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Synthesis of graft and block copolymers via olefin metathesis ; Surface modification of poly(vinylchloride)/

Richard L. Norton
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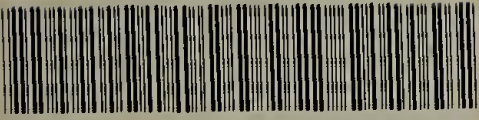
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I. SYNTHESIS OF GRAFT AND BLOCK COPOLYMERS
VIA OLEFIN METATHESIS

II. SURFACE MODIFICATION OF POLY(VINYLCHLORIDE)

A Dissertation Presented

by

RICHARD L. NORTON

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 1989

Polymer Science and Engineering

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Approved as to style and content by :



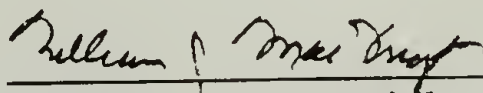
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I owe thanks to many people. This is only a partial listing of who I should thank and why.

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The pressures of the final months of graduate school seem to cause temporary insanity in most people. In my case they were perhaps the sanest part of graduate school because of Sarah. I have to say a special thank you to her.

Finally I must thank my family: Mom, Dad, brothers (Tom, Pete, John, Pat and Mark), aunts, uncles and cousins. Their caring and support have been important to me throughout my life.

ABSTRACT

I. SYNTHESIS OF GRAFT AND BLOCK COPOLYMERS VIA OLEFIN METATHESIS

II. SURFACE MODIFICATION OF POLY(VINYLCHLORIDE)

MAY 1989

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Poly(norbornenamer-g-styrene) graft copolymers were prepared by olefin metathesis copolymerization of norbornene and ω -norbornenyl-polystyrene, a macromonomer, using tungsten(VI) chloride/tetramethyltin catalysis. The molecular architecture of the graft copolymers was controlled in three ways: the backbone (poly(norbornenamer)) degree of polymerization by use of 1-octene as a chain transfer agent, the graft chain (polystyrene) degree of polymerization by the anionic macromonomer synthesis and the graft density by adjusting the ratio of norbornene to macromonomer.

Two methods for the synthesis of block copolymers by olefin metathesis using tungsten(VI) chloride/tetramethyltin catalysis were investigated. One method involved the complete polymerization of norbornene and then the addition of a second monomer, either bicyclo[4.2.0]oct-7-ene or cyclooctene. Some block copolymer was formed when bicyclo[4.2.0]oct-7-ene was used because of the occurrence of a small

amount of chain transfer. When cyclooctene was used, too much chain transfer occurred leading to formation of only slightly blocky copolymer. In the second method ω -vinylpolystyrene was used as a polymeric chain transfer agent in the polymerization of norbornene. The product contained some block copolymer of styrene and norbornene.

The surface of poly(vinylchloride) was partially converted to polyethylene by reduction with tributyltinhydride. The course of the reaction was followed by X-ray photoelectron spectroscopy and attenuated total reflection infrared spectroscopy. The surface reduced material was found to be resistant to conditions which caused extensive elimination at the surface of poly(vinylchloride). Surface reduction did not prevent dissolution of the poly(vinylchloride) film in tetrahydrofuran or swelling in dichloromethane. The reduced surface was shown to be oxidized by chromic acid (as is the surface of polyethylene) while the underlying PVC was unaffected.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iv
ABSTRACT.....	v
LIST OF TABLES.....	xii
LIST OF FIGURES.....	xiv
LIST OF SCHEMES.....	xvi
PART I. SYNTHESIS OF GRAFT AND BLOCK COPOLYMERS VIA OLEFIN METATHESIS	
CHAPTER	
I INTRODUCTION	1
Olefin Metathesis Background	2
Mechanism.....	2
Catalysts	9
Polymers	10
Block Copolymers	12
References	15
II EXPERIMENTAL	18
Materials	18
Materials Handling.....	19
Methods.....	20
Graft Copolymer Synthesis	20
Model Compound Synthesis.....	20
ω -Norbornenylpolystyrene Synthesis	21
Copolymerization of Model Compound and Norbornene.....	22

Comparison of 1-Octene and <i>cis</i> -2-Hexene as Chain Transfer Agents.....	22
Poly(norbornenamer- <i>g</i> -styrene) Synthesis	23
Poly(norbornenamer) synthesis	23
Casting of Polymer Films.....	23
Block Copolymer Synthesis.....	24
Effect of Cyclohexene on Catalyst Activity.....	24
Bicyclo[4.2.0]oct-7-ene Synthesis.....	24
Concurrent Addition Copolymerization of Norbornene and Cyclooctene.....	26
Sequential Addition Copolymerization of Norbornene and Cyclooctene.....	27
Concurrent Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene.....	27
Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene.....	28
Polymerization of Bicyclo[2.2.2]oct-2-ene	29
Polymerization of Phenylacetylene.....	29
Polymerization of Phenylnorbornene	29
Synthesis of ω -Vinylpolystyrene	30
Polymerization of Norbornene with ω -Vinylpolystyrene.....	30
Reference and Note	32
III RESULTS AND DISCUSSION	33
Graft Copolymer Synthesis	33
Model Compound Synthesis.....	35
Macromonomer Synthesis.....	35
Copolymerization of Model Compound and Norbornene.....	42

Copolymerization of the Macromonomer and Norbornene	45
Block Copolymer Synthesis.....	56
Catalyst Activity Studies	56
Block Copolymer Synthesis by Sequential Monomer Addition Introduction.....	59
Copolymerizations of Norbornene and Cyclooctene	67
Copolymerizations of Norbornene and Bicyclo[4.2.0]oct-7-ene	72
Other Monomers	79
Block Copolymer Synthesis by Reaction of a Polymeric Chain Transfer Agent Introduction	80
Synthesis of ω -Vinylpolystyrene	81
Polymerization Reaction.....	84
References and Notes.....	88
IV CONCLUSIONS AND SUGGESTIONS.....	90
Graft Copolymer Synthesis	90
Block Copolymer Synthesis.....	91
Reference	93
PART II. SURFACE CHEMISTRY OF POLY(VINYLCHLORIDE)	
CHAPTER	
V. INTRODUCTION.....	94
Objectives of This Research.....	96
Poly(vinylchloride) Background.....	97
Chemical Modification of PVC	97
Surface Modification of PVC.....	98
Reduction of Alkyl Chlorides with Tributyltin Hydride.....	99

Polymer Surface Analytical Techniques.....	101
UV-vis Spectroscopy.....	101
Attenuated Total Reflection Spectroscopy (ATR-IR)	102
X-Ray Photoelectron Spectroscopy (XPS).....	104
Contact Angle.....	107
References	109
VI. EXPERIMENTAL	112
Materials	112
Material Handling	113
Methods.....	114
Reduction of PVC Film with Tributyltin Hydride.....	114
Initial Reductions Using AIBN.....	114
Reduction at 45 °C.....	118
Reductions with AMBN as Initiator.....	118
Kinetic Study of Reduction Using Tributyltin Hydride	119
Reduction Control Experiments.....	121
Stronger Reduction Conditions	121
Reductions Using UV Light to Dissociate AMBN	122
AMBN Dissociation Kinetics	123
Other Reductions of PVC.....	124
Reduction of PVC Film with Triethylsilane	124
Reduction of PVC film with Chromium (II) Chloride	125
Attempted Reduction of PVF2 Film.....	125
Studies of the Properties of Reduced PVC	127
Base Treatment of PVC and Reduced PVC	127
Solvent Resistance Tests of PVC and Reduced PVC.....	128
Oxidation of PVC, Reduced PVC and PE	128

