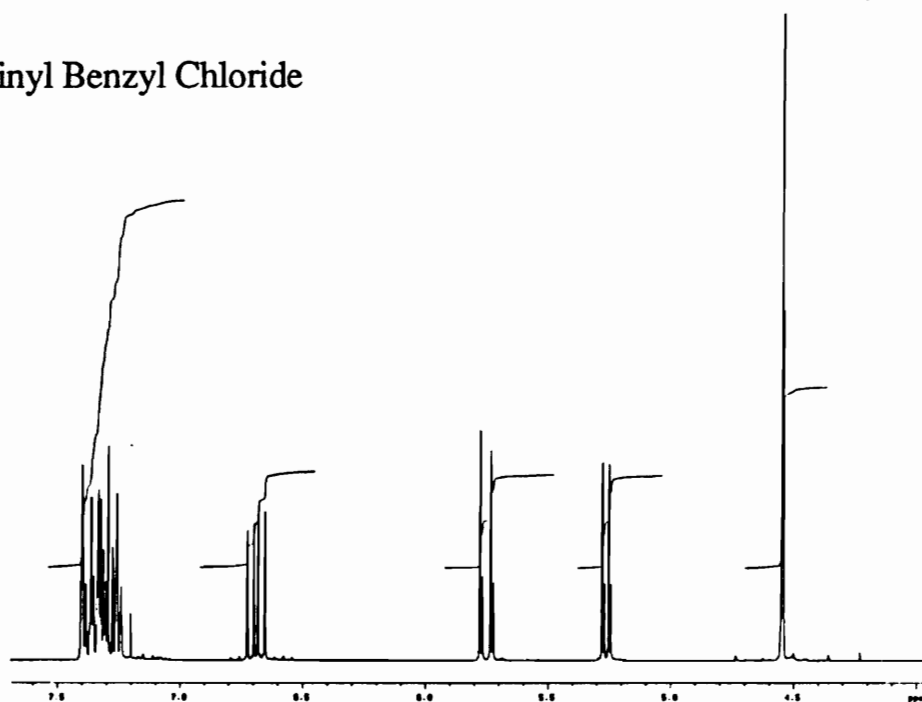


Figure 4.3.4 ¹H NMR of a) Vinyl Benzyl Chloride (VBC)
b) VBC/HI Adduct + Methyl Vinyl Ether
(t = 2 hrs.)

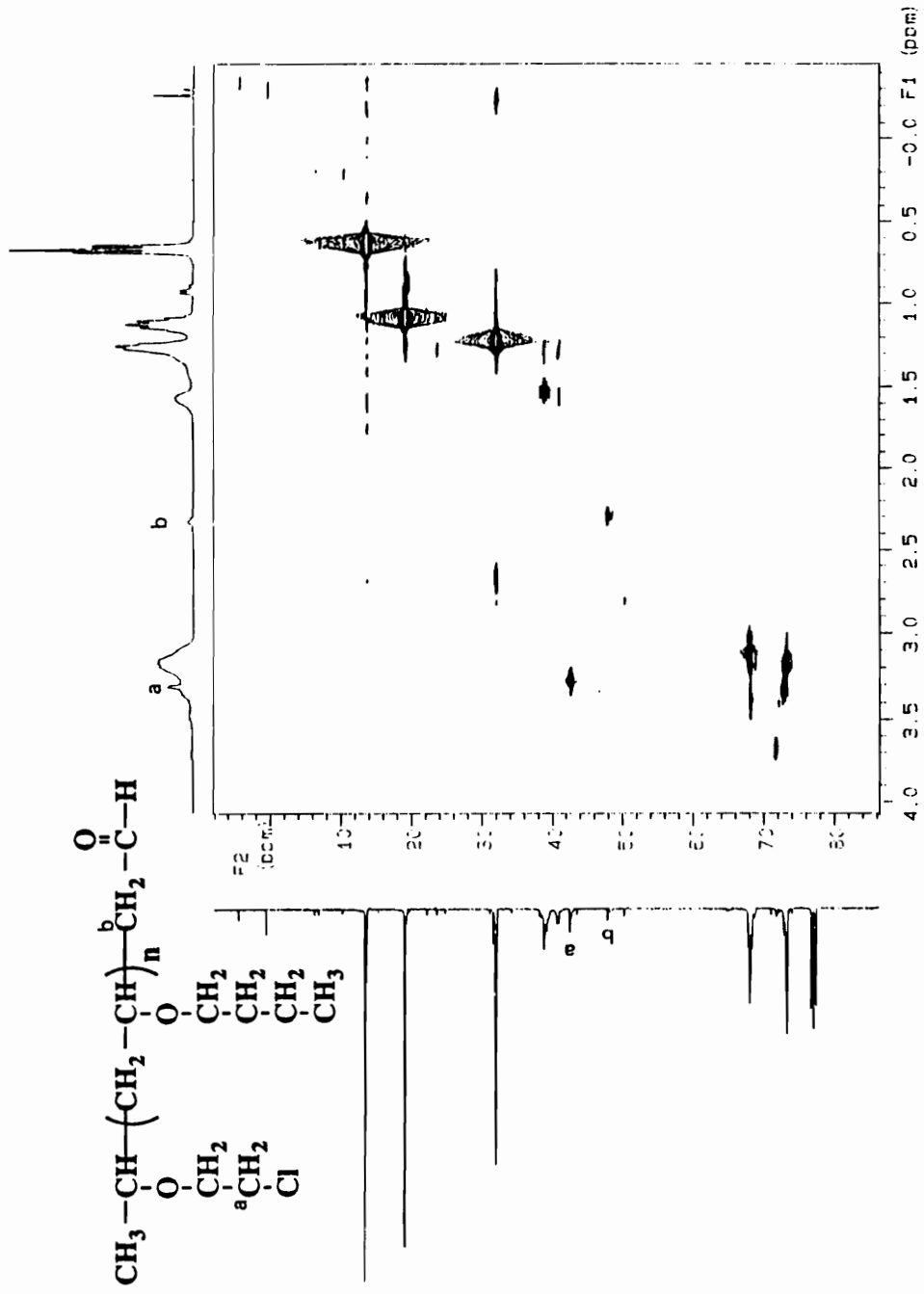


Figure 4.3.5 Identification of endgroups of PBVE (1K) by 2-D NMR

a carbon connected to a chloride), i.e. 43ppm, 68ppm, and 73ppm. Only the 43ppm peak on the ^{13}C axis is in the chemical shift region corresponding to methylene carbons bonded to chloride¹⁸⁶. Thus the 43ppm peak on the carbon spectrum was identified as the methylene carbon connected to the chloride. The chemical shifts of nonfunctional endgroups were determined using DEPT. Figure 4.3.6 depicts the DEPT spectra of a 2K PMVE. Based on their concentrations, only small peaks were attributed to endgroups. Two small peaks, labeled a and g, appear due to methyl carbons (the unlabeled methyl peak is residual toluene). Peak a has been assigned to the methyl carbon at the chain head. Peak g is further downfield, indicative of a methyl carbon connected to a heteroatom, and thus must be the last methoxy methyl. Similar logic was used when methylene carbons were assigned. Peak d had been determined by 2-D NMR as described above. Peaks c and f are assigned to carbons connected to heteroatoms. Since inductive effects decrease as the distance between bonds increases, peak c, which is further downfield than peak f, was assigned to the methylene carbon α to oxygen and β to chloride at the chain head, while peak f was assigned to the methylene carbon α to one oxygen and γ to another oxygen at the chain end. The only small peak remaining, e, had to be due to the methylene at the chain end. There was only one small methine carbon peak, b, assigned to the only methine in the endgroups. The fact that all resonances in the ^{13}C NMR spectra could be assigned, together with the fact that all

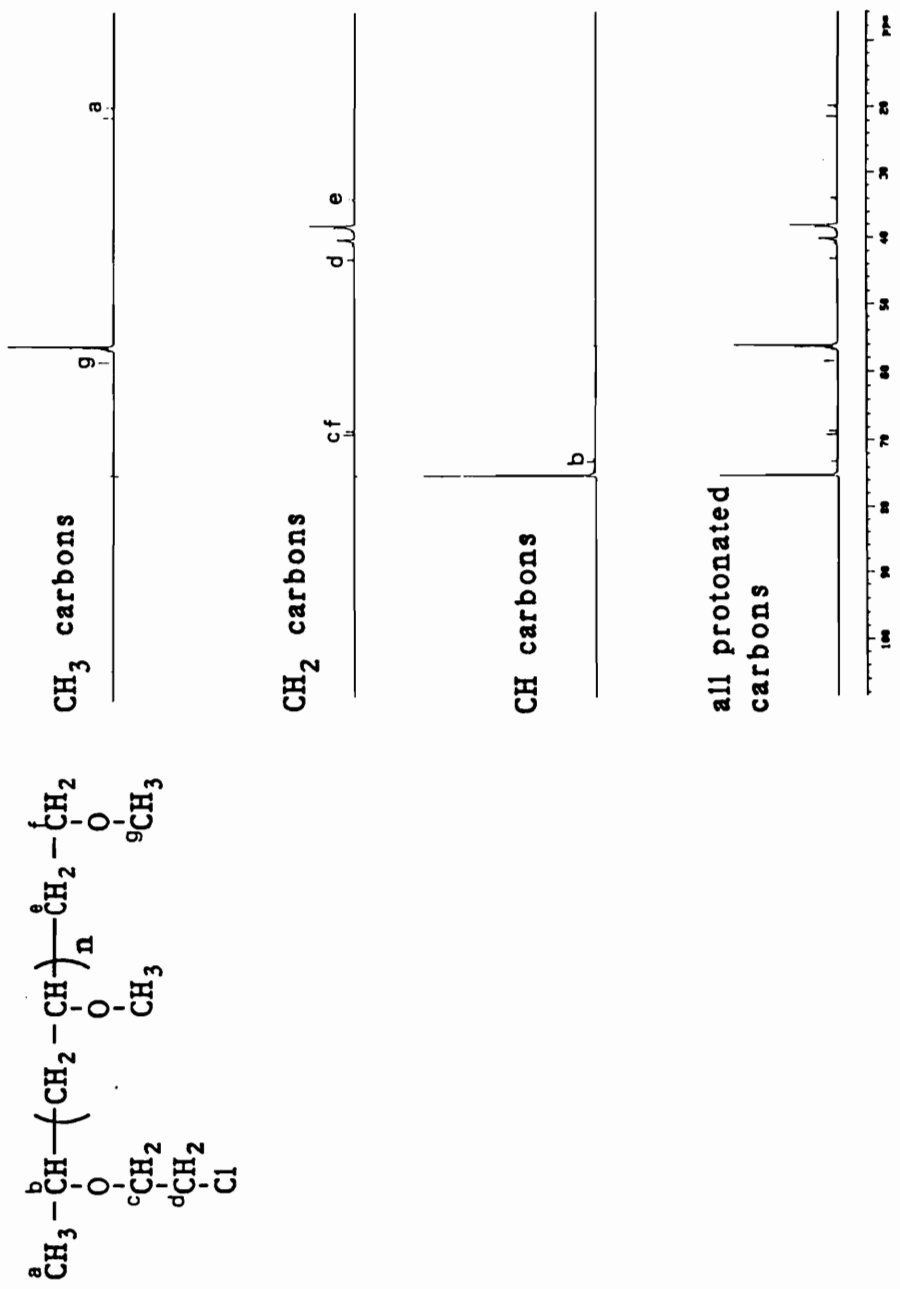


Figure 4.3.6 Identification of endgroups of monofunctional PMVE by DEPT

expected endgroup structures were accounted for, provided strong evidence (within the detection limits of ^{13}C NMR) that initiation and termination steps had proceeded as described. A quantitative ^{13}C NMR spectrum of the same 2K PMVE oligomer used in the DEPT experiment is shown in Figure 4.3.7. Integrations due to the endgroups correspond on a 1:1 basis as expected, i.e., the total number of chain heads equals the total number of chain ends, indicating quantitative functionalization. Thus termination using hydride under the conditions described was selective, without side reactions or replacement of chloride functionality.

A series of monofunctional PBVE and PMVE oligomers were prepared using the above procedures and used as macroinitiators to polymerize 2-ethyl-2-oxazoline, affording poly(alkyl vinyl ether-2-ethyl-2-oxazoline) block copolymers (scheme 4.3.4). The conditions for the polymerization of 2-ethyl-2-oxazoline using model initiators have been discussed in section 4.1. The use of NaI was, again, to convert the ethyl chloride functionality on the monofunctional poly(alkyl vinyl ether) to the more reactive ethyl iodide since ethyl chloride does not initiate the polymerization of 2-ethyl-2-oxazoline (section 4.1). Excess NaI (100% molar excess) was used to ensure complete reaction. However, without NMP added to the reaction mixtures, the polymerizations using the macroinitiators did not proceed as quickly as those using 1-chlorobutane as initiator. For example, to make 5K PEOX, it took more than twice as long when monofunctional 1K PBVE was used instead of 1-chlorobutane as the

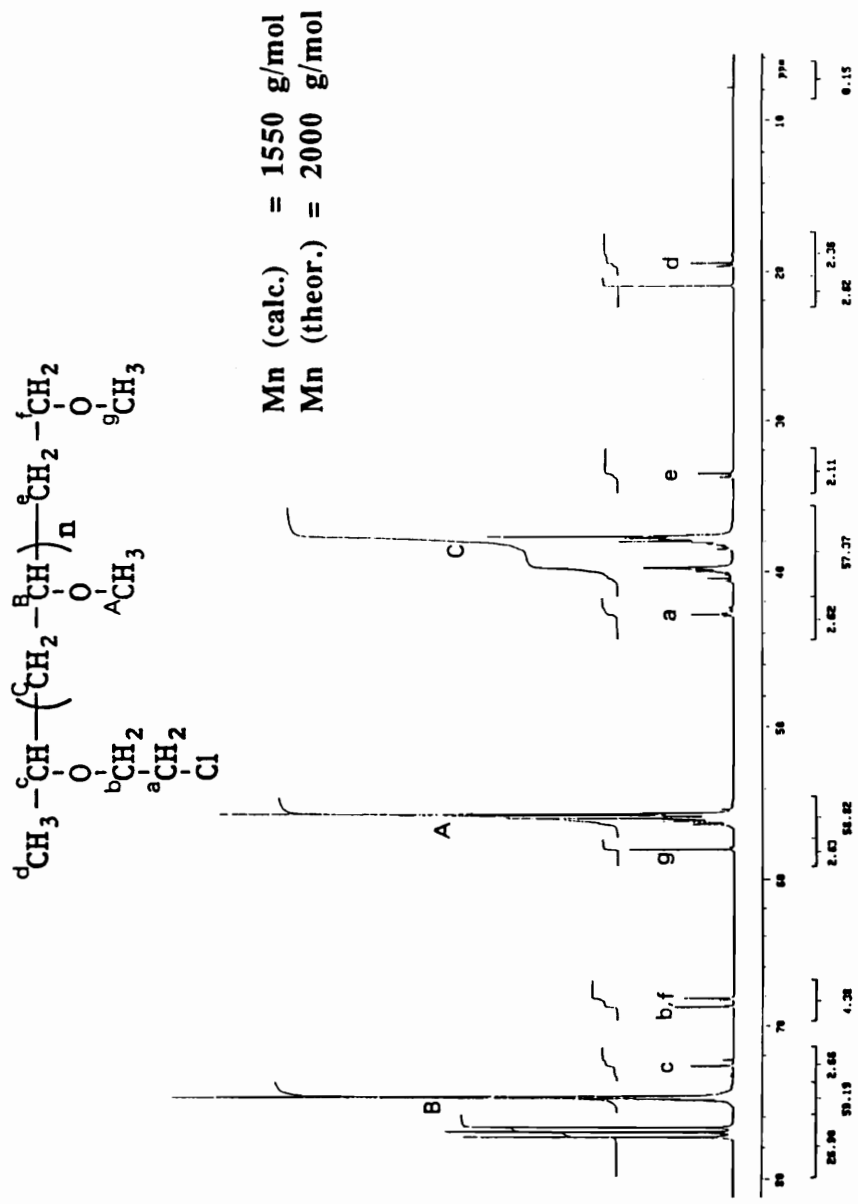
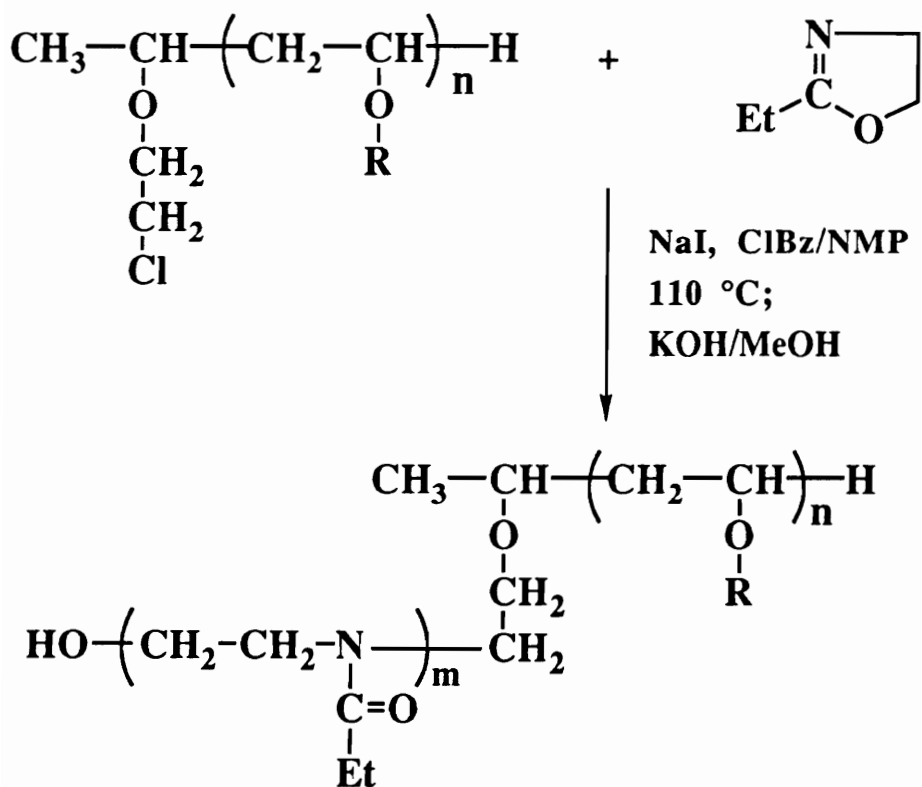