Note.....	130
VII. RESULTS AND DISCUSSION	131
Reduction of the Surface of PVC with Tributyltin hydride.....	131
Initial Reductions.....	131
Kinetic Study of Reduction.....	134
Reduction Control Experiments.....	146
Harsher Reduction Conditions	149
Reductions Employing UV initiation	150
Other Reductions of PVC.....	151
Attempted Reduction of PVC Film with Triethylsilane.....	151
Reduction of PVC Film with Chromium (II) Chloride	152
Attempted Reduction of Poly(vinylidene fluoride)	152
Studies of the Properties of Reduced PVC	153
Base Treatment of PVC and Reduced PVC	153
Solvent Resistance of Reduced PVC.....	155
Oxidation of Reduced PVC, PVC and PE	156
References and Notes.....	162
VIII. CONCLUSIONS AND SUGGESTIONS	164
References	166

LIST OF TABLES

Table 2.1: 1-Octene versus cis-2-Hexene as Chain Transfer Agents, GPC Data.....	23
Table 3.1: Macromonomer GPC Data	37
Table 3.2: Graft Copolymerization Data.....	50
Table 3.3: Graft Copolymerization GPC Data.	55
Table 3.4: Cyclooctene Metathesis after Aging with or without Cyclohexene Kinetic Data.	58
Table 3.5: Concurrent Copolymerization of Norbornene and Cyclooctene NMR Data.....	69
Table 3.6: Sequential Addition Copolymerization of Norbornene and Cyclooctene NMR Data.....	71
Table 3.7: Concurrent Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene NMR Data.	73
Table 3.8: Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene NMR Data.....	77
Table 3.9: Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene GPC Data.....	79
Table 3.10: ω -Vinylpolystyrene GPC Data	82
Table 3.11: Norbornene and ω -Vinylpolystyrene Reaction GPC Data.....	85
Table 6.1: Reaction Conditions and XPS Data for PVC Reduction.....	115
Table 6.2: Reaction Conditions and XPS Data for PVC Reduction.....	116
Table 6.3: Reaction Conditions and XPS Data for PVC Reduction.....	117
Table 6.4: Reaction Conditions and XPS Data for PVC Reduction.....	118
Table 6.5: Reaction Conditions and XPS Data for PVC Reduction.....	119
Table 6.6: XPS Data for PVC Reduction Kinetic Study.....	120
Table 6.7: Contact Angle Data for PVC Reduction Kinetic Study	120
Table 6.8: Conditions and XPS Data for Reduction Control Experiments.....	121
Table 6.9: Reaction Conditions and XPS Data for PVC Reduction.....	122

Table 6.10: Reaction Conditions and XPS Data for PVC Reduction	123
Table 6.11: Kinetics of AMBN Dissociation Data.....	124
Table 6.12: Reaction Conditions and XPS Data for PVC Reduction	124
Table 6.13: XPS Data for PVC Reduction using Chromium (II) Chloride	125
Table 6.14: Reaction Conditions and XPS Data for PVF2 Reduction.....	126
Table 6.15: Reaction Conditions and XPS Data for PVF2 Reduction.....	126
Table 6.16: XPS Data for Base Treatment of PVC and Reduced PVC	127
Table 6.17: XPS Data for Oxidized Samples.....	129
Table 6.18 Contact Angle Data for Oxidations.....	129
Table 7.1: Reaction Conditions and XPS Chlorine to Carbon Ratios for Initial Reductions.....	133
Table 7.2: Reduction Kinetic Study XPS Data.....	135
Table 7.3: Apparent PVC fraction data for kinetics experiments.....	142
Table 7.4: Conditions and XPS Data for Reduction Control Experiments.....	146
Table 7.5: Reaction Conditions and Apparent PVC Fractions for Harsher Reductions	149
Table 7.6: Reaction Conditions and Apparent PVC Fractions for Reductions with UV Initiation.....	150
Table 7.7: XPS Data for Base Treatment of PVC and Reduced PVC	155
Table 7.8: Contact Angle and XPS Data for Oxidations.....	158

LIST OF FIGURES

Figure 2.1: Reaction tube for UV photolysis.	25
Figure 3.1: IR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).....	38
Figure 3.2: ^{13}C NMR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).....	40
Figure 3.3: ^1H NMR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).	41
Figure 3.4: ^{13}C (upper) and ^1H NMR (lower) spectra of the copolymer of norbornene and the ethyl ester of 5-norbornene-2-carboxylic acid.	44
Figure 3.5: GPC of (a) ω -NBPS-DP29, (b) Methanol precipitated copolymerization product, (c) purified copolymerization product and (d) poly(norbornenamer) with a DP of 500.....	46
Figure 3.6: ^1H NMR spectrum of poly(norbornenamer- <i>g</i> -styrene).....	48
Figure 3.7: Mole percent styrene in product versus mole percent styrene in feed for graft copolymerization of norbornene and ω -NBPS-DP29.	52
Figure 3.8: Observed average number of grafts per chain versus predicted number from feed for graft copolymerization of norbornene and ω -NBPS-DP29.	52
Figure 3.9: ^{13}C NMR spectrum of the product of concurrent addition copolymerization of norbornene and cyclooctene.....	68
Figure 3.10: ^{13}C NMR spectrum of the product of sequential addition copolymerization of norbornene and cyclooctene.....	71
Figure 3.11: ^{13}C NMR spectrum of the product of concurrent addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.	73
Figure 3.12: ^{13}C NMR spectrum of product of sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.....	75
Figure 3.13: ^{13}C NMR spectrum of the product of sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.....	76

Figure 3.14: GPC of poly(norbornenamer) before addition of bicyclo[4.2.0]oct-7-ene (upper) and the product after the addition (lower).....	78
Figure 3.15: ^1H NMR spectrum of ω -vinylpolystyrene.....	83
Figure 3.16: GPC of products of norbornene and ω -vinylpolystyrene metathesis.	85
Figure 3.17: ^1H NMR spectrum of purified product of metathesis of norbornene and ω -vinylpolystyrene.	86
Figure 5.1: ATR-IR schematic.....	102
Figure 5.2: XPS schematic.....	106
Figure 5.3: Contact angle schematic.....	108
Figure 7.1: XPS survey spectra of PVC (upper)and 32 hour reduced PVC (lower)(take off angle = 75°).....	136
Figure 7.2: C_{1s} region of the XPS spectrum (take off angle = 15°) of PVC and reduced PVC.....	137
Figure 7.3: ATR-IR spectra of 32 hour reduced PVC (upper) and PVC (lower).	139
Figure 7.4: ATR-IR spectra carbon hydrogen stretching region of samples reacted different times. (Time of reaction indicated in hours.)...	140
Figure 7.5: Apparent PVC fraction by ATR-IR and XPS plotted versus reaction time for reduction kinetic study.	143
Figure 7.6: Transition state of reduction.....	144
Figure 7.7: ATR-IR spectrum of AMBN control sample.....	148

LIST OF SCHEMES

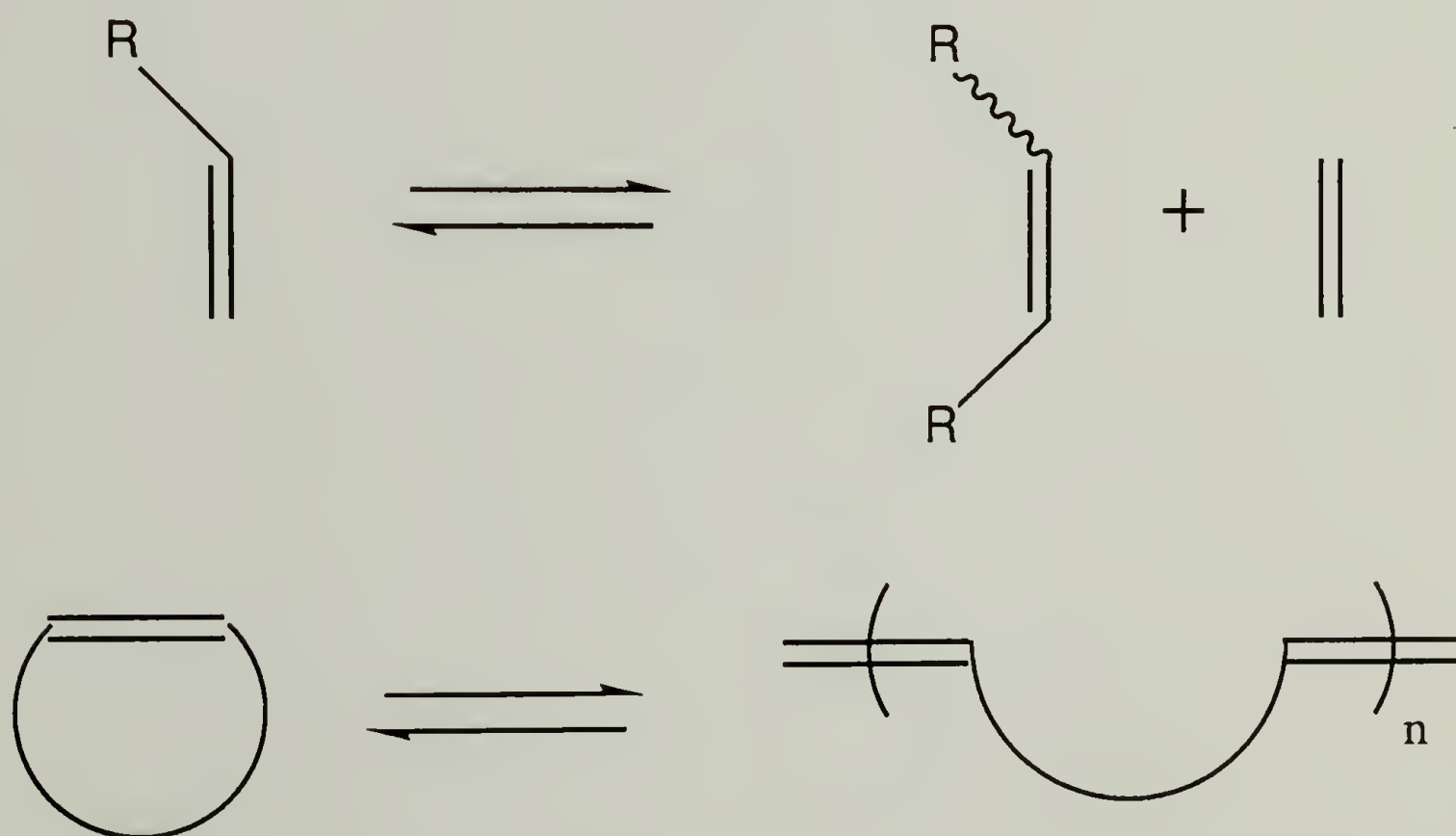
Scheme 1.1: Olefin Metathesis Reactions.	1
Scheme 1.2: Acyclic olefin metathesis catalytic cycle.....	3
Scheme 1.3: Cyclic olefin metathesis catalytic cycle.	4
Scheme 1.4: Olefin metathesis equilibrium.....	6
Scheme 1.5: Chain transfer involving another polymer chain.	7
Scheme 1.6: Chain transfer involving an acyclic olefin.	8
Scheme 1.7: Carbene formation mechanism for $WCl_6/SnMe_4$	9
Scheme 3.1: Poly(norbornenamer-g-styrene) synthesis.	34
Scheme 3.2: Synthesis of the ethyl ester of 5-norbornene-2-carboxylic acid.	35
Scheme 3.3: Synthesis of ω -norbornenylpolystyrene.....	36
Scheme 3.4: Copolymerization of norbornene and the ethyl ester of 5-norbornene-2-carboxylic acid.	43
Scheme 3.5: Sequential addition copolymerization schematic	61
Scheme 3.6: Polymer and carbene structures.....	64
Scheme 3.7: Bicyclo[4.2.0]oct-7-ene synthesis.....	65
Scheme 3.8: Concurrent addition copolymerization of norbornene and cyclooctene.	67
Scheme 3.9: Sequential addition copolymerization of norbornene and cyclooctene.	70
Scheme 3.10: Concurrent addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.	72
Scheme 3.11: Sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.	74
Scheme 3.12: Olefin metathesis of norbornene and ω -vinylpolystyrene.	80
Scheme 3.13: Synthesis of ω -vinylpolystyrene.....	81
Scheme 5.1: Surface reduction of PVC.....	97

Scheme 5.2: Reaction Steps in Reduction of Alkyl Chlorides with HSnBu ₃	100
Scheme 7.1: Base treatment of PVC and reduced PVC.....	154
Scheme 7.2: Oxidation of PE, PVC and reduced PVC.....	157
Scheme 7.3: Oxidation of PVC surface.....	159

PART I: SYNTHESIS OF BLOCK AND GRAFT COPOLYMERS VIA OLEFIN METHATHESIS

CHAPTER I INTRODUCTION

Olefin metathesis is a unique reaction. Carbon-carbon double bonds, often the strongest bonds in the molecule, are broken by a catalyst. The resultant molecular fragments are then recombined by formation of new double bonds.¹⁻³ Metathesis of an asymmetric acyclic olefin yields a mixture of olefins. When a cyclic olefin reacts, the new double bonds formed link the ring opened units together to form a polymer. These reactions, which are reversible, are shown in Scheme 1.1.



Scheme 1.1: Olefin Metathesis Reactions.