Figure 4.3.7 ¹³C NMR of ethyl chloride monofunctional PMVE

**Scheme 4.3.4 Synthesis of
Poly(alkyl vinyl ether-b-2-ethyl-2-oxazoline)s**



R = Bu, Me

initiator (76^+ hrs vs. ca. 36 hrs) under similar initiator and polymer concentrations. In fact, almost no poly(2-ethyl-2-oxazoline) could be detected after 12 hours of heating when the macroinitiator used. By contrast above 30% conversion was observed within the same period of time when 1-chlorobutane was used. It was reasoned that the exchange of iodide for chloride was causing an induction period. Since sodium iodide did not dissolve completely in the reaction mixture (macroinitiator, 2-ethyl-2-oxazoline, chlorobenzene), the rather poor solubility of sodium iodide was assumed to be the cause of the slow exchange. Thus, a small amount of NMP (1/6 v/v, of chlorobenzene) was added to dissolve sodium iodide. Then the solution of NaI in NMP was added to the solution of PMVE in chlorobenzene (36% wt/v). The mixture remained clear until it was heated at 110°C for ca. one hour. The appearance of cloudiness indicated the generation of sodium chloride, the product of iodide-chloride exchange. It has been determined in the model study (section 4.1) that only two hours were sufficient for complete iodide-chloride exchange. The macroinitiator reaction mixture was 1/3 as concentrated as the model reaction, thus it was heated for ca. 8 hours (more than the necessary $3 \times 2 = 6$ hrs) to ensure complete exchange. Then 2-ethyl-2-oxazoline monomer was added and the polymerization monitored by ^1H NMR. It took only ca. 36 hours to complete the polymerization of PEOX block with M_n of 10,000g/mol as compared to 72^+ hrs for PEOX block with M_n of 5000g/mol without NMP. Following propagation, the PEOX living ends were

terminated by KOH/MeOH. The copolymers were then washed with a saturated aqueous solution of Na_2SO_3 and then deionized water. Emulsion formation was observed during washing, indicating that these copolymers are surface active. The solvent combination, hexanes/toluene of 3/1 (v/v), which was initially used to precipitate the polymer solutions, resulted in copolymer fractionation. Therefore the copolymers were recovered by precipitating into hexanes. For high PMVE percentages in the copolymer i.e. 10K PMVE-5K PEOX, cold hexanes was used in order to obtain solid polymers as precipitants.

4.3.2 Characterization

A. Molecular weight and molecular weight distribution

The molecular weights and molecular weight distributions of monofunctional PBVE and PMVE were characterized by GPC, using polystyrene standards. Typical GPC peaks as shown in Figure 4.3.8 are sharp and symmetrical. The experimental molecular weights correlated well with the theoretical molecular weights calculated based on the feed ratio of monomer to initiator and the molecular weight of one repeating unit (Table 4.3.1). The molecular weight distributions are very narrow for these monofunctional oligomers, indicative of the living characteristics of the polymerization of BVE and MVE via the HI/CIEVE/ ZnI_2 initiating system.

In inspecting Table 4.3.1 more closely, it was noticed that the molecular weight distributions of PMVE began to broaden at an Mn

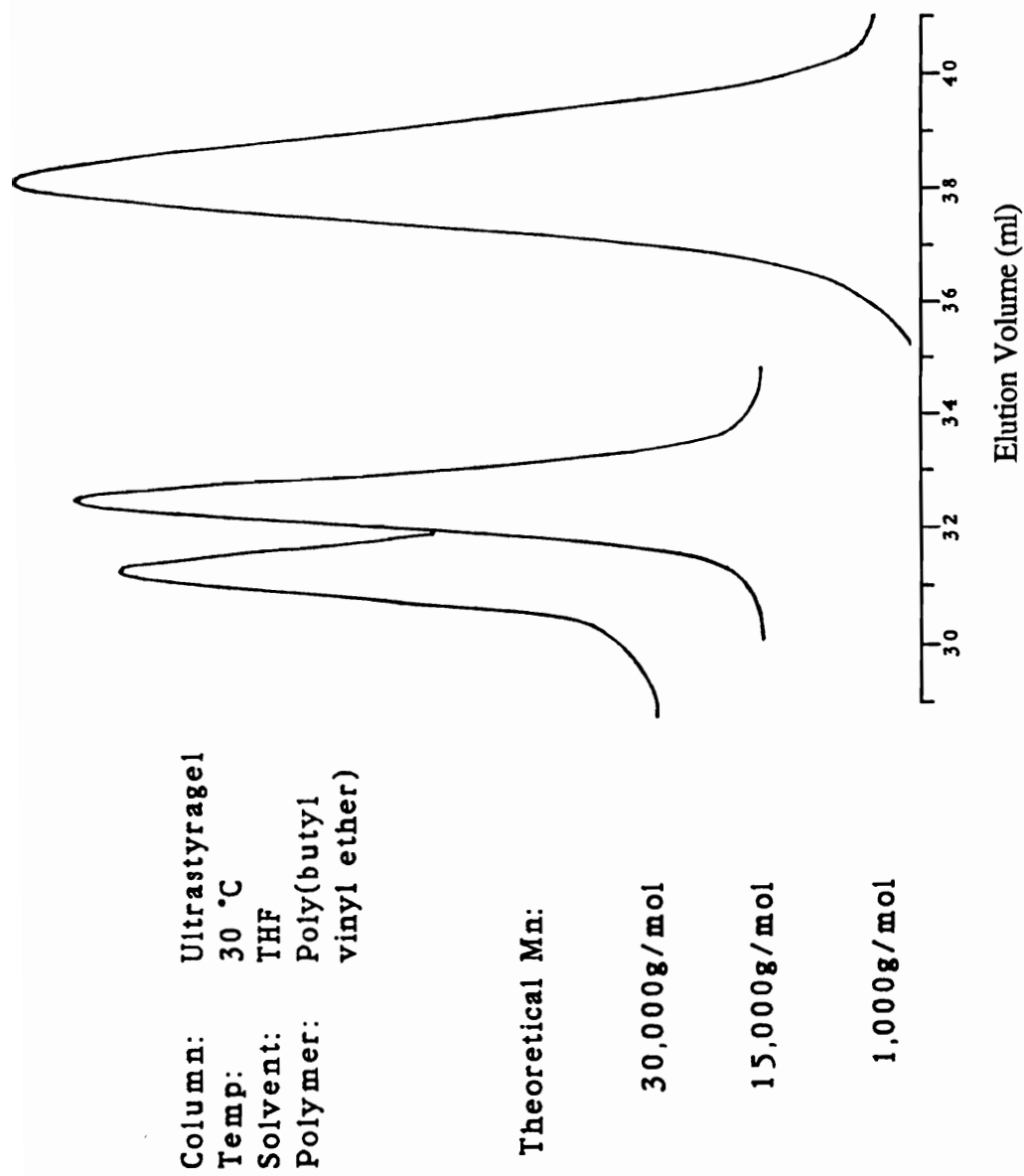


Figure 4.3.8 GPC of monofunctional PBVE with indicated theoretical number average molecular weights

Table 4.3.1 Molecular Weights of Monofunctional Poly(alkyl vinyl ether) Oligomers

polymer	theoretical Mn*	GPC** Mn	GPC Mw/Mn	VPO Mn	¹ H NMR Mn
PBVE	1000	1100	1.15		910
PBVE	15000	15600	1.05		
PBVE	30000	23600	1.11		
PMVE	2000	1800	1.12		1500
PMVE	5000	4200	1.08	4400	4990
PMVE	10000	8800	1.2	7600	

* unit = g/mol

** based on polystyrene standard

of ca.10,000 g/mol. To determine if there is a molecular weight limit, beyond which the living characteristics of the polymerization start to deteriorate, a nonfunctional PMVE was synthesized with a initial targeted molecular weight of 60,000 g/mol. To obtain a reasonable polymerization rate with this low concentration of living ends, the polymerization was carried out at -10°C (the boiling point of MVE is about 5 - 6°C). At ca. 96 hours and 76.6% conversion (analyzed by ¹H NMR), the polymer was terminated using LiBH₄. The calculated Mn at 76.6% conversion was ca. 46,000 g/mol. The GPC trace for this polymer was much broader than that of the analogous lower molecular weight materials (Figure 4.3.9). The number average molecular weight based on polystyrene standards was 25,100 g/mol and <Mw>/<Mn> was 1.89. Clearly, side reactions became more important as the polymerization time increased. Therefore the living nature of these polymerization systems is limited to those polymers with medium to low molecular weights.

The molecular weights of monofunctional PMVE oligomers were also determined by ¹H NMR and/or VPO. These results are also listed in Table 4.3.1. Good agreement was found between theoretical values and the observed ones. Thus it was concluded that monofunctional PMVE oligomers could be synthesized with controlled molecular weights and narrow molecular weight distributions using the method described. The success in preparing PMVE-PEOX diblock copolymers using these monofunctional PMVE oligomers as macroinitiators was demonstrated by GPC of the copolymers in

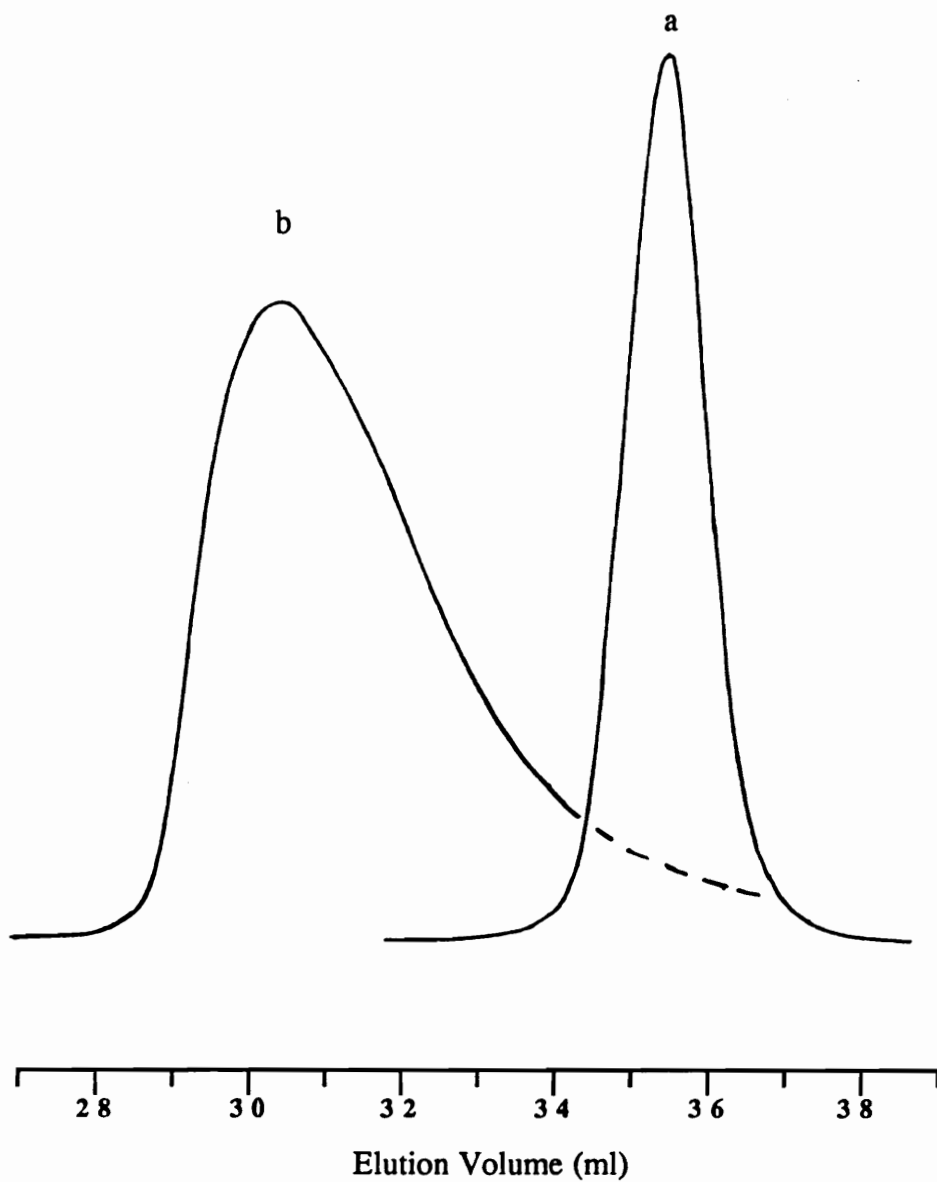


Figure 4.3.9 GPC of PMVE with theoretical Mn of a) 5K, b) 46K

contrast to that of the oligomers (see Figure 4.3.10). Shift of the GPC curve of the copolymer (5K PMVE-10K PEOX) to a lower elution volume, i.e. higher molecular weight, relative to that of the oligomer (5K PMVE) indicates formation of the desired block copolymer. The molecular weights and molecular weight distributions of PMVE oligomers and their copolymers with PEOX were also analyzed by GPC using a universal calibration (Table 4.3.2). Even though the absolute values for the copolymers need to be viewed with caution, the relative values are all in the right order when comparing the copolymers with their precursors.