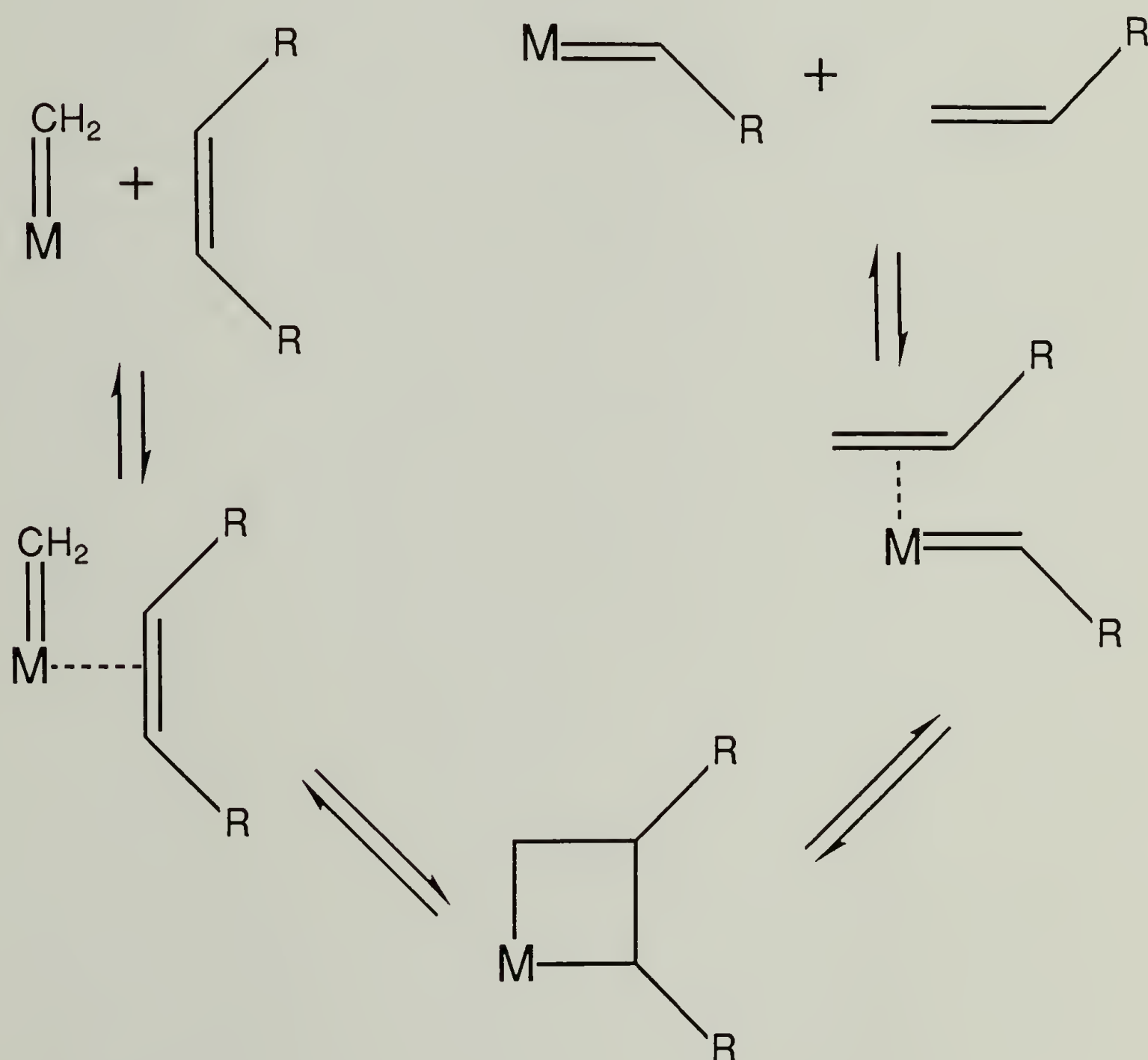
The synthesis of graft and block copolymers via olefin metathesis is the objective of the work described here. This is part of an ongoing effort to demonstrate that a variety of molecular architectures can be achieved with this versatile reaction. The graft copolymer, poly(norbornenamer-*g*-styrene), was synthesized by copolymerization of norbornene and ω -norbornenylpolystyrene, a macromonomer. This synthesis is the first example of a well defined graft copolymer being formed by olefin metathesis. When this research began there was no available method for synthesizing well defined block copolymers by olefin metathesis. Some syntheses of block copolymers employing living metathesis systems were reported during the course of this research.⁴⁻⁷ Two methods for synthesizing block copolymers which are complementary to the use of living metathesis systems were investigated in this research. Both of these rely on chain transfer reactions to form block copolymer. In the first method, one metathesis monomer is polymerized and then a second monomer is added. If the proper amount of chain transfer occurs during the polymerization of the second monomer, multiblock copolymer is formed. In the second method a metathesis monomer is polymerized in the presence of ω -vinylpolystyrene, which acts as a polymeric chain transfer agent. Chain transfer causes the formation of diblock and triblock copolymers of styrene and norbornene.

Olefin Metathesis Background

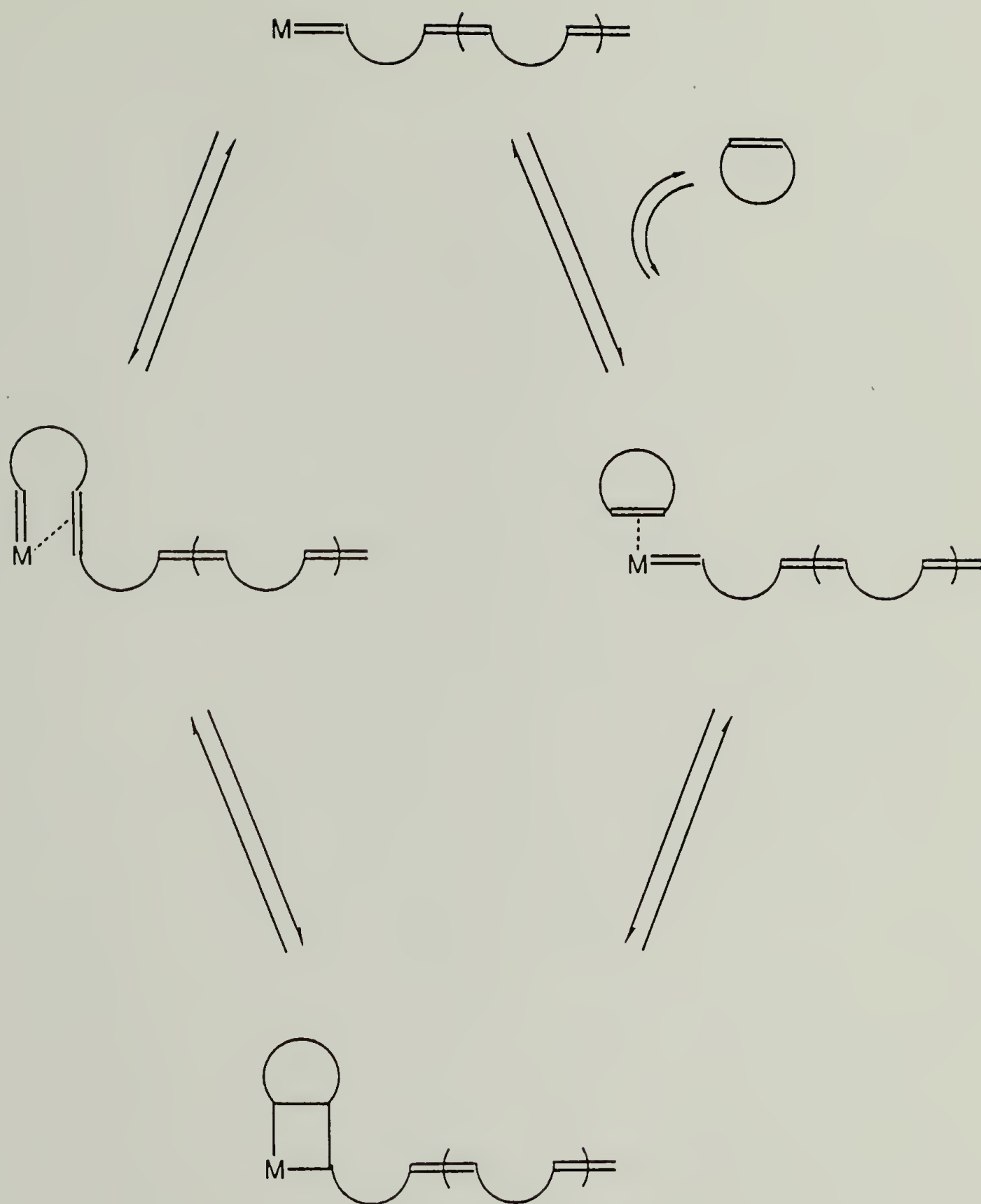
Mechanism

The currently accepted general mechanism of olefin metathesis, involving metal carbenes and metallocyclobutanes, was first proposed in 1970.⁸ Experimental support for this mechanism includes studies of the

initial products formed,^{2,9} the catalytic activity of some isolable metal carbenes^{5,10,11} and metallocyclobutanes,^{12,13} and of spectroscopically observed metal carbenes^{14,15} and metallocyclobutanes.¹⁵ The catalytic cycles of metathesis of an acyclic olefin and a cyclic olefin are shown in Schemes 1.2 and 1.3. It is important to note that the same fundamental steps are involved.



Scheme 1.2: Acyclic olefin metathesis catalytic cycle.

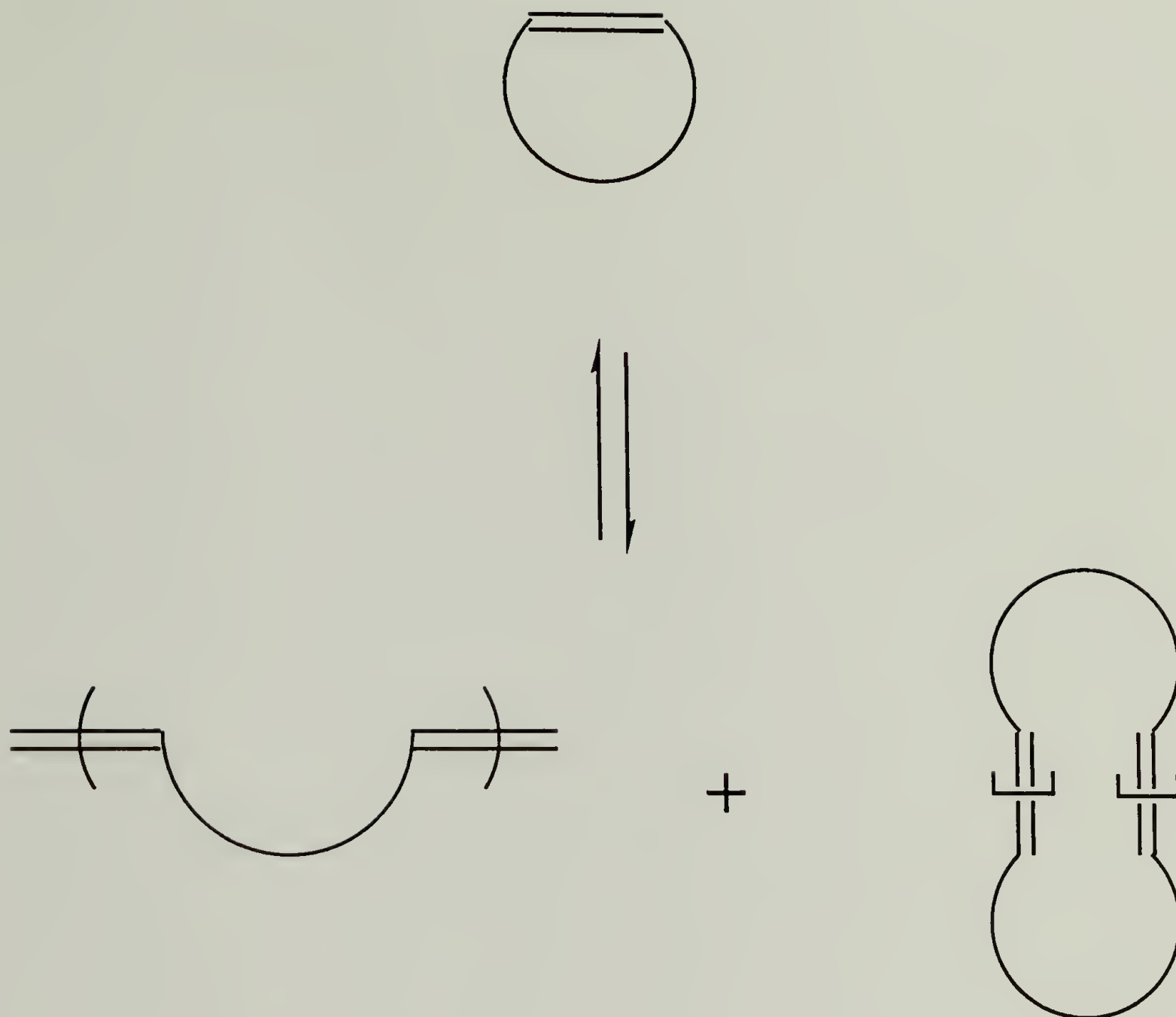


Scheme 1.3: Cyclic olefin metathesis catalytic cycle.

The formation of the various products obtained by the metathesis of an acyclic olefin is explained by the reaction of all the possible combinations of carbenes and reacting olefin in the catalytic cycle. Since the products of this reaction can also serve as reactants, the reaction is reversible and an equilibrium mixture of olefins can be obtained. An equilibrium mixture is not always obtained: many catalysts exhibit selectivity in the olefins reacted and produced.¹ This allows kinetic control of the products obtained.

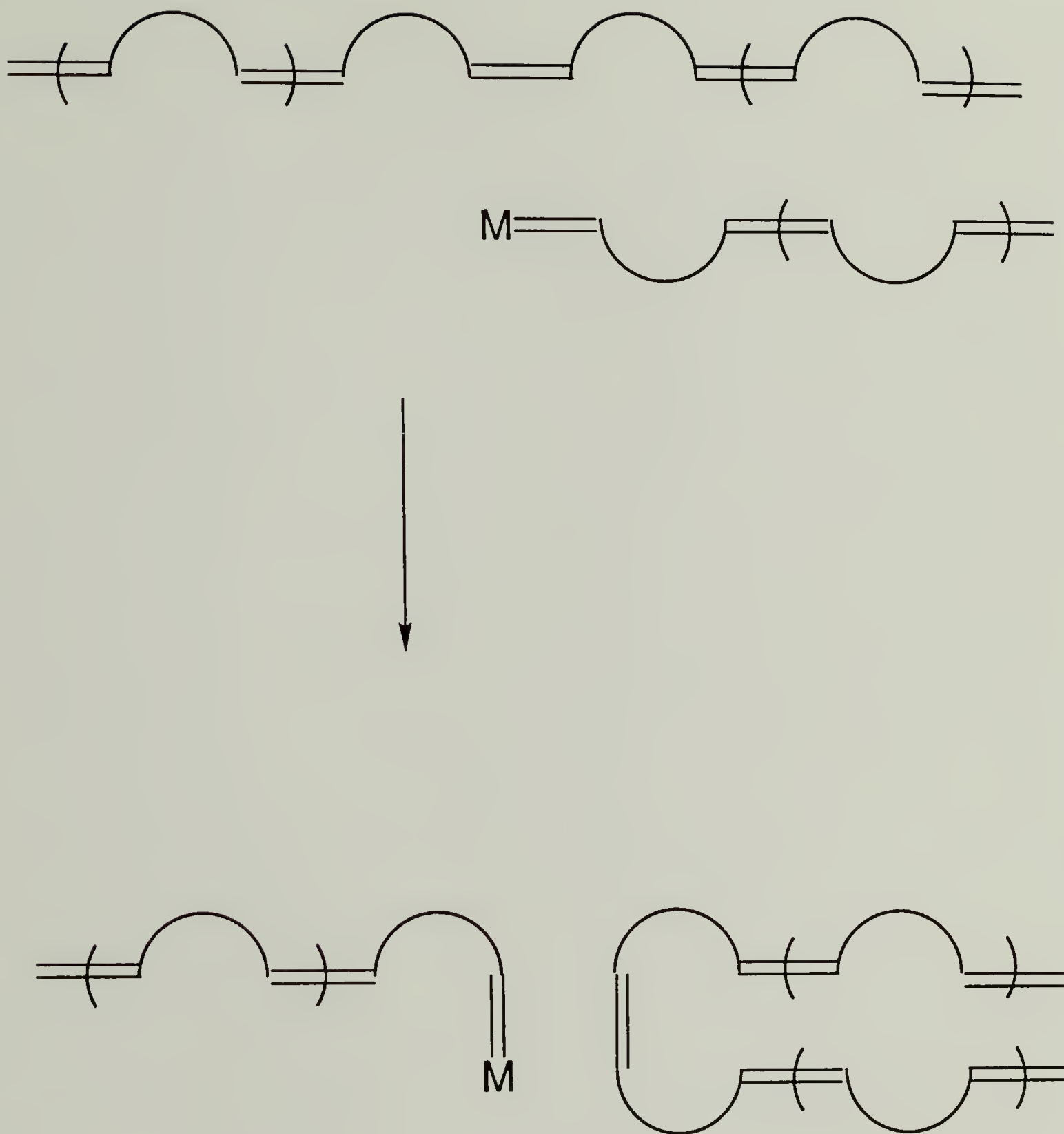
Metathesis of a cyclic olefin gives a mixture of monomer, cyclic oligomer and polymer at equilibrium as shown in Scheme 1.4. The distribution of the products at equilibrium depends on thermodynamic parameters such as: temperature, pressure, concentration and the enthalpies and entropies of the monomer, oligomers and polymer. Kinetic control of the product mixture is possible. For example, some catalysts initially form high polymer exclusively and later depropagation yields cyclic oligomers. Other catalysts establish the equilibrium cyclic concentration first and then form polymer.³