B. Compositions

The compositions of isolated PMVE-PEOX block copolymers were determined by proton NMR in CDCl_3 and ^{13}C solid state NMR. The results are listed in Table 4.3.3. The methylene protons of the PMVE main chain at $\delta 1.5\text{-}1.9\text{ppm}$ and the methylene protons of the PEOX pendent group at $\delta 2.2\text{-}2.45\text{ppm}$ were well separated (Figure 4.3.11). Based on integration of these peaks, compositions of the block copolymers were calculated according to the following relation:

$$\text{wt \% PMVE} = \frac{A_1 \times 58}{A_1 \times 58 + A_2 \times 99}$$

where A_1 is the integration of the peak at $\delta 1.5\text{-}1.9\text{ppm}$, A_2 is the integration of the peak at $\delta 2.2\text{-}2.45\text{ppm}$, 58 is the MW of one PMVE repeat unit and 99 is the MW of one PEOX repeat unit.

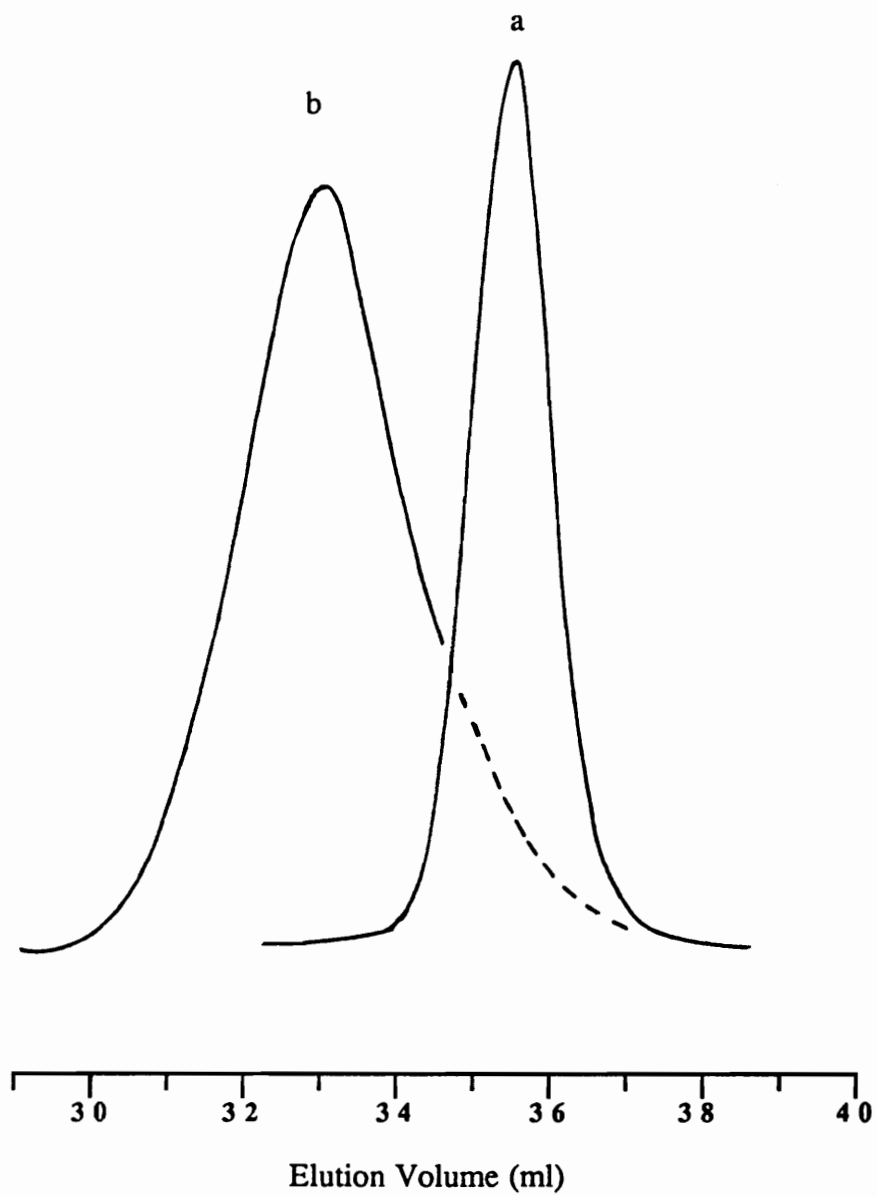


Figure 4.3.10 GPC of a) 5KPMVE, b) 5KPMVE-10KPEOX

Table 4.3.2 Molecular Weights of Monofunctional Poly(methyl vinyl ether) Precursors and PMVE-PEOX Copolymers

polymer	theoretical Mn*	GPC** Mn	GPC MW/Mn
PMVE 5K	5000	5800	1.16
PMVE 10K	10000	11100	1.12
PMVE 5-PEOX 5	5000-5000	13700	1.3
PMVE 5-PEOX 10	5000-10000	17900	1.39
PMVE 10-PEOX 5	10000-5000	17600	1.35

* unit = g/mol

** based on universal calibration method

Table 4.3.3 Composition of PMVE-b-PEOX Copolymers

Sample (kg/mol)	Theoretical (%)	¹ H NMR (%)	¹³ C S.S. NMR (%)
PMVE 5-PEOX 5	50	36.6	42
PMVE 5-PEOX 10	33	24.6	31
PMVE 10-PEOX 5	67	67.5	

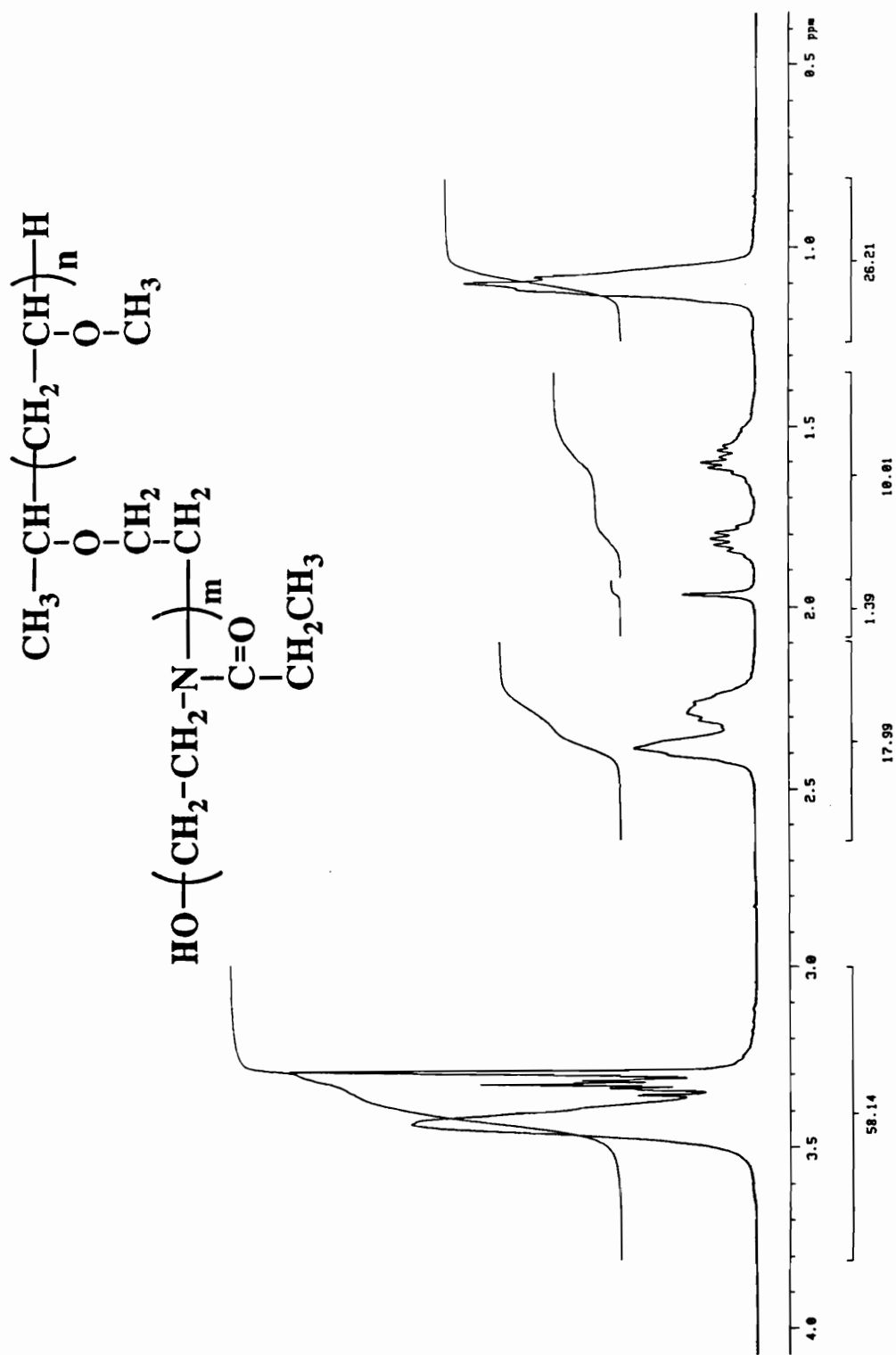


Figure 4.3.11 ^1H NMR of 5KPMVE-10KPEOX block copolymer

The compositions determined by ^1H NMR are in the right order compared to theoretical values (Table 4.3.3). But the compositions of PMVE 5K-PEOX 10K and PMVE 5K-PEOX 5K copolymers are lower in PMVE content than the theoretical ones. To eliminate possible error caused by micelle-formation (section 4.2), ^{13}C solid state NMR was used to confirm the composition for these two copolymers. An exemplary spectrum is shown in Figure 4.3.12. In this spectrum, the methoxy carbon of the PMVE side group at $\delta 56.5$ ppm and the methylene carbon of the PEOX pendent group at $\delta 26$ ppm were somewhat separated from other peaks and used for the calculation of the composition using basically the same relation as the one used above. Slightly higher PMVE contents were found by solid state NMR as compared to solution NMR. The values were still lower than the theoretical ones, probably because some of the higher PMVE content copolymers were removed in the precipitation and work-up steps.

C. Physical properties

a. Thermal stability

The thermal and thermo oxidative stability of PMVE homopolymers (functional and nonfunctional) and the PMVE-PEOX block copolymers was evaluated using dynamic TGA. The temperature at 5% weight loss in nitrogen as well as in air for these polymers are listed in Table 4.3.4. There was no significant difference in temperature at 5% weight loss in nitrogen between the PMVE oligomers and PMVE-PEOX block copolymers. The

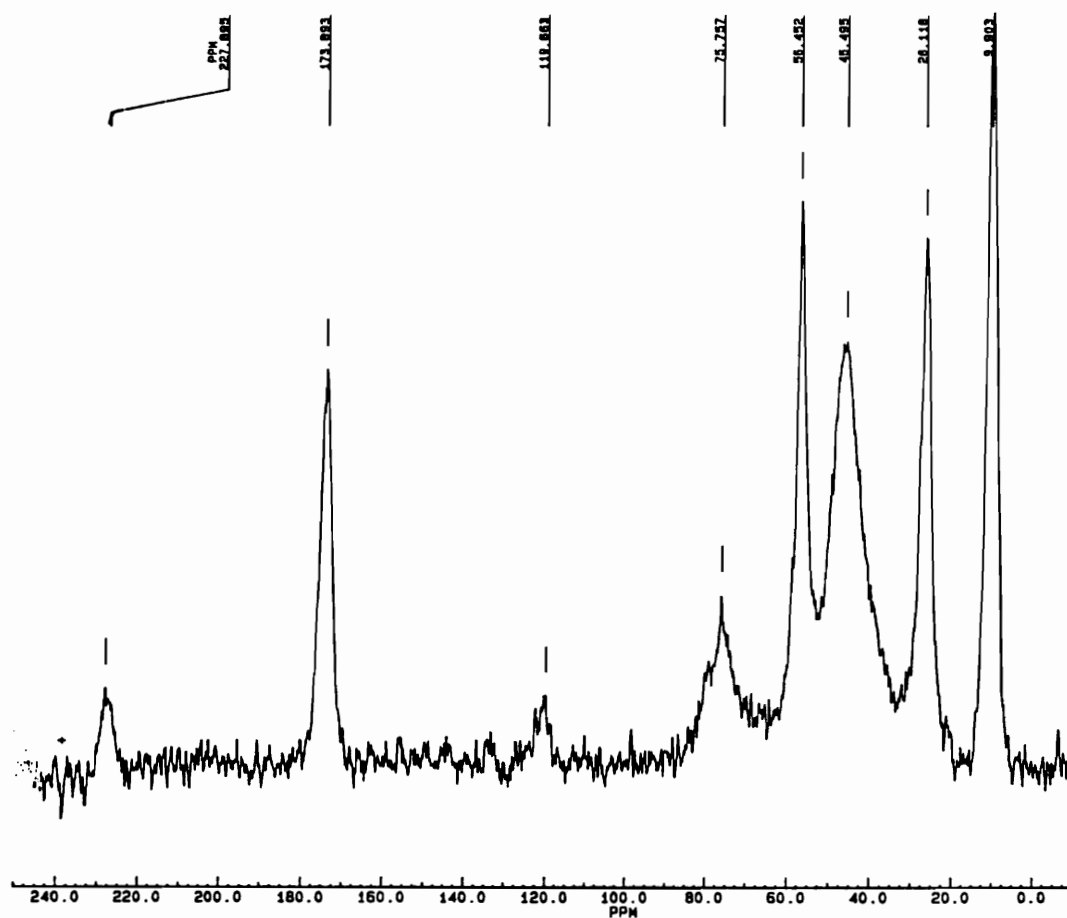
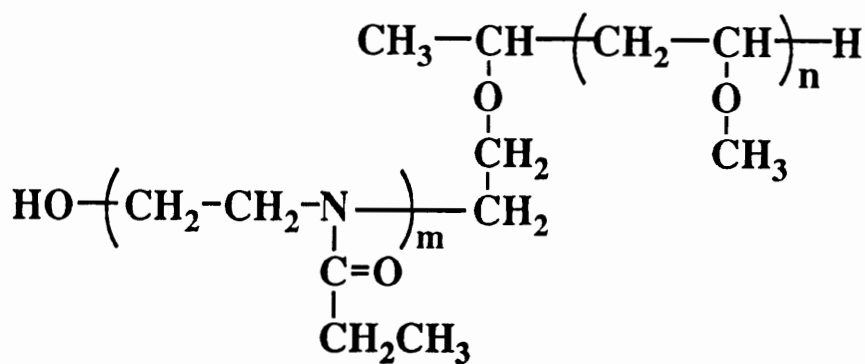


Figure 4.3.12 ^{13}C S. S. NMR of 5KPMVE-b-5KPEOX

Table 4.3.4 Thermal Stabilities of PMVE, PEOX
Homopolymers and Block Copolymers

Sample (kg/mol)	5% wt. loss in nitrogen (°C)	5% wt. loss in air (°C)
PMVE 5	373	273
PMVE 10	349	295
PMVE 46	347	
PMVE 10-PEOX 5	361	314
PMVE 5-PEOX 5	387	340
PMVE 5-PEOX 10	401	379
PEOX 5		370

temperatures at 5% weight loss in air were lower than that in nitrogen in all cases, but the temperature drop was greater for PMVE oligomers than for the block copolymers. The higher thermo-oxidative stability of PEOX increased the thermo-oxidative stability of the copolymers as compared to that of PMVE oligomers. Figure 4.3.13 clearly shows the difference in thermo-oxidative stability between 5K PMVE oligomer and its copolymer with two block lengths of PEOX, 5K and 10K.