The formation of polymer, cyclic oligomer and monomer occurs by the catalytic cycle outlined in Scheme 1.3. Propagation is the result of going through the cycle clockwise. Going through the cycle counterclockwise gives depropagation. If depropagation occurs as drawn monomer is reformed. A cyclic oligomer is formed if the carbene reacts with a double bond further back in the chain. This intramolecular chain transfer process is known as backbiting.



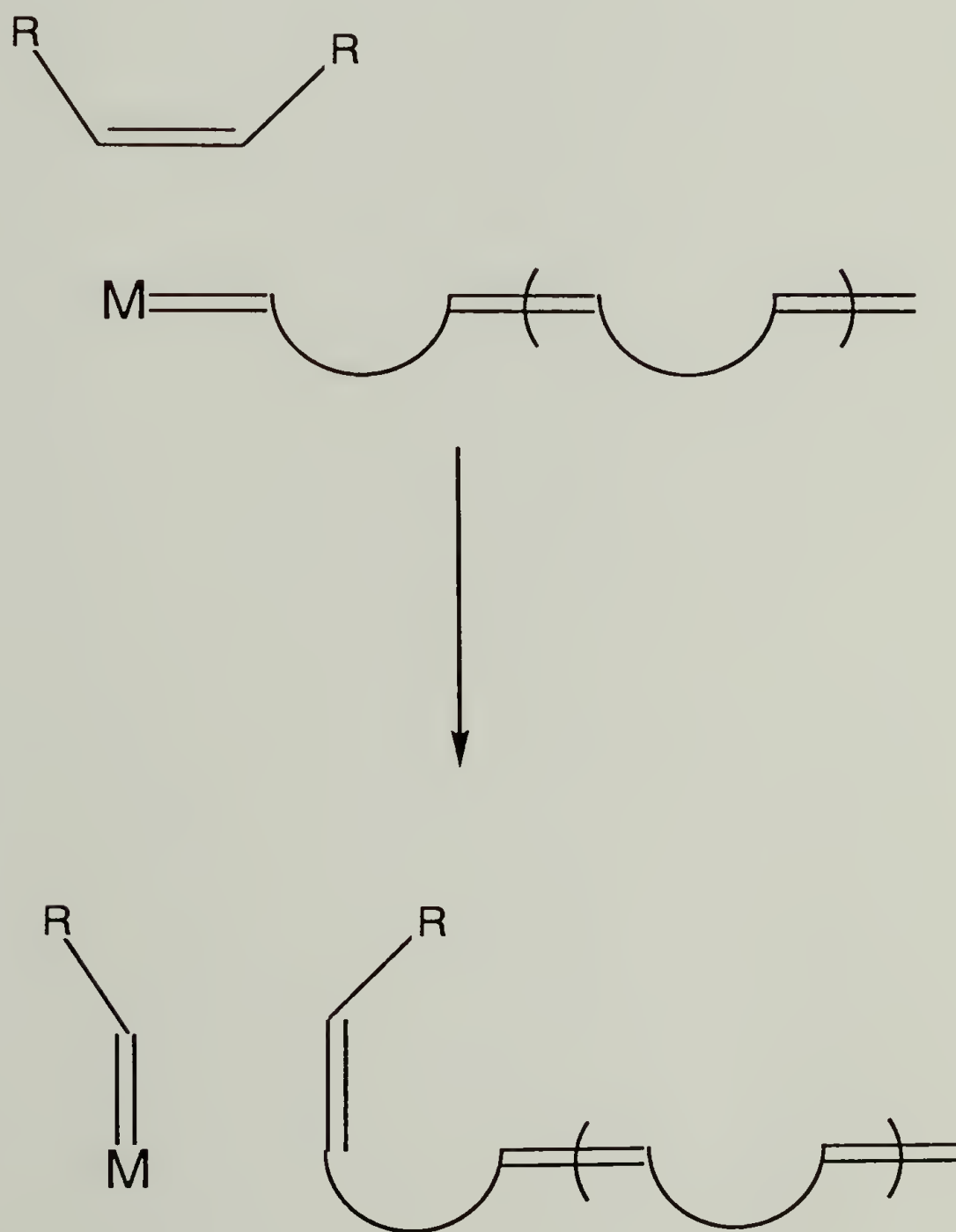
Scheme 1.4: Olefin metathesis equilibrium.

Intermolecular chain transfer processes also occur. A double bond in another polymer can react with a carbene as shown in Scheme 1.5. This scrambles the initial polymer structure and prevents formation of polymers with a narrow molecular weight distribution. Acyclic olefins are added to metathesis polymerization to serve as chain transfer agents which limit the molecular weight of the polymer.



Scheme 1.5: Chain transfer involving another polymer chain.

Reaction of an acyclic olefin with a growing chain terminates that chain and forms a new carbene (Scheme 1.6) which can initiate further polymerization or bite into another chain. In this way each acyclic olefin reacted forms two chain ends. The number average molecular weight of the polymer produced is determined by the ratio of monomer reacted to acyclic olefin reacted. The mechanism of these chain transfer processes is the same as that of metathesis of an acyclic olefin.