Since poly(alkyl vinyl ether) are known to be labile toward free radical reactions, the rather low thermo-oxidative stability of poly(methyl vinyl ether) and its effects on copolymers was expected. Although these block copolymers were not designed for high temperature applications, it is important to know the limits of these copolymers in terms of thermo-oxidative stability.

b. Thermal transitions

Poly(alkyl vinyl ether)s were the first reported stereoregular polymers¹⁸⁷⁻¹⁹⁰. Heterogeneous as well as homogeneous catalysts produced semicrystalline poly(methyl vinyl ether)s, even though the homogeneous catalysts yielded PMVE with lower isotacticities and lower T_m 's. The initiator system used in this study, HI/ZnI₂ is also a homogeneous catalyst. It was interesting to find that the poly(methyl vinyl ether)s synthesized in this study are also semicrystalline materials. These polymers formed clear solutions in toluene. Upon drying under vacuum at 40-60°C, some of the

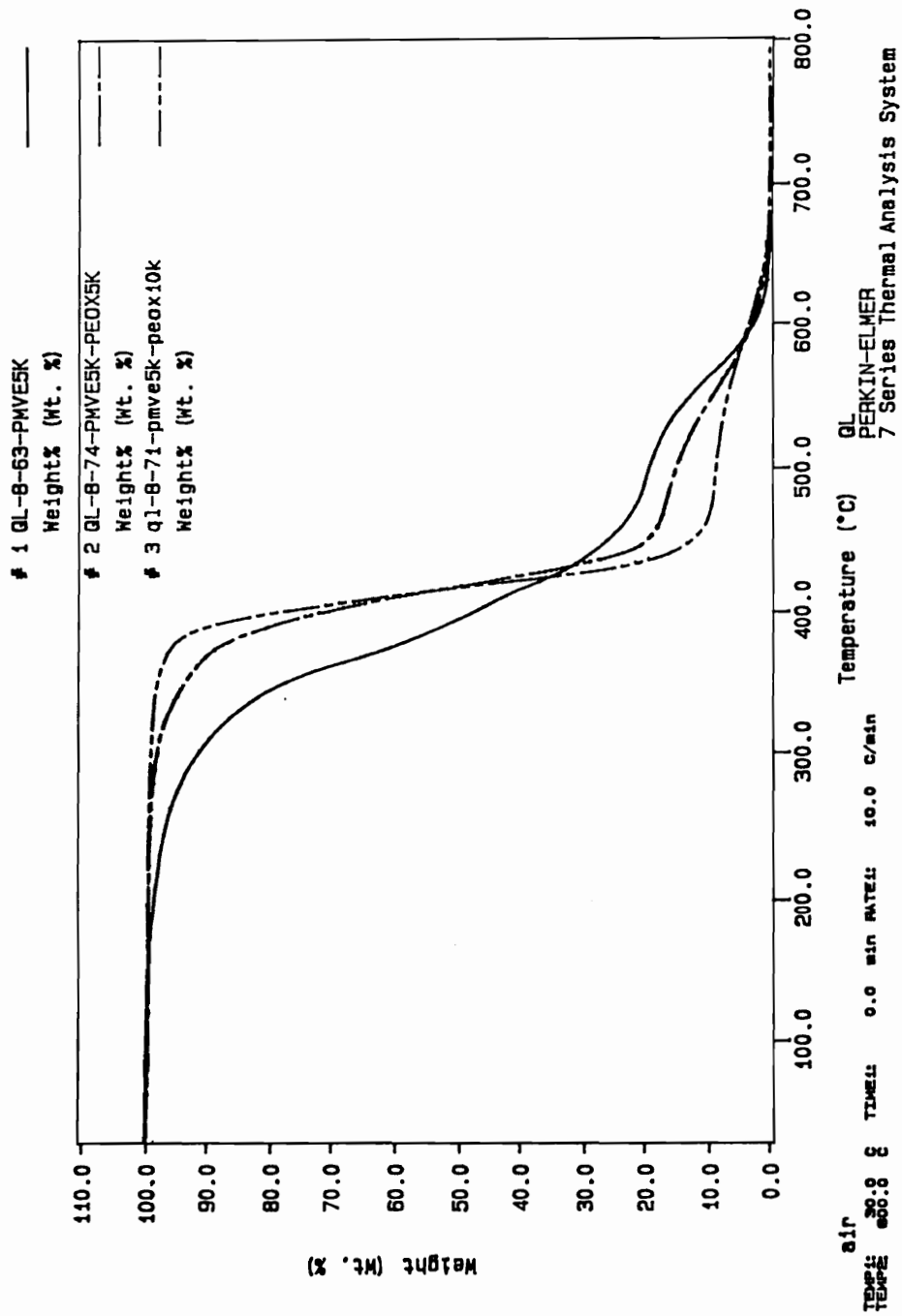


Figure 4.3.13 TGA thermograms of 5KPMVE, 5KPMVE-5KPEOX and 5KPMVE-10KPEOX

oligomers became hazy. All PMVE synthesized in this study became hazy upon aging at room temperature, implying that crystallization may have taken place. At room temperature, PMVE oligomers with Mn's of 2000 and 5000 are hazy and tacky, while PMVE materials with Mn's of 10,000 and 46,000 are hazy and rubbery. Crystallinity in these polymers was explored by DSC. A T_m was detected in the first heating cycle for all these polymers (Table 4.3.5). The higher melting point of the two melting peaks, as shown in Figure 4.3.14, is probably due to the annealing effect during drying as well as solvent induced crystallization. After the polymers were heated above the higher T_m and crystallized at room temperature for more than 10 days, only the lower T_m was detectable (Figure 4.3.14).

Crystallization of these polymers was so sluggish that no T_m was detected in the second heating cycle after slow cooling from the melt. Comparison with the values reported in the literature, (also included in Table 4.3.5), is difficult to interpret, because the T_m's reported are not equilibrium melting points (T_m⁰) and the thermal history of these samples is unknown. However above observance of melting points for the PMVE material synthesized in this study did imply some stereoregularity in those polymers. ¹H and ¹³C NMR spectra of these polymers were analyzed to determine the relative content of isotactic, heterotactic and syndiotactic triads. In the proton spectra, the methoxy peak was deconvoluted to yield the triads content directly. Peak assignment was based on previous work by Ramey¹⁹¹ and Dombroski¹⁹², as shown in Figure 4.3.15. In the ¹³C spectrum,

Table 4.3.5 Thermal Transitions of PMVE Homopolymers

Sample (kg/mol)	T _g (°C)	T _m * (°C)	T _m ** (°C)
PMVE 2	-34	45, 73	
PMVE 5	-31	45, 71	46, 58
PMVE 10	-28	45, 83	46, 51
PMVE 46	-25	47	46
Ref. 187		144	
Ref. 200		70	

* After drying.

** Crystallized at room temperature from melt.

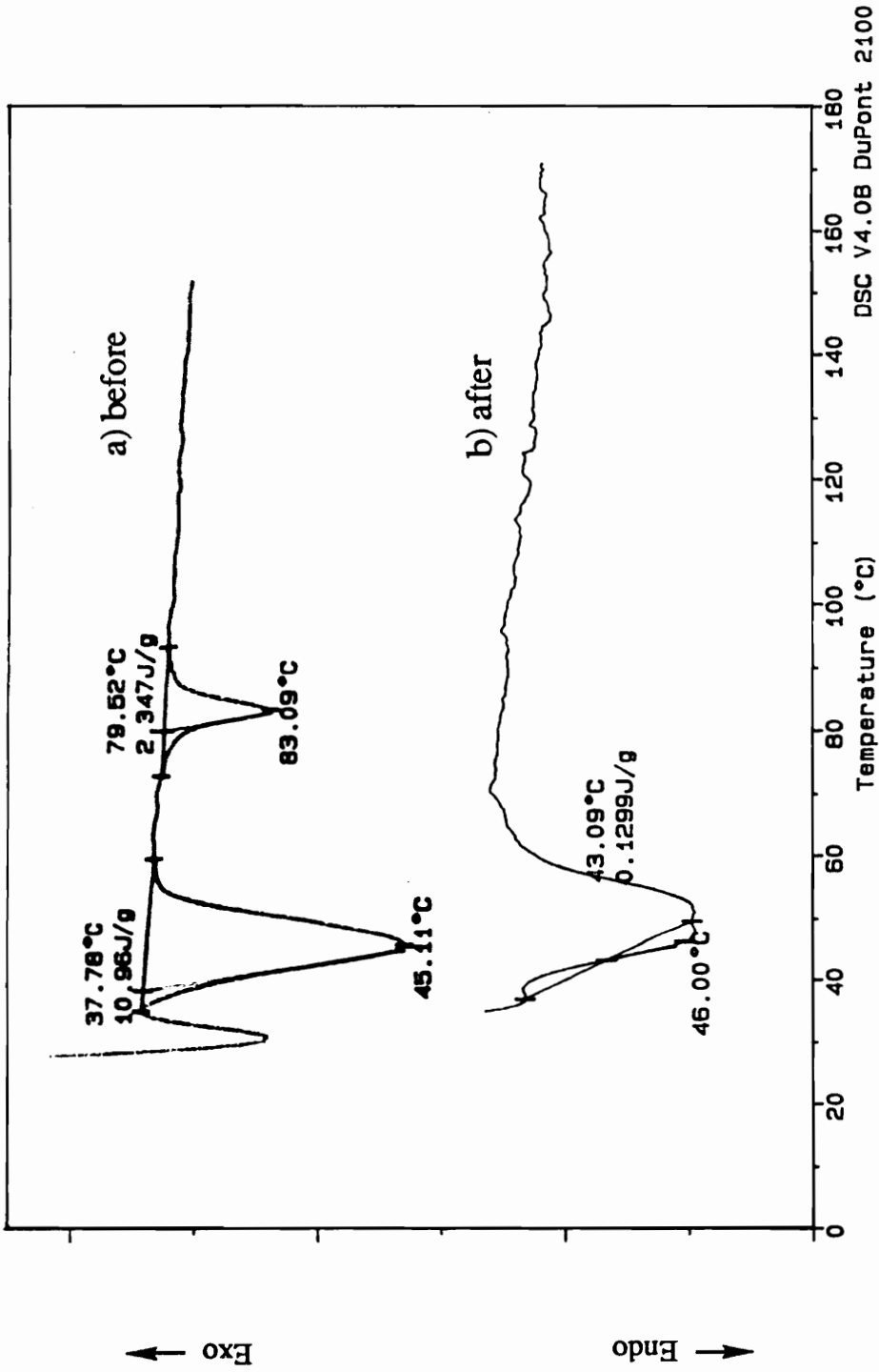
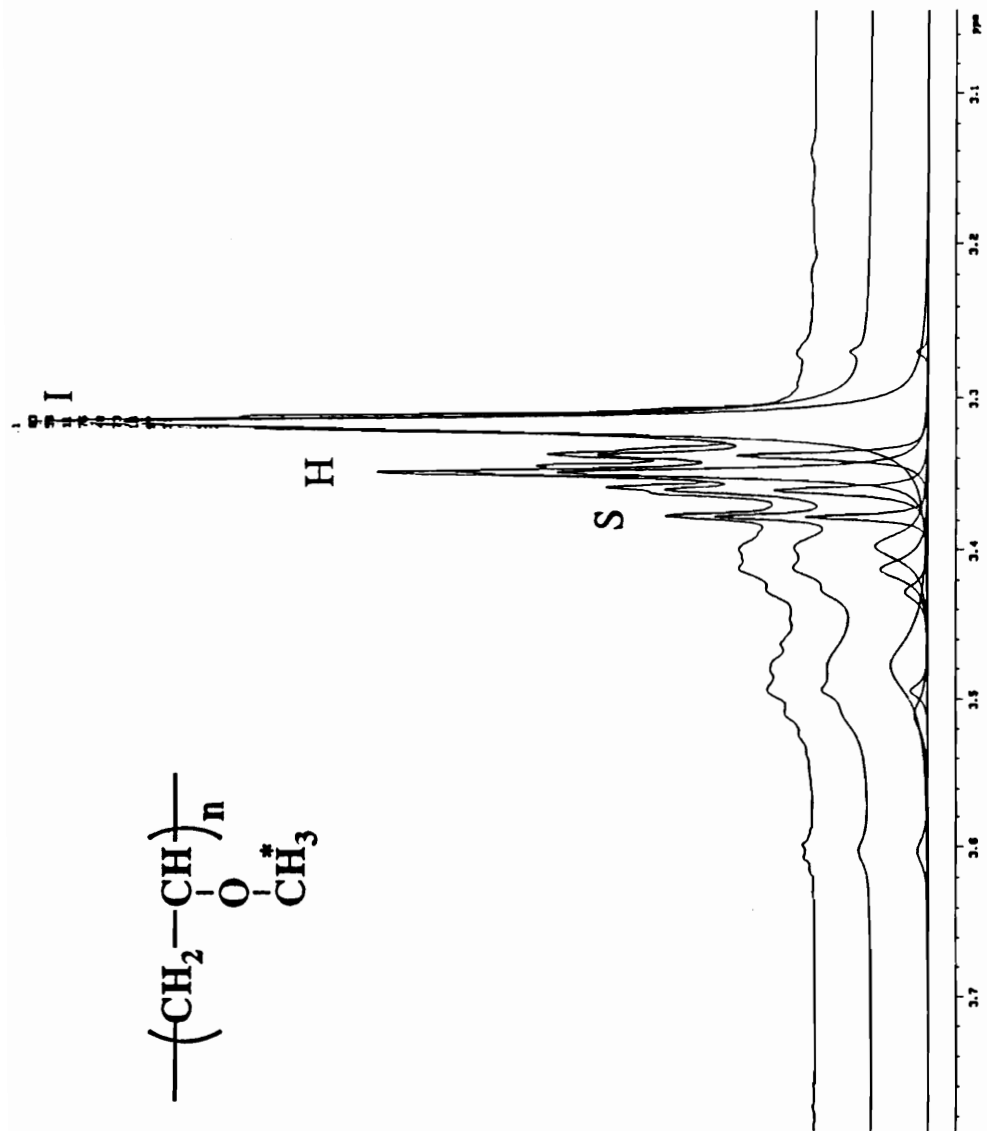


Figure 4.3.14 DSC of 10K PMVE a) before, and b) after heat treatment.

the methylene ^{13}C peak was comprised of two separated peaks (Figure 4.3.16), due to the meso and racemic diads^{193,194}. The methine ^{13}C peak in PMVE could not be used to obtain the tacticity information as in the case of poly(butyl vinyl ether), because the chemical shifts due to different tacticity exhibited opposite trend to what is expected based on those of poly(butyl vinyl ether)s. In the methoxy region, much finer splitting was observed. They were believed to correspond to pentad sequences^{193,194} and only tentative peak assignments were made. Therefore, the more defined methylene ^{13}C peak was used to determine the tacticity of PMVE. To compare the results from ^1H and ^{13}C measurements, the triad contents determined from ^1H spectra were converted into diad contents according to the following statistical relations: $m = mm + mr = I + (1/2)H$ and $r = rr + mr = S + (1/2)H$. The only assumption required for these relations to hold is the reversibility relationship, that is, mr and rm are indistinguishable, which is true experimentally^{194,195}. In addition, the triad contents were calculated from diad values determined from ^{13}C spectra assuming a Bernoullian model, i.e. the stereochemistry of the newly formed diad is not affected by the stereochemistry of the last diad on the chain. The consequent equations are: $I = mm$, $H = 2mr$, and $S = rr$. Results from both methods are listed in Table 4.3.6. Slightly more than 50% isotactic triads were observed for all the PMVE samples irrespective of molecular weight differences. The heterotactic triads comprised more than 30%. The diad and triad contents determined by both



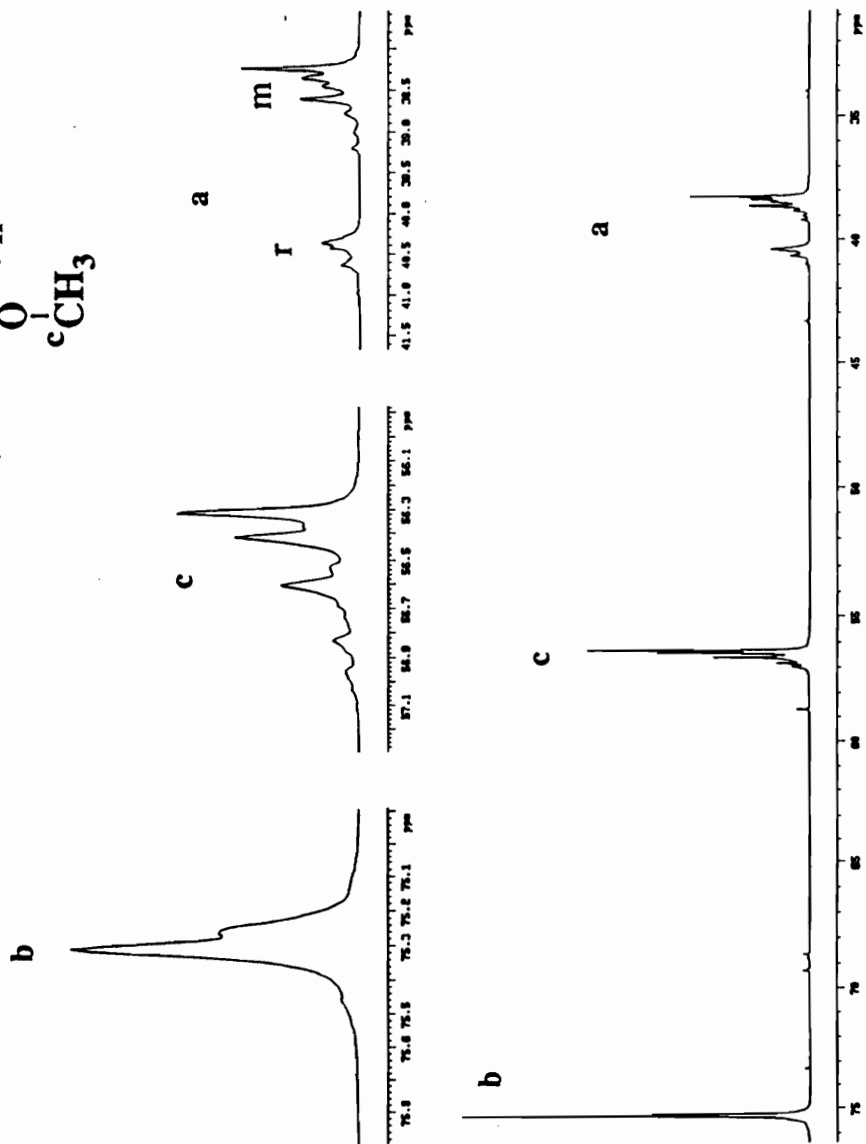
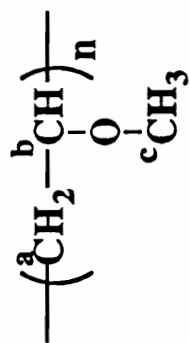


Figure 4.3.16 ^{13}C of 5KPMVE for tacticity analysis

Table 4.3.6 Tacticity of Poly(methyl vinyl ether)s

Sample (kg/mol)	Triads obsd (¹ H)			Triads calcd ^a (¹³ C)			Diads obsd (¹³ C)			Diads calcd ^b (¹ H)		
	I (%)	S (%)	H (%)	I (%)	S (%)	H (%)	m (%)	r (%)	m (%)	r (%)	m (%)	r (%)
2	61	4	35	52	8	40	72	28	78	22	78	22
5	61	4	35	56	6	38	75	25	79	21	79	21
10	60	4	36	52	8	40	72	28	78	22	78	22
46	61	4	35	53	7	40	73	27	78	22	78	22

a. I, S and H were calculated using $I = mm$, $S = rr$, $H = 2mr$.

b. m and r were calculated using $m = I + (1/2)H$, $r = S + (1/2)H$.

methods basically agree. As discussed earlier, no assumption except reversibility was made in converting triad content derived from ^1H spectra to diad contents. The discrepancy in diad content between the two methods (proton vs. carbon spectra) may be due to experimental errors involved in the measurements, especially those in deconvolution of proton spectra. Therefore the assumed Bernollian's model may be the mechanism of stereoregulation in these polymerizations. Interestingly, similar triad contents (55% I, 35% H and 10% S) were reported for PMVE prepared using a different homogeneous initiator, $\text{BF}_3\cdot\text{OEt}_2$ ¹⁹². The moderate amount of isotactic triads in these polymers is probably the cause of low T_m 's and slow crystallization behavior of poly(methyl vinyl ether)s.

The glass transition temperatures of PMVE oligomers and homopolymers, PMVE-b-PEOX copolymers, and separately synthesized PEOX homopolymers were determined by DSC. The results are summarized in Table 4.3.7. For both PMVE and PEOX homopolymers, T_g increases as the theoretical number average molecular weight increases, suggesting the molecular weights are less or equal to the critical molecular weight for each system. Two glass transition temperatures were obtained for PMVE-b-PEOX copolymers, with block length listed in the table, indicating these block copolymers are microphase separated systems. The T_g values of the PMVE blocks are higher than that of corresponding PMVE precursors, suggesting partial phase mixing or lose of chain mobility at the interphase due to the covalent bonding between PMVE and

Table 4.3.7 DSC Results on PMVE, PEOX homopolymers and block copolymers

Sample (kg/mol)	PEOX Tg (°C)	PMVE Tg (°C)	PMVE Tm (°C)
PEOX 5	50		
PEOX10	54		
PEOX 30	56		
PMVE 5		-31	46, 58
PMVE 10		-28	46, 51
5-5*	51	-24	44, 46**
5-10	55	-24	46**
10-5	43	-25	

* 5-5 = 5kg/mol PMVE-5kg/mol PEOX

** Apparent melting, please see text for explanation.

PEOX block. In contrast to that of PMVE, T_g of PEOX block is harder to define, especially for 5K PMVE-5K PEOX and 5K PMVE-10K PEOX. There seems a melting peak in thermograms for both copolymers in addition to baseline shift at the temperature region of PEOX T_g. This apparent melting peak is absent in the thermogram of 10K PMVE-5K PEOX (Figure 4.3.17). The presence of the peak(s) is hard to explain, since the samples were melted at 100°C for at least 5 minutes and quenched (200°C/min) before DSC scanning. The temperatures at the peaks are similar to T_m of PMVE precursors (Table 4.3.7).

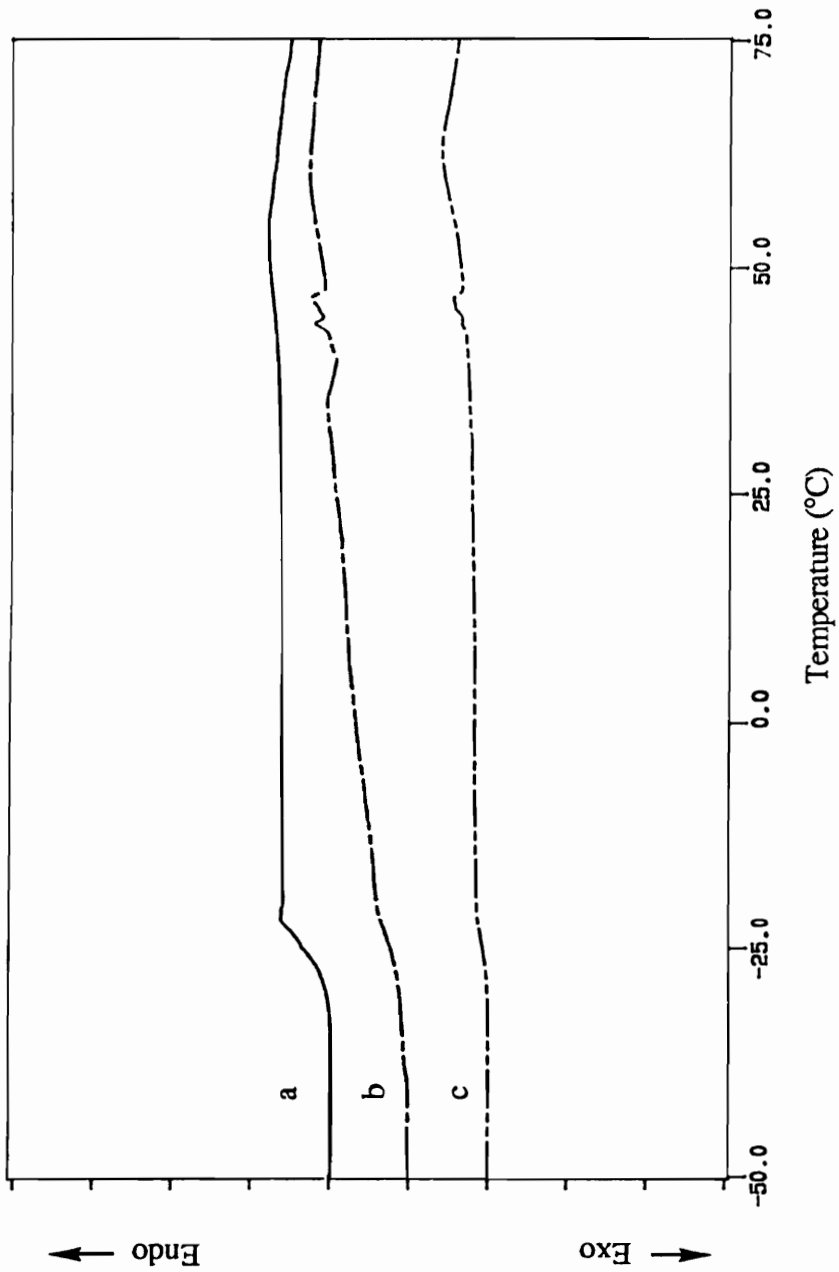


Figure 4.3.17 DSC of a) PMVE10K-b-PEOX5K, b) PMVE5K-b-PEOX5K, and c) PMVE5K-b-PEOX10K

4.4 Synthesis of Copolymeric Blend Emulsifiers

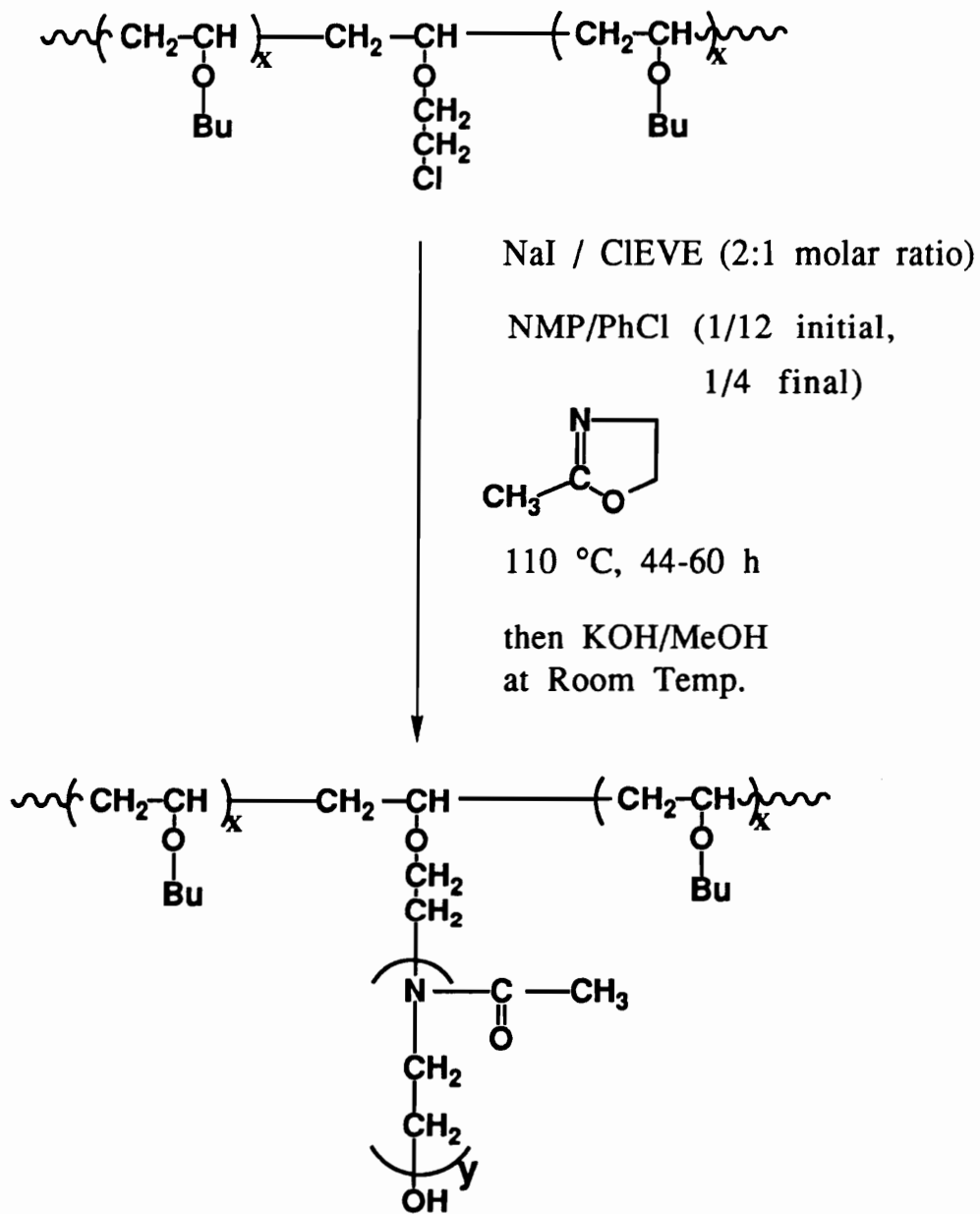
This section discusses the synthesis of two types of copolymers designed for use as polymer blend emulsifiers.

4.4.1 Poly(n-butyl vinyl ether-2-methyl-2-oxazoline) Graft Copolymers

The synthesis of poly(n-butyl vinyl ether-2-methyl-2-oxazoline) graft copolymers involved collaborative work with a fellow graduate student, Mr. John Bronk. The first step in the synthesis was to prepare poly(n-butyl vinyl ether) with a minor amount (ca. 3 mole%) of chloroethyl vinyl ether incorporated throughout the chain. The preparation of this random copolymer involved polymerizing n-butyl vinyl ether and 3 mole % of chloroethyl vinyl ether in toluene at 10°C using ca. 5% by wt. of aluminum hydrogen sulfate catalyst. This was performed by Mr. Bronk, and the details can be found in his thesis¹⁹⁶.

The graft copolymers with poly(n-butyl vinyl ether) (PBVE) as the backbone and poly(2-methyl-2-oxazoline) (PMOX) grafts were prepared according to scheme 4.4.1. The pendent ethyl chloride groups served as initiators for the polymerization of 2-methyl-2-oxazoline in the presence of sodium iodide. Again, as in section 4.3, the function of the iodide salt was to convert the halides to the more active alkyl iodides in situ. A binary solvent system was required due to the large difference in polarity between the poly(n-butyl vinyl ether) backbone and the poly(2-methyl-2-oxazoline) grafts.