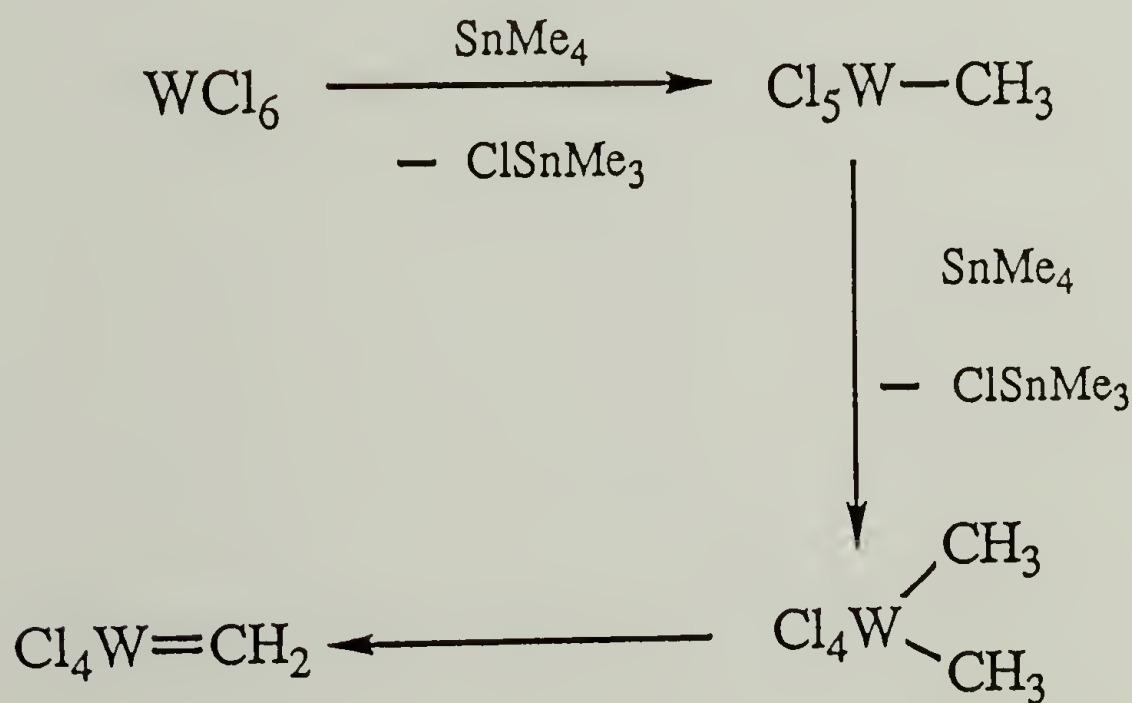


Scheme 1.6: Chain transfer involving an acyclic olefin.

Catalysts

A large number of catalyst systems have been used for olefin metathesis.¹⁶ The catalysts can be homogeneous or heterogeneous (supported or nonsupported). Some catalysts are discrete, isolable metal carbenes^{5,11,16} or metallocyclobutanes.^{12,13} More usually the catalyst is formed in situ by reaction of two or more catalyst precursors.

The formation of the catalytic species in the tungsten hexachloride and tetramethyltin catalyst system ($\text{WCl}_6/\text{SnMe}_4$), which was used in this research, has been studied.¹⁷⁻²² The accepted reaction path for formation of a metal carbene is shown in Scheme 1.7. Labeling studies^{17,20,21} have determined that only a small portion (0.7, 1.4 and 8 percent) of the tungsten atoms actually participate in olefin metathesis. This has been attributed to the inefficiency of the reactions outlined in Scheme 1.7.¹⁸⁻²⁰ Another possible factor is that not all the metal carbenes formed are catalytically active.



Scheme 1.7: Carbene formation mechanism for $\text{WCl}_6/\text{SnMe}_4$.

There are a number of indications that the actual catalytic species in this and other catalytic systems is not a simple metal carbene. There is theoretical evidence that reaction with water or oxygen is needed for formation of an active catalyst in some catalyst systems.^{2,23} It has also been proposed that bimetallic bridged complexes are the actual catalytic species.²⁷⁻²⁹ There is evidence that some catalytic species are bimetallic: Addition of an aluminum trihalide to a metal carbene has been shown to greatly increase olefin metathesis activity.²⁹ There are significant differences in different WCl_6 based catalyst systems that could be explained by cocatalyst involvement in a bimetallic catalyst: The percentage of *cis* double bonds formed in polymerization of norbornene by WCl_6 based catalyst systems varies from 39 to 74 percent³⁰ and the $\text{WCl}_6/\text{SnMe}_4$ catalyst system is compatible with many functional groups that other WCl_6 based systems are not.³¹

The $\text{WCl}_6/\text{SnMe}_4$ catalyst system was chosen for use in this research because it is compatible with many functional groups³¹⁻³⁴ and relatively easily prepared. The actual catalyst is formed in situ on mixing the two commercially available precursors under anaerobic conditions. Functional group compatibility and ease of use are important since the objective of this work is to demonstrate the versatility of olefin metathesis.

Polymers

Monocyclic olefins of 4 members and higher (with the exception of 6 membered rings) have been polymerized. Cyclohexene, other 6 membered rings, and some substituted rings of other sizes do not polymerize under normal conditions because of thermodynamics. The change in enthalpy with

the opening of these only slightly strained rings is not enough to offset the loss of entropy which occurs upon polymerization. The free energy of polymerization is not negative and therefore polymer is not formed. Lowering the temperature attenuates the effect of the entropy loss. Cyclohexene has been oligomerized and copolymerized at low temperature.³⁵ Every cyclic olefin has a theoretical ceiling temperature above which it will not polymerize because of the temperature dependence of the free energy. The interplay of enthalpy and entropy is also responsible for equilibrium concentrations of monomer and cyclic oligomers.

A number of bicyclic olefins and multicyclic olefins have been polymerized. Many polymerization studies have been done with norbornene, (bicyclo[2.2.1]hept-2-ene), and its derivatives. Polymerization of norbornene is heavily favored thermodynamically, because it is a strained ring system. It is very rapidly polymerized (with at least $\text{WCl}_6/\text{SnMe}_4$) because it forms a very active carbene.³⁶ A great deal of olefin metathesis research involves norbornene or norbornene derivatives because of the above factors and the fact that it is a commercially used monomer.

The structure of olefin metathesis polymers is most often studied by ^{13}C NMR. The ratio of *cis* to *trans* double bonds is commonly determined by looking at the olefin carbon region of the spectrum. Other structural features that can be examined by ^{13}C NMR include tacticity, the amount of head to tail additions and copolymer structure.

Metathesis polymers of cyclic olefins are called poly(alkenamer)s in general. Specific polymers are named using the monomer name (without the

cyclo- prefix) and the -amer suffix which indicates that it is a ring opened polymer. The metathesis polymer of cyclooctene is poly(octenamer). The metathesis polymer of norbornene is poly(norbornenamer). This nomenclature is generally used and will be used in this dissertation. An alternate nomenclature, which follows the IUPAC conventions, refers to the aforementioned polymers as poly(1-octenylene) and poly(1,3-cyclopentylene-vinylene).

There are examples of commercial uses of olefin metathesis polymers. Poly(octenamer) is used in blends with other elastomers to improve the strength of unvulcanized materials and to decrease the viscosity of the blends during processing.³⁷ Poly(norbornenamer) is an unusually soft rubber which is used as a sound and vibration damping material and as a sealant.³⁸ It is used in powder form as an oil absorbant: it can absorb 10 times its weight in aromatic petroleum oils.³⁹

Block Copolymers

Several strategies of olefin metathesis block copolymerization have been investigated. Ill defined block and/or graft copolymers have been formed by addition of poly(butadiene) or a styrene/butadiene copolymer to a metathesis polymerization.^{40,41} The blocks or grafts are formed by chain transfer involving the double bonds in the added polymer. Sequential addition of 5-cyanonorbornene, cyclopentene and 5-cyanonorbornene has been claimed to have resulted in block copolymer formation.⁴² This is unlikely since the polymerization was done below the cyclopentene equilibrium monomer concentration. A block copolymer of styrene and cyclopentene has been formed by addition of polystyryllithium to WCl_6 and

cyclopentene.⁴³ Presumably the polystyryllithium acts as a cocatalyst in formation of the initial carbene.

Block copolymers of acetylene and another monomer have reported by olefin metathesis. Addition of polystyryllithium to WCl_6 and acetylene has yielded a styrene/acetylene block copolymer.⁴⁴ Addition of acetylene to a cyclopentene polymerization has yielded a block copolymer of these two monomers.⁴⁵

In the above examples there is little control of block copolymer structure and probably significant amounts of homopolymer formed. Synthesis of well defined block copolymers by sequential monomer addition requires use of a living initiator and the avoidance of chain transfer. All of the chains formed in the polymerization of the first monomer must remain able to initiate polymerization of the second monomer.