Scheme 4.4.1
 Synthesis of Poly(butyl vinyl ether-g-2-methyl-2-oxazoline) copolymers



The polymerization was conducted at 110°C to achieve a fast polymerization rate. Since the boiling point of 2-methyl-2-oxazoline is 109.5-110.5 °C, a pressure reactor was used to prevent the loss of monomers. The resultant graft copolymers were recovered by precipitation of the reaction mixture into diethyl ether, which removes any unreacted PBVE homopolymers. Graft copolymers with 50% and 75% by weight of PMOX were prepared. The corresponding graft length is 3300 g/mol and 10000 g/mol respectively assuming all the pendent ethyl chloride groups reacted. The molecular weights of the PBVE backbones were very high, ranging from approximately 300,000 -500,000 <Mn> as measured by polystyrene standards. Thus, the molecular weights of the graft copolymers were correspondingly high. The dried graft copolymers were not soluble in conventional solvent and no GPC measurement could be made. This is attributed at least partially to the abnormally high molecular weights. The presence of both copolymer components was confirmed by ¹³C solid state NMR, as shown in Figure 4.4.1. The compositions of the graft copolymers were determined using the integration of peaks in Figure 4.4.1 according to the following equation:

$$\text{wt \% PMOX} = \frac{(\text{G and B} - \text{A}) \times 85}{(\text{G and B} - \text{A}) \times 85 + \text{A} \times 100 + \text{A} \times 3.2\% \times 71}$$

where G and B stands for the area under overlapped peak G and B, G is due to the methyl carbon on PMOX side chain, and B is due to the methylene carbon on PBVE side chain overlapped with G, and A

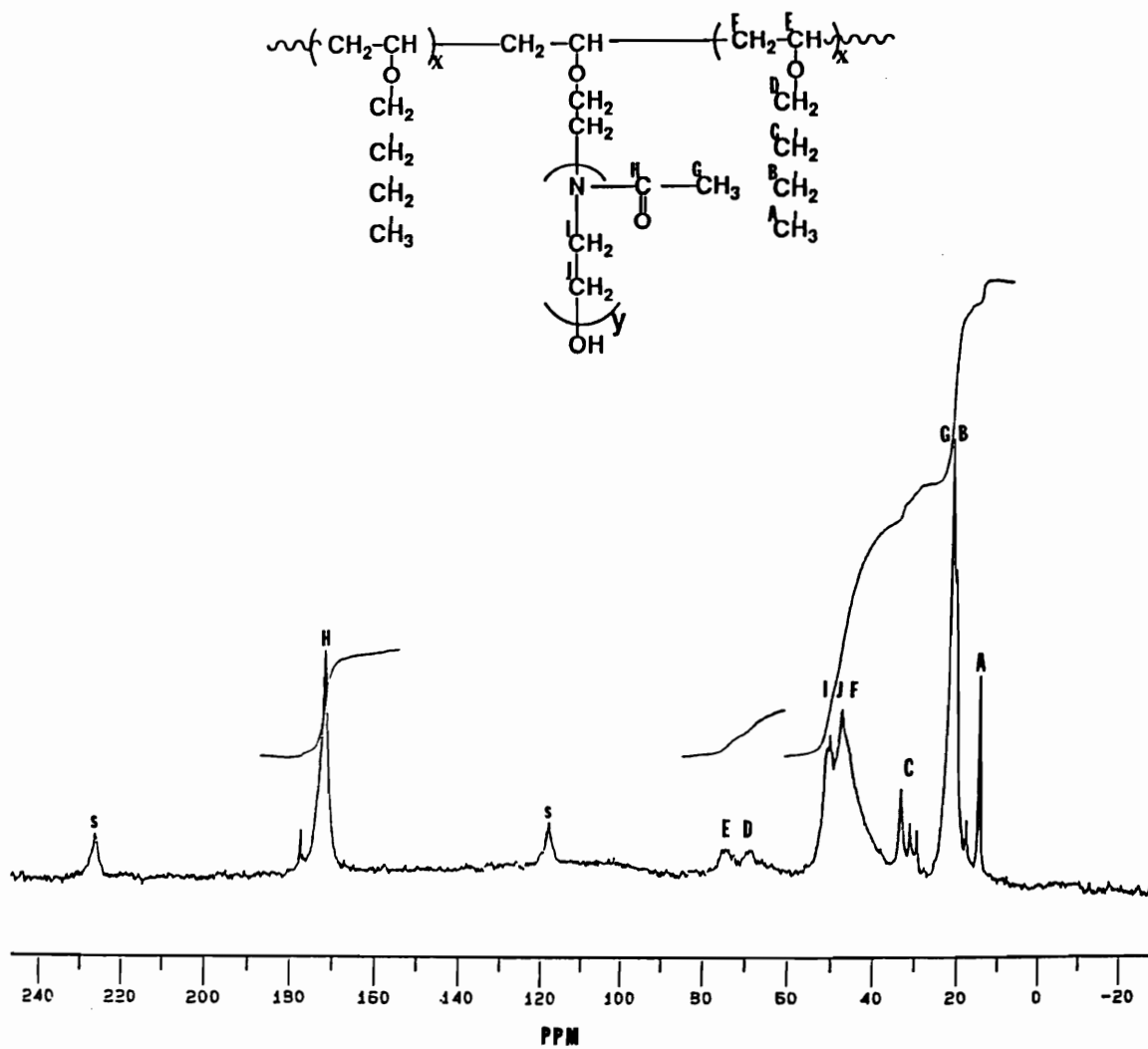


Figure 4.4.1 ^{13}C Solid State NMR of Poly(butyl vinyl ether-g-2-methyl-2-oxazoline)

refers to the area under peak A due to the methyl carbon on PBVE side chain. The molecular weights of repeat units for PMOX and PBVE are 85 and 100 respectively. The molecular weight of chloroethyl vinyl ether without the chloride is 71; and there are 3.2 mole% of these units along the PBVE backbone. In the calculation, the assumption that area B must be equal to area A was used. Alternatively, deconvoluting peak G and B yielded the same results. To ensure quantitative integration of the alkyl carbons in the NMR experiments, a relaxation time of 106 s was used. This is more than five times that of the spin relaxation time for similar alkyl carbons in general. The observed compositions are listed in Table 4.4.1. These basically agree with the theoretical values, but have a slightly higher wt. percentage of PMOX in both compositions. Therefore it was concluded that the majority of PBVE reacted with 2-methyl-2-oxazoline monomer and formed the graft copolymers.

DSC thermograms showed two glass transitions for the materials indicative of microphase separated systems. An example is given in Figure 4.4.2. This is one of the most important factors for a copolymer to be an effective blend emulsifier.

Polymer blends prepared using a 25/75 wt% PBVE - PMOX graft copolymer as a blend emulsifier will be discussed in a later section.

4.4.2 Poly(2-methyl-2-oxazoline- ϵ -caprolactone) Diblock Copolymers

Table 4.4.1 Composition of PBVE-g-PMOX copolymers

Sample	Theoretical Mn of PMOX graft (g/mol)	Theoretical (wt% of PMOX)	¹³C S.S. NMR (wt% of PMOX)
1	3300	50	55
2	10000	75	82

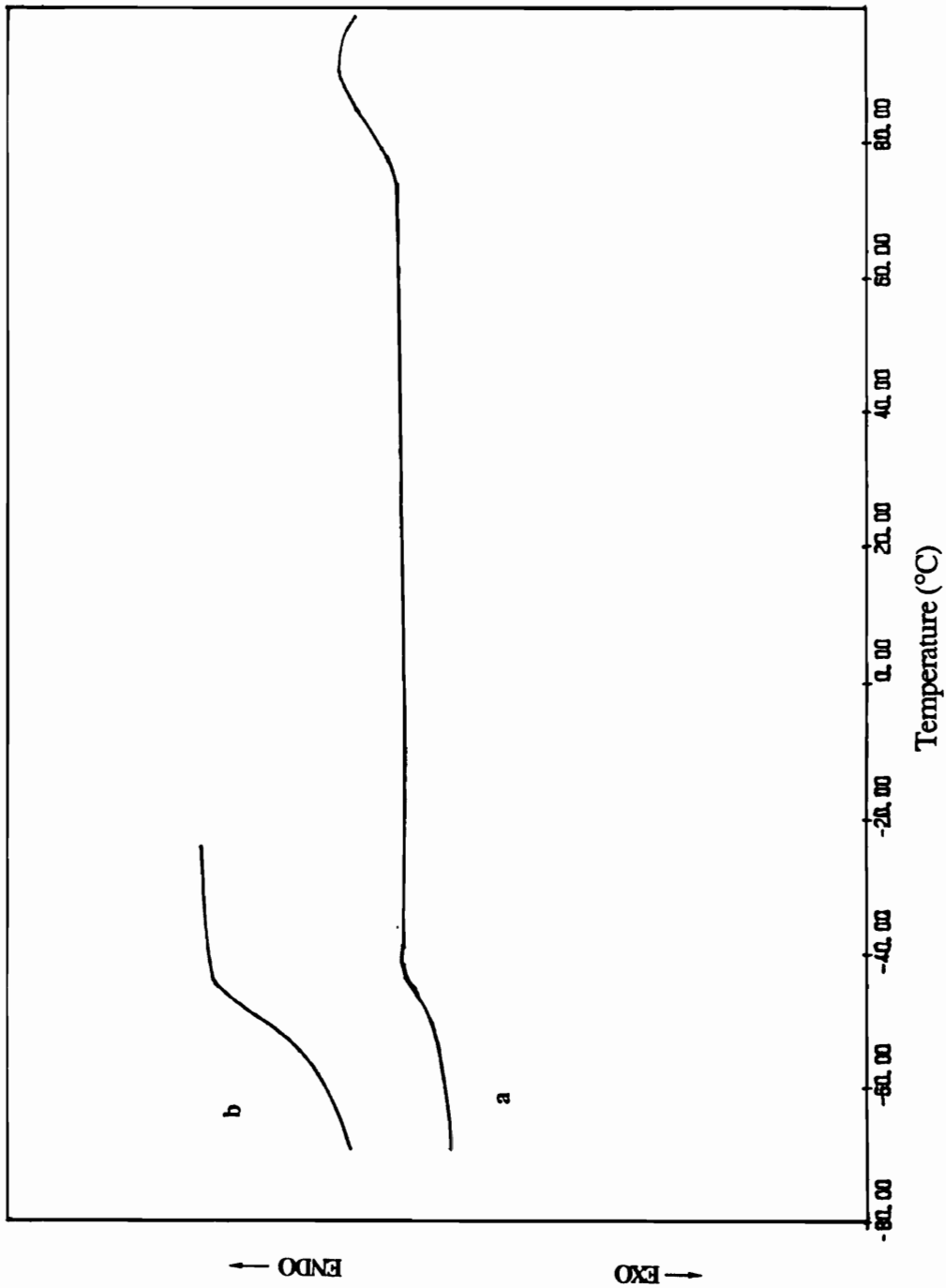
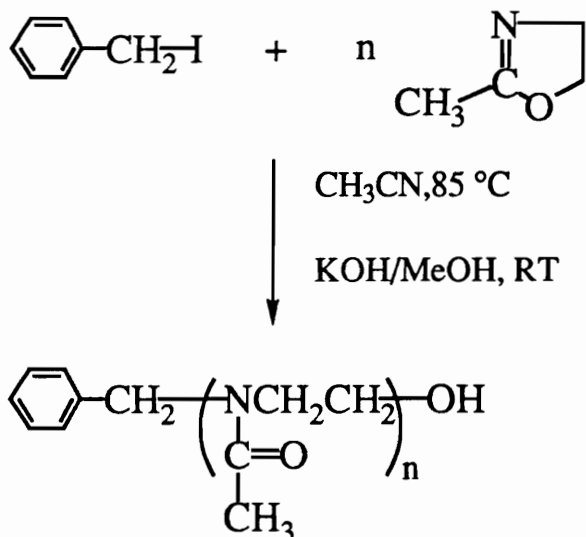


Figure 4.4.2 DSC thermogram of a) PBVE-g-PMOX (50/50 wt./wt.)
b) PBVE precursor

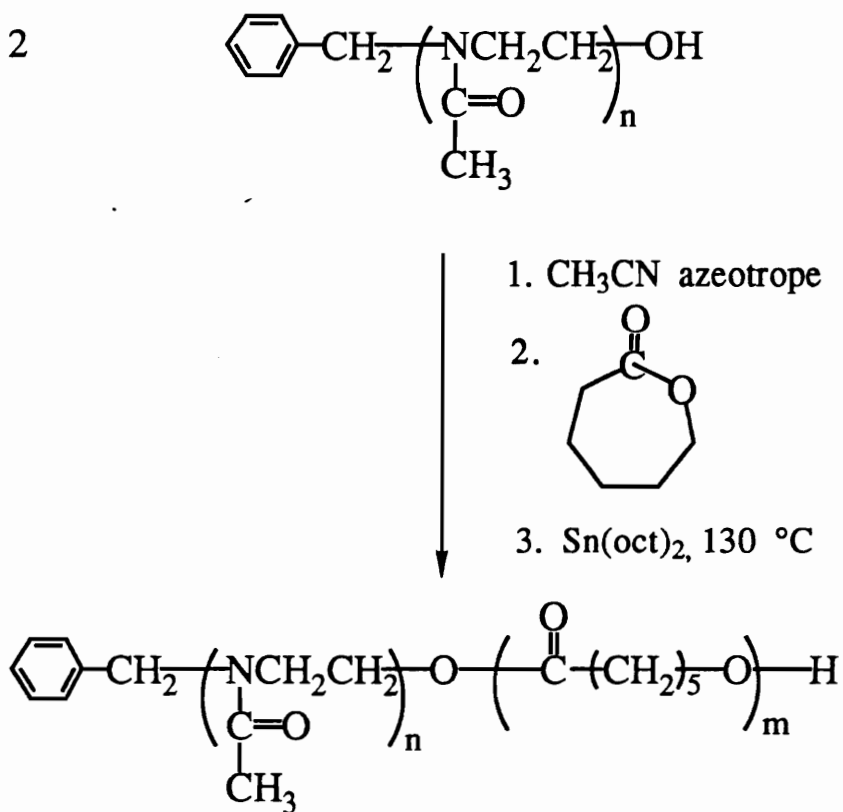
It has been established that hydroxy-terminated poly(2-ethyl-2-oxazoline) can be used as a macroinitiator for ϵ -caprolactone to yield corresponding block copolymers¹⁹⁷. Analogous diblock materials with poly(2-methyl-2-oxazoline) as the polyamide block were prepared (Scheme 4.4.2). However, the increased polarity of poly(2-methyl-2-oxazoline) complicates the process because the choice of an "ideal" solvent for the polymerization proved elusive. Poly(2-methyl-2-oxazoline) is only soluble in extremely polar solvents. Polar aprotic solvents such as N-methylpyrrolidinone are unsuitable for the copolymerization reaction because the ring-opening of ϵ -caprolactone proceeds extremely slowly in these types of solvents. This was believed due to interactions between the stannous octoate catalyst and the carbonyl group of the solvent which preclude activation of the ester ring. Consequently, this copolymerization was performed in the absence of a solvent. In order to control the viscosity of the copolymerizations, the reactions were terminated at low ϵ -caprolactone conversions and precipitated into diethyl ether to remove unreacted monomer. Acetonitrile was used as an azeotrope solvent to remove any trace of water in the polymerization system. Even though poly(2-methyl-2-oxazoline) could be synthesized using acetonitrile as the solvent, the polymer became insoluble once it was dried. This behavior suggested the possibility of crystallization of PMOX during the drying process. However, no obvious melting behavior was detected by DSC on this dry polymer. It is interesting to note, though, that several melting

Scheme 4.4.2 Synthesis of
Poly(2-methyl-2-oxazoline-b- ϵ -caprolactone) Copolymers

Step 1



Step 2



peaks were observed on the annealed poly(2-methyl-2-oxazoline- ϵ -caprolactone) block copolymer (Figure 4.4.3). These high melting points (154°C, 172°C, and 189°C) relative to that of poly(ϵ -caprolactone), whose melting point is about 60°C, are believed to be due to the poly(2-methyl-2-oxazoline) block.

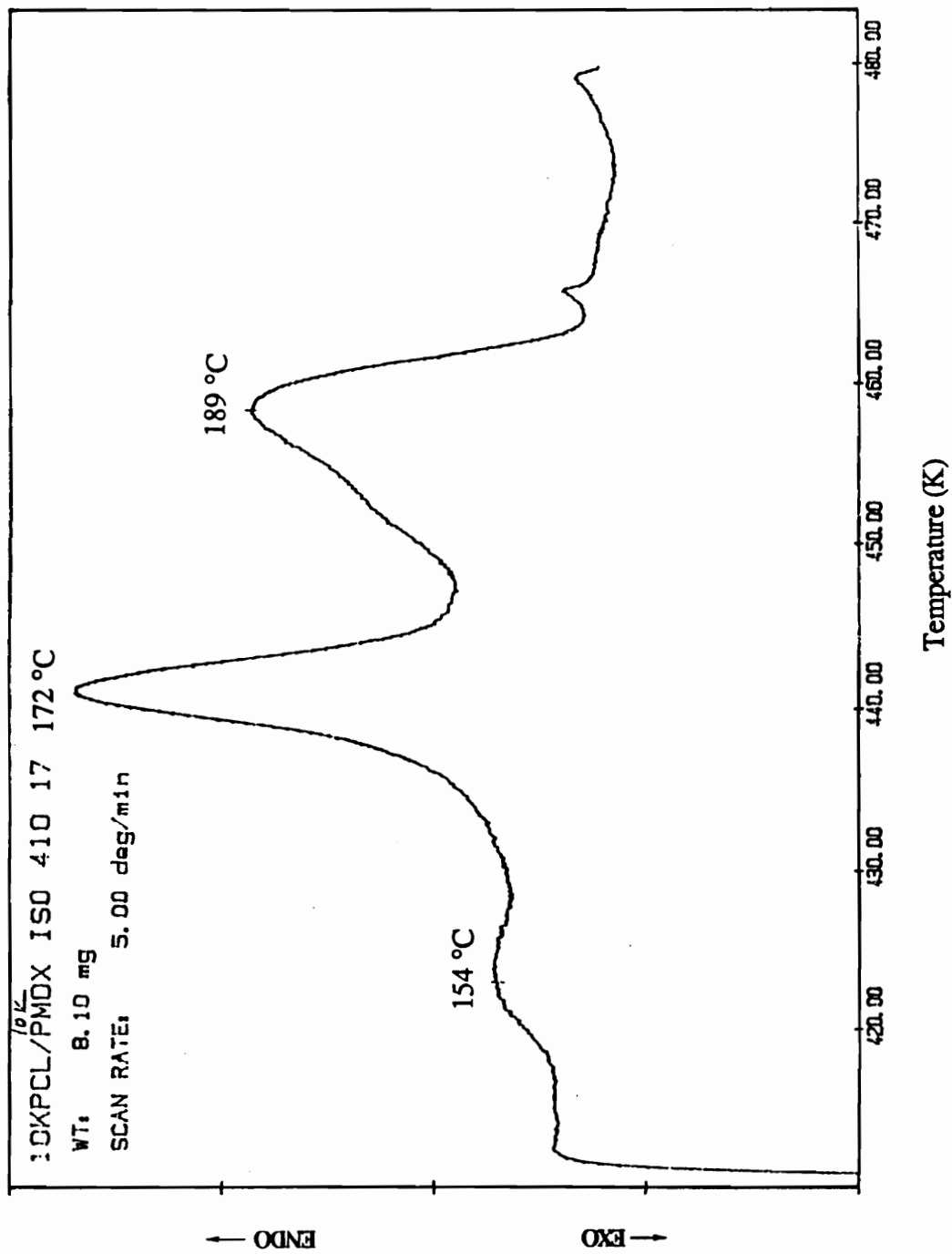


Figure 4.4.3 DSC thermogram of 10KPCL after annealing 17 hr. at 137 °C

4.5 Blends

Polymer blends are of widespread industrial importance because of their potential to yield new families of materials utilizing existing polymers. Due to entropic reasons, many polymer pairs are thermodynamically immiscible. This is not necessarily a disadvantage, since synergetic effects can be achieved in immiscible blends provided the morphology and adhesion between phases can be adequately controlled. To prepare a compatible blend of two immiscible polymers, the use of polymeric emulsifiers, either generated in situ or pre-prepared in the form of copolymers, has potential. The work has centered on pre-formed copolymers in order that the blends can be analyzed from a more fundamental point of view.

This study is focused on compatibilization of immiscible blends comprised of poly(ϵ -caprolactam) (nylon 6) and isotactic poly(propylene). The initial phase of the research was concentrated on identifying suitable emulsifier components which would adhere to each homopolymer in the blends. In addition, a plausible synthetic pathway had to be found to link these two components together. Based on these criteria, a number of polymer structures were selected for potential emulsifier components, as listed in Table 4.5.1. Of these, the copolymers of 2-alkyl-2-oxazoline with alkyl vinyl ether and with ϵ -caprolactone were synthesized and their efficiency as blend emulsifiers was investigated.

Table 4.5.1 Proposed Compatibilizers
for Nylon6/Poly(propylene) Systems

Poly(propylene)	Nylon 6
Atactic Polypropylene $\left[\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]_n$	Poly(ϵ -caprolactam) $\left[\text{NH} - (\text{CH}_2)_5 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n$
Poly(ϵ -caprolactone) $\left[\text{O} - (\text{CH}_2)_5 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Poly(2-alkyl-2-oxazoline) $\left[\text{N} - \underset{\text{C}=\text{O}}{\underset{\text{R}}{ }} - \text{CH}_2 - \text{CH}_2 \right]_n$
Poly(Vinyl alkyl ether) $\left[\text{CH}_2 - \underset{\text{OR}}{\text{CH}} \right]_n$	R = methyl, ethyl
R = methyl, ethyl, butyl	

Due to the scope and the amount of work required, the overall research was conducted through teamwork. In the following, the work completed by the author will be discussed in detail and the results by other colleagues will be included when necessary to complete the conclusions.

4.5.1 Blends of Poly(ϵ -caprolactam) with Poly(2-oxazoline) and Poly(2-alkyl-2-oxazoline)s

Because the aliphatic polyamide structure of the poly(2-alkyl-2-oxazoline)s was similar to that of poly(ϵ -caprolactam), it was reasoned that one or more of these materials might be miscible with poly(ϵ -caprolactam). Thus poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) homopolymers with number average molecular weights of 30,000 g/mol were prepared (as described in section 4.1) and melt blended individually with nylon 6. However, the investigations on the miscibility between poly(2-alkyl-2-oxazoline)s have been inconclusive. Several typical methods for determining blend miscibility were not applicable for these blends. First of all, the difference between the Tg of nylon 6 (56°C) and that of poly(2-ethyl-2-oxazoline) (in the range of 60°C) and poly(2-methyl-2-oxazoline) (in the range of 70°C) is small. Tg's less than 20°C apart cannot be very well resolved by various techniques¹⁹⁸. Secondly, the refractive index for nylon 6 and that for poly(2-alkyl-2-oxazoline)s are probably close due to their structure similarities. Consequently, though no secondary phase in the melt blend was

observed under an optical microscope, this does not necessarily indicate a miscible blend nor a secondary phase too small to observe by the microscope. Third, the crystallization of nylon 6 is very fast. The crystal growth rate of nylon 6 relative to that of the blends cannot be monitored under a microscope using crosspolarizers. No melting point depression was observed between nylon 6 and the blends.. Therefore SEM was used to probe the topography of freeze-fractured surfaces of the blends. As shown in Figure 4.5.1, the diameter of the dispersed phase was approximately 0.5μ for the poly(2-methyl-2-oxazoline)/nylon 6 (30/70 w/w) blend and $5-10\mu$ for the analogous poly(2-ethyl-2-oxazoline)/nylon 6 (30/70 w/w) blend. The significant decreased domain size in the poly(2-methyl-2-oxazoline) blend relative to the poly(2-ethyl-2-oxazoline) blend suggested that poly(2-methyl-2-oxazoline) has more affinity for nylon 6 than the ethyl derivative and, hence, may perform more effectively as an anchor segment in a copolymeric emulsifier. As the substituents changed from ethyl to methyl, the domain sizes decreased. Therefore it was of theoretical interest to know what the effect would be if the substituent was simply a proton. However, as described in section 4.1, unsubstituted 2-oxazoline polymer crystallized out of the polymerization solution, and only low molecular weight polymer was obtained. Nevertheless, this polymer was melt blended with nylon 6 and its freeze-fracture surface analyzed by SEM. From observation of the fracture surfaces of this blend, it was found that the domain size (Figure 4.5.2) was

a)



5 μ m bar

b)

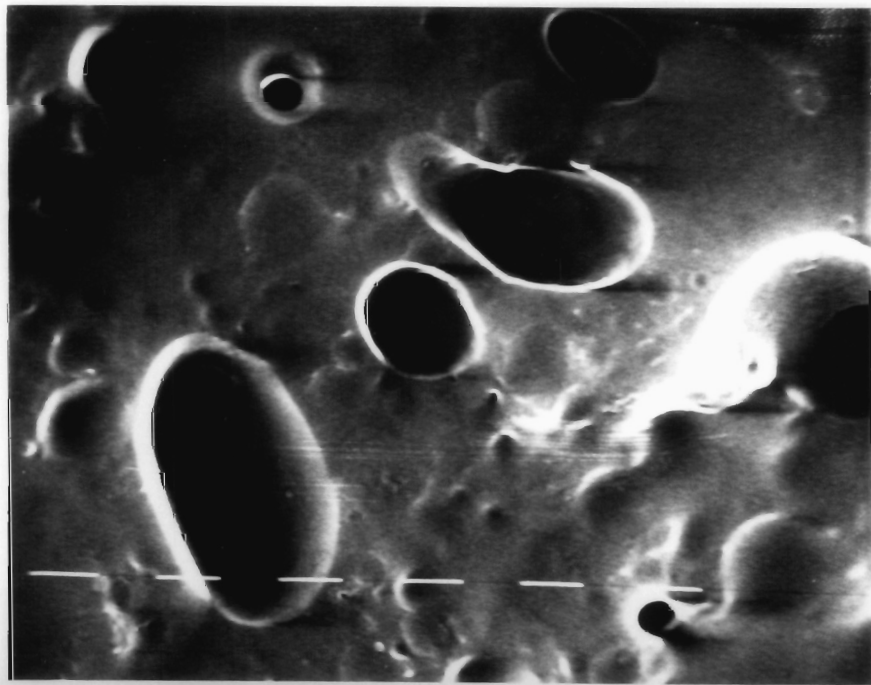


Figure 4.5.1 SEM of fracture surfaces of blends of
a) Nylon 6/Poly(2-methyl-2-oxazoline) (70/30, wt./wt.)
b) Nylon 6/Poly(2-ethyl-2-oxazoline) (70/30, wt./wt.)

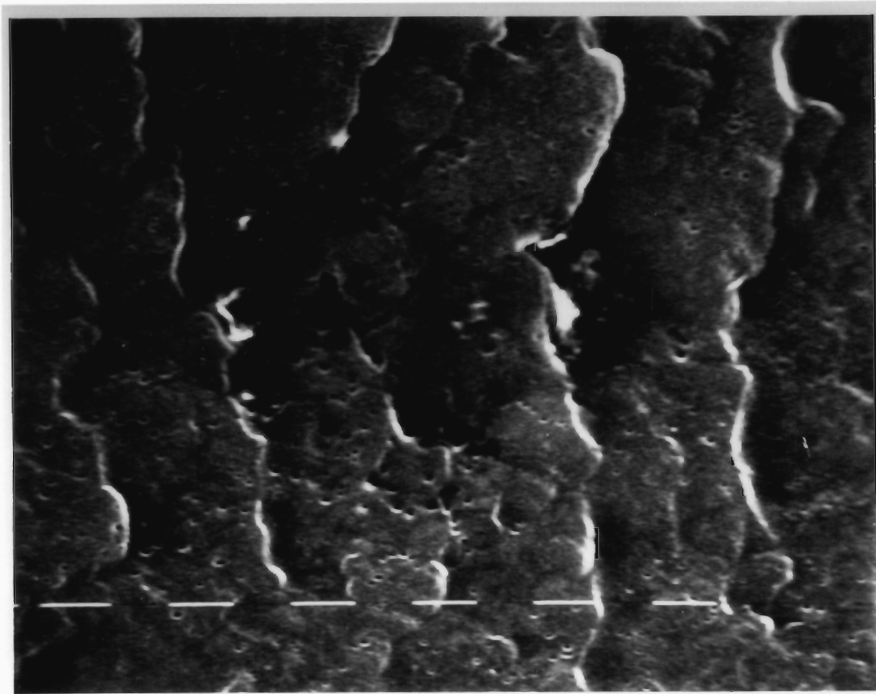


Figure 4.5.2 SEM of fracture surfaces of blends of Nylon 6/Poly(2-oxazoline) (90/10 by wt.)

comparable to that found in poly(2-methyl-2-oxazoline)/nylon 6 blends. The molecular weight difference between poly(2-methyl-2-oxazoline) and poly(2-oxazoline) complicates the interpretation of these results to some extent, but since poly(2-oxazoline) crystallizes easily, it can still be concluded that poly(2-methyl-2-oxazoline) is a better choice as part of an emulsifier.

4.5.2 Blends of Poly(propylene) and Poly(alkyl vinyl ether)s

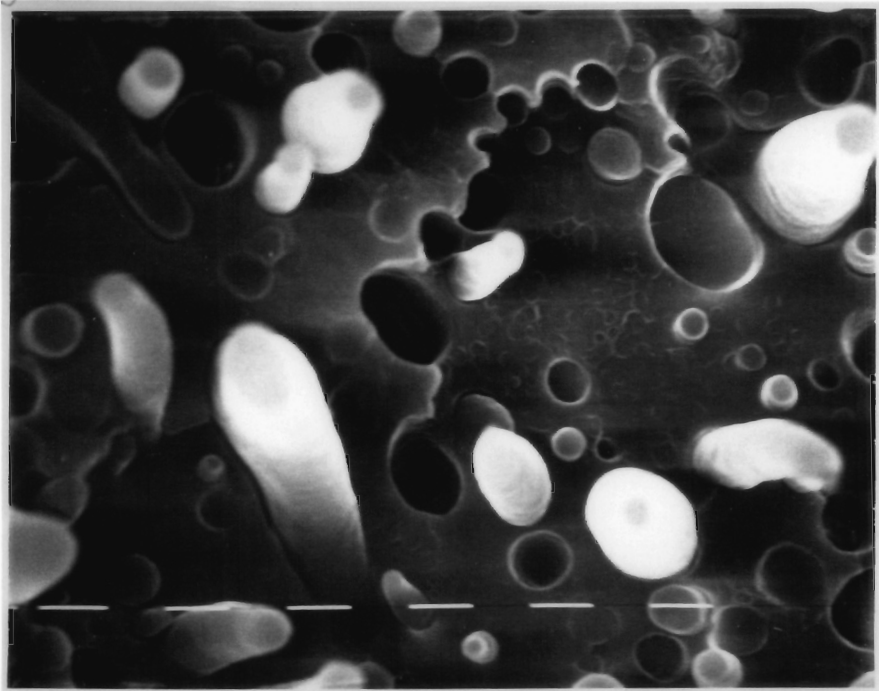
Due to the known lability of poly(propylene) and poly(alkyl vinyl ethers) toward free radical reactions, the possibility of melt grafting reactions between these materials was investigated by colleagues. They found that the domain size of poly(n-butyl vinyl ether) in poly(n-butyl vinyl ether)/poly(propylene) blends decreased substantially with increasing blending time, suggesting that some reaction had taken place between the two components. They also found that under identical conditions, the dispersed phase diameter of a poly(methyl vinyl ether)/poly(propylene) blend showed significantly larger poly(methyl vinyl ether) domains relative to poly(n-butyl vinyl ether). The reason for this latter point is not clear.

4.5.3 Blends of Poly(ϵ -caprolactam), Poly(propylene), and Emulsifiers

Based on the encouraging blend results described above, poly(n-butyl vinyl ether-g-2-methyl-2-oxazoline) copolymers were selected as potential emulsifier structures. To enhance the reaction between poly(propylene) and the poly(n-butyl vinyl ether) component, a master blend composed of poly(propylene) and poly(n-butyl vinyl ether-g-2-methyl-2-oxazoline) copolymers was prepared prior to blending with nylon 6. Figure 4.5.3 compares the fracture surfaces of nylon 6/poly(propylene) blends with 3% by wt. of a poly(n-butyl vinyl ether-g-2-methyl-2-oxazoline) copolymer as emulsifier with an analogous nylon 6/poly(propylene) control blend. It can be seen from the figure that addition of the copolymer decreased the size of the dispersed poly(propylene) phase substantially.

Although co-crystallization of poly(ϵ -caprolactone) with poly(propylene) has been previously proposed¹⁹⁹, blend studies using poly(2-alkyl-2-oxazoline-b- ϵ -caprolactone) copolymers were not encouraging. Large domains of dispersed poly(propylene) have been observed when either poly(2-ethyl-2-oxazoline-b- ϵ -caprolactone) or poly(2-methyl-2-oxazoline-b- ϵ -caprolactone) was used as an emulsifier (Figure 4.5.4). This was attributed to a lack of adhesion between poly(propylene) and poly(ϵ -caprolactone).

a)



5 μ m bar

b)

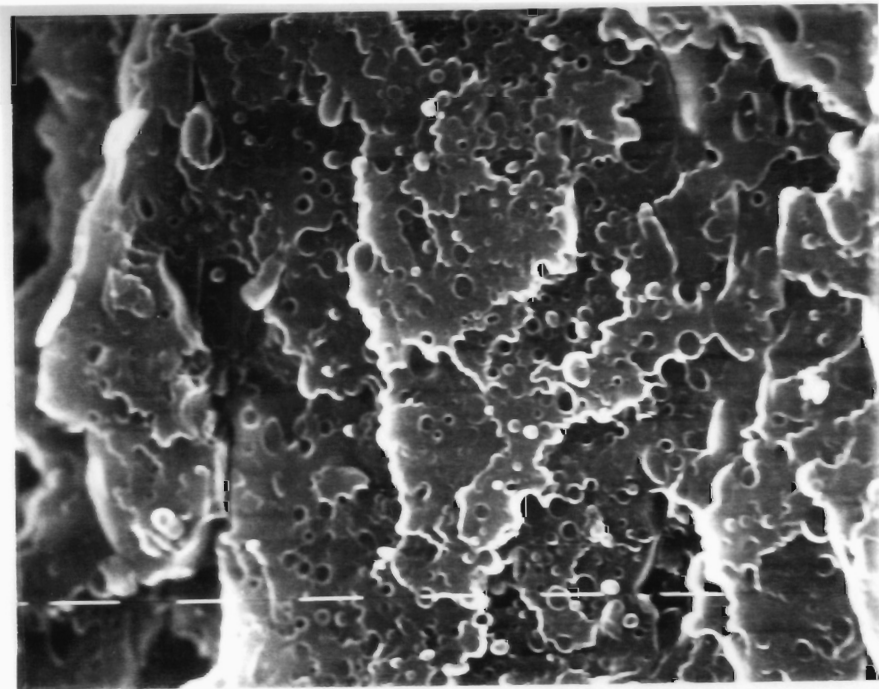
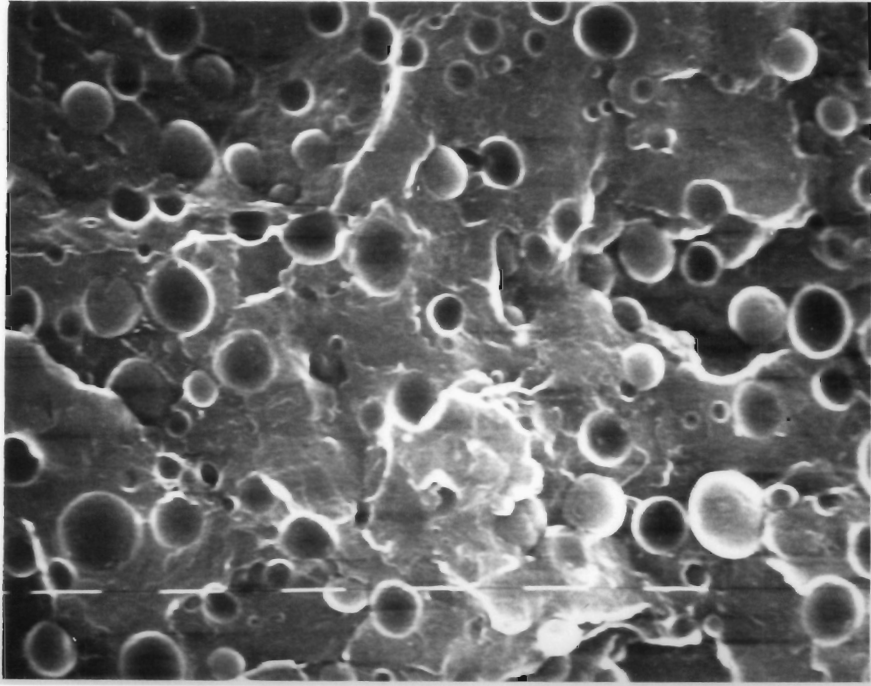


Figure 4.5.3 SEM of fracture surfaces of blends of
a) Nylon 6/Poly(propylene) control (70/30 by wt.)
b) Nylon 6/Poly(propylene)/PBVE-g-PMOX (70/27/3 by wt.)

a)



b)

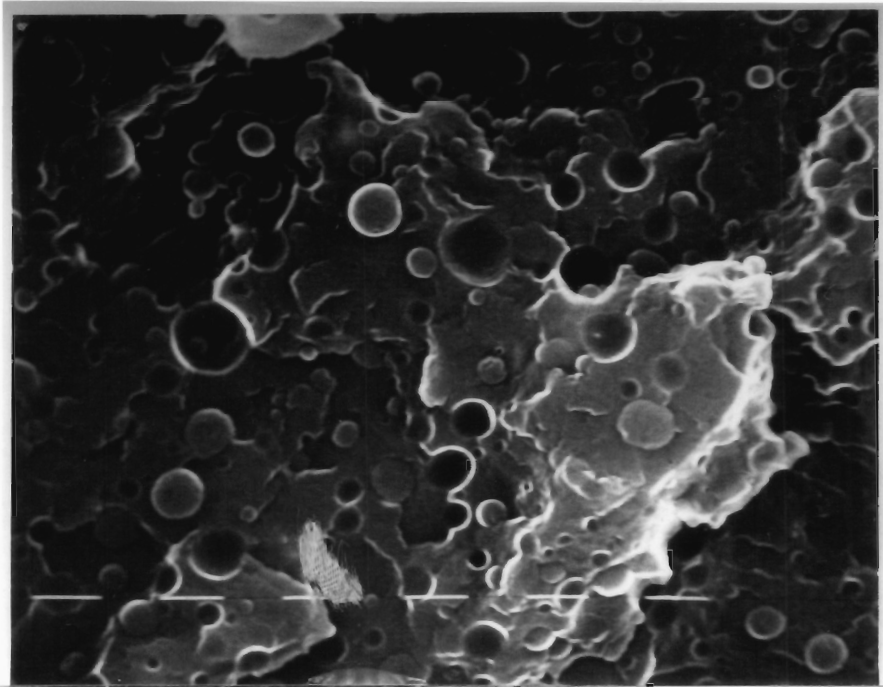


Figure 4.5.4 SEM of fracture surfaces of blends of
a) Nylon 6/Poly(propylene)/PEOX-b-PCL (90/9/1 by wt.)
b) Nylon 6/Poly(propylene)/PMOX-b-PCL (90/9/1 by wt.)

Chapter V

Conclusions

The emphasis of this thesis is on the preparation of block copolymers containing poly(2-alkyl-2-oxazoline) components which have well defined chemical and architectural structure. Because molecular weight distributions of each segment are difficult to analyze when blocks have been combined to make copolymers, the polymerization of 2-alkyl-2-oxazolines was studied using model initiators which approximate the macroinitiators used in the copolymerizations. Thus, conclusions from this work can be drawn which relate to both homopolymerization of 2-alkyl-2-oxazolines under specified conditions, and also to block copolymerization of such materials.

The living nature of poly(2-ethyl-2-oxazoline) in chlorobenzene has been investigated using activated halides such as benzyl iodide and benzyl chloride/NaI, and using the unactivated alkyl halide system, chloroethyl ethyl ether/NaI. Monomer conversion vs. molecular weight was analyzed for the case of benzyl iodide at 110°C up to a targeted M_n of 40,000 g/mol. Number average molecular weight was found to vary linearly with conversion, indicative of a living system. However, molecular weight distribution ranged from approximately 1.3 - 1.5, increasing toward the end of polymerization (approximately 100% conversion). The initial propagation step(s) was found to be rate determining. Subsequent propagation steps are

4-7 times faster than the rate limiting step. Thus, relative rates of initiation and propagation should not cause this broadening of the distributions. With our present knowledge of reactions taking place in this system, we cannot speculate as to the reason for very minor amounts of side reactions which might cause this molecular weight distribution broadening toward the end of the reaction. The living nature of these types of polymerizations was further demonstrated using the benzyl chloride/NaI and chloroethyl ethyl ether/NaI initiating systems by performing sequential monomer addition experiments. In all cases, the number average molecular weight increased as expected with sequential monomer addition following monomer depletion.

The effect on molecular weight distributions of poly(2-ethyl-2-oxazoline)s using different initiator systems was of particular interest in this work for two reasons. First, from a synthetic standpoint, it was only possible to use a limited number of different functional groups on the ends of the poly(dimethylsiloxane) and poly(alkyl vinyl ether) oligomers. Within these possible synthetic limits, we wanted to choose the best functional group to use on the ends of these macroinitiators for initiation of the oxazoline block. The property which was of most interest was the molecular weight distribution of the oxazoline component. Secondly, because one of the major intended applications for the final block copolymers was as steric suspension stabilizers, and making relatively low molecular weight polyoxazoline blocks was the interest. This, of course, is the

range of molecular weight where the relative rates of initiation vs. propagation would have the most effect.

The kinetics and mechanisms of these 2-ethyl-2-oxazoline polymerizations have investigated in chlorobenzene using iodide as the counterion. Results indicate that at very early stages of propagation (up to at least two repeat units on the chain) the active species is covalent. After that very early stage of propagation, ionic species are present and the overall propagation rate increases. Saegusa suggests^{19,20} that the carbonyl group on the penultimate unit provides a stabilizing influence on the oxazolinium ion of 2-methyl-2-oxazoline in acetonitrile as the solvent. In this work, the driving force for conversion of the endgroup to the ionic form is not clear, but the data is consistent with Prof. Saegusa's suggestion. Unfortunately, it was not possible to quantitatively determine the relative amounts of covalent vs. ionic "active" endgroups during these reactions. It is evident that the ionic form is contributing substantially to propagation. The extent of contribution from any remaining covalent endgroup is not yet clear.

It is important to understand the reactions taking place using both iodobutane and benzyl iodide as initiators in these polymerizations because these functional groups are related to those used on the poly(dimethylsiloxane) and poly(alkyl vinyl ether) macroinitiators used for the copolymerizations. Three stages of polymerization (initiation, initial propagation, and subsequent propagation) can be separately considered for the case of benzyl

iodide as the initiator. The initial propagation steps are clearly rate determining. If this were also the case for using iodobutane as the initiator, then the structure of the initiator should have relatively little effect on molecular weight distributions as long as the same counterion was present. For the case of iodobutane, the initiation and initial propagation stages cannot be separated. However, it is clear that the overall initiation rate constant at 80°C in the iodobutane case is slower than even the slowest step using benzyl iodide by approximately a factor of 20. Thus, the structure of the alkyl group on the initiator becomes quite important.

The actual macroinitiator systems used for copolymerization were benzyl chloride/NaI for the cases of the poly(dimethylsiloxane-*b*-2-ethyl-2-oxazoline)s and chloroethyl ethyl ether/NaI for the poly(alkyl vinyl ether-*b*-2-ethyl-2-oxazoline)s. Thus, homopolymerizations of 2-ethyl-2-oxazoline were also studied using benzyl chloride/NaI and chloroethyl ethyl ether/NaI. For the benzyl case, exchange of iodide for chloride was so fast at the polymerization temperature that it was not measurable. Thus, it was concluded that the initiating species was benzyl iodide and that the exchange reaction of iodide for chloride had been effectively separated from the processes of initiation and propagation. It is also clear that most of the chloride precipitates during the exchange step. The effect on molecular weight distributions using the direct comparison of benzyl iodide vs. benzyl chloride/NaI remains under investigation. However, the molecular weight distribution of a

poly(2-ethyl-2-oxazoline) oligomer prepared with a targeted M_n of 1000 g/mol using benzyl chloride/2 NaI was found to be narrow (1.19). As expected, the exchange rate of iodide for chloride on chloroethyl ethyl ether was much slower than on benzyl iodide. Thus, in order to separate the processes of exchange from initiation, chloroethyl ethyl ether was allowed to quantitatively react with sodium iodide prior to the addition of monomer. Again, the molecular weight distribution of a poly(2-ethyl-2-oxazoline) oligomer prepared in this manner with a targeted M_n of 1000 g/mol was found to be quite narrow (1.21).

Based on the knowledge of 2-ethyl-2-oxazoline homopolymerizations described above, copolymers of two types were prepared. Narrow distribution poly(dimethylsiloxane) oligomers terminated with benzyl chloride endgroups were used as macroinitiators in conjunction with sodium iodide for the growth of 2-ethyl-2-oxazoline blocks. Relatively narrow copolymer molecular weight distributions were found in all cases. Following extraction with hexane, a good solvent for the poly(dimethylsiloxane) portion, no fractionation was observed. This at least provides supporting evidence that the compositional distribution in these materials is also relatively uniform.

Poly(methyl vinyl ether) oligomers with Poisson distributions and precisely terminated on one end with a chloroethyl ether functional group were used in conjunction with sodium iodide to polymerize 2-ethyl-2-oxazoline blocks. In order to insure effective

initiation and to narrow the copolymer molecular weight and compositional distributions, the chloride to iodide conversion was made prior to the addition of monomer. A series of these diblock materials was prepared wherein the molecular weight distributions ranged from 1.3 - 1.4.

Both types of the materials described above are currently being utilized for studying the parameters important for steric stabilization of inorganic particles in polar media. The well defined nature of the copolymers is important in order to derive information relating the chemical structure and block lengths of the stabilizers to the properties of the suspensions.

A less defined series of materials was also prepared having poly(n-butyl vinyl ether) backbones and poly(2-methyl-2-oxazoline) grafts. These were found to be effective polymer blend emulsifiers in melt blends of isotactic poly(propylene) with Nylon 6.

Chapter VI

Recommendations for Future Study

Many interesting directions have evolved as a result of this research, and need to be pursued in the future. As demonstrated in this study, the molecular weight distributions of living poly(2-ethyl-2-oxazoline) initiated by benzyl iodide in chlorobenzene were not as narrow as a Poisson distribution. This broadening is probably caused by equilibria among various active species and should be explored further.

It has also been established in this research that the rate determining step(s) occurred at early stage(s) in the polymerization of 2-ethyl-2-oxazoline in chlorobenzene initiated by benzyl iodide or butyl iodide. The effects of more polar solvents and different counter-anions, such as iodide/NaCl (in the case of benzyl chloride/NaI as initiator) vs. iodide (benzyl iodide as initiator) should be investigated to identify possible mechanism changes and manipulation of initiation and propagation rates.

In the course of this research, it has also been observed that chloroethyl ethyl ether/NaI may be a more reactive initiating system than 1-chlorobutane/NaI for the polymerization of 2-ethyl-2-oxazoline. Because of the practicality of using alkyl chloride initiators for the preparation of block and graft copolymers, initiation rate constants using chlorine functionality should be pursued. It is also evident that in situ conversion of chlorine to iodide prior to

monomer addition is important. This necessitates the use of small amounts of dipolar aprotic solvents as diluents. The effect on rate constants, equilibria between chlorine and iodine, and mechanism is not understood at this point.

The unexplained surface activity of the low molecular weight block copolymer (0.5KPDMS-2KPEOX) should also be studied. This may become important in applications where complete surface coverage may be critical, such as for design of blood contacting cardiovascular implant material surfaces. The behavior of these low molecular weight components in solution is also of great interest.

Using the established procedures for the copolymerization of poly(methyl vinyl ether) and 2-ethyl-2-oxazoline, well defined poly(butyl vinyl ether-2-methyl-2-oxazoline) block copolymers need to be prepared. The application of these copolymers as blend compatibilizers for Nylon 6/poly(propylene) and other blends of polar/nonpolar polymer pairs should be explored further.

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