The first example of a living metathesis system involved the initial formation of block copolymers of norbornene derivatives using a tungsten catalyst.¹⁴ The only analysis of this system was NMR spectroscopy of the metal carbenes and the polymer, which indicated that block copolymer was formed initially but that the copolymer structure was scrambled by later chain transfer reactions. Some discrete and isolable metal carbenes^{5,11} and metallocyclobutanes^{12,13} were shown to act as living initiators in the olefin metathesis polymerization of norbornene or norbornene derivatives. These living systems have all the attributes of an anionic living polymerization: the molecular weight of the polymer is determined by the ratio of monomer to initiator, the molecular weight distribution of the product is narrow, the

living polymer can be endcapped and well defined block copolymers can be synthesized quantitatively.

Formation of well defined block copolymers by sequential monomer addition has been reported with these living systems.⁴⁻⁷ Two other methods of synthesizing block copolymers using a living system have been demonstrated: termination of a living polymer with a polymeric endcapping reagent and transformation of the living end of an olefin metathesis polymer to a Ziegler-Natta initiator and subsequent olefin polymerization.⁴⁶

There are limitations to these living systems. Living behavior has only been demonstrated with norbornene, norbornene derivatives and other monomers which produce sterically hindered double bonds on ring opening. The avoidance of chain transfer, which is necessary for living behavior, may depend both on the initiator and the double bond structure of the monomer and polymer. This could severely limit the number of monomers that could be used in this manner. It is reported with one system that cyclopentene is polymerized but that the molecular weight distribution is broad.⁷

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CHAPTER II

EXPERIMENTAL

Materials

Acetophenone (Aldrich) was distilled from calcium hydride.

Benzene (Fisher) was distilled from sodium/benzophenone dianion.

Bicyclo[2.2.2]oct-2-ene (Aldrich) was dissolved in chlorobenzene. This solution was then distilled from calcium hydride.

sec-Butyllithium (Aldrich) was used as received, a cyclohexane solution in a Sure-Seal™ bottle.

Calcium hydride (Aldrich) was used as received.

Chlorobenzene (Aldrich) was distilled from calcium hydride.

3-Chloropropene (Aldrich) was distilled trap-to-trap from calcium hydride.

Cyclohexene (Aldrich) was distilled from calcium hydride.

1,3-Cyclooctadiene (Aldrich) was distilled from calcium hydride.

Cyclooctene (Aldrich) was distilled from calcium hydride.

Ethanol (Pharmco) was distilled from magnesium, which had been activated by reaction with iodine.

Ethylene oxide (Eastman Kodak) was distilled from calcium hydride.

Heptane (Aldrich) was distilled from calcium hydride.

Heptane (Aldrich) was distilled trap-to-trap from calcium hydride.

cis-2-Hexene (Wiley) was distilled trap-to-trap from calcium hydride.

Magnesium (Fisher) was used as received.

Norbornene (Aldrich) was dissolved in chlorobenzene. This solution was then distilled from calcium hydride.

5-Norbornene-2-carbonyl chloride (Pfaltz & Bauer) was used as received.

Octane (Aldrich) was distilled trap-to-trap from calcium hydride.

1-Octene (Aldrich) was distilled trap-to-trap from calcium hydride.
Phenylacetylene (Aldrich) was distilled from calcium hydride.
Phenylnorbornene (Wiley) was distilled from calcium hydride.
Styrene (Aldrich) was distilled from calcium hydride.
Tetramethyltin (Aldrich) was distilled trap-to-trap from calcium hydride.
Tungsten (VI) chloride (Aldrich) was used as received.

Materials Handling

All solutions, distilled reagents and distilled solvents were stored under nitrogen in flasks sealed with Teflon stopcocks. All transfers of these liquids were done under nitrogen by syringe or cannula. Solutions were prepared by standard Schlenk techniques except for the two exceptions noted below.

Solutions of tungsten (VI) chloride (WCl_6) in chlorobenzene were prepared in the following manner: In a glove bag, an ampule of WCl_6 was opened and a portion of the solid placed in a tared round bottom flask, which contained a stir bar. The flask was stoppered with a rubber septum (also tared), taken from the glove bag and weighed. The amount of chlorobenzene needed to make a solution of the desired molarity was then added. The WCl_6 was dissolved by stirring under a positive pressure of nitrogen for 30 minutes. The solution was then transferred to a Teflon stopcock equipped storage flask.

Chlorobenzene solutions of norbornene and bicyclo[2.2.2]oct-2-ene were prepared and purified in the following manner: A solution of the solid

compound of the desired molarity was prepared with undistilled chlorobenzene in air. This solution was then distilled from calcium hydride into a storage flask equipped with a Teflon stopcock. The concentrations of the original and distilled solutions were compared by gas chromatography.

Methods

NMR spectra, ^1H and ^{13}C , were obtained of deuteriochloroform solutions of the sample with either a Varian XL-200 or XL-300 spectrometer. Gel permeation chromatography (GPC) was carried out using Polymer Laboratories PL gel columns (10^4 , 10^3 , 10^2 angstrom), a Rainin Rabbit Pump, a Knauer 98 refractive index detector and toluene as the mobile phase. GPC data accumulation was performed using Interactive Microware GPC software and an Apple IIe computer. Molecular weight data is reported relative to a polystyrene calibration. Gas chromatography was carried out using a Hewlett Packard 5790A instrument and either an Analabs 15% AN-600 or DC-200 column.

Graft Copolymer Synthesis

Model Compound Synthesis

(6-43)¹ 5 mL of 5-Norbornene-2-carbonyl chloride (30 mmol) was added by cannula to a nitrogen-purged round bottom flask. Then 2 mL of ethanol (33 mmol) was added dropwise by cannula. After 20 minutes the reaction mixture was washed with 2 N sodium hydroxide in water (3 times). The mixture was dried over first calcium chloride and then magnesium sulfate. The ester was then distilled from calcium hydride. All the above

procedures were done under nitrogen because of the stench of the norbornene derivatives.

ω -Norbornenylpolystyrene Synthesis

(6-44) Benzene (40 mL) was added to a nitrogen-purged, crown-capped pressure bottle containing a Teflon stir bar. The appropriate amount (for the desired polymer molecular weight) of *sec*-butyllithium was introduced. Styrene (3 mL) was then added dropwise at room temperature and the polymerization mixture was stirred for 30 minutes. Ethylene oxide was then introduced into the reaction bottle as a vapor in a stream of nitrogen until the red color of the polystyryllithium was discharged. A slight molar excess (based on *sec*-butyllithium) of 5-norbornene-2-carbonyl chloride was then added. After 10 minutes the reaction was stopped.

The lowest molecular weight sample was isolated in the following manner: The reaction solution was transferred to a separatory funnel and washed with water (twice), saturated sodium bicarbonate solution (twice) and saturated sodium chloride solution. The solution was dried with magnesium sulfate. The benzene was then removed, first by rotary evaporation and then by drying on a vacuum line.

The other samples were isolated and purified by precipitation in methanol, dissolution in tetrahydrofuran and reprecipitation in methanol. The samples were then dried at reduced pressure.

Copolymerization of Model Compound and Norbornene

(6-49) Chlorobenzene (2.6 mL) and 1.6 mL of 0.07 M tetramethyltin (SnMe_4) in chlorobenzene (0.11 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. This was placed in an 80 °C oil bath. After 5 minutes 0.8 mL of 0.07 M WCl_6 in chlorobenzene (0.05 mmol) and 0.1 mL of 1.0 M *cis*-2-hexene in chlorobenzene (0.1 mmol) were added. After another 5 minutes, A mixture of 0.4 mL of the ethyl ester of 5-norbornene-2-carboxylic acid (2 mmol) and 4 mL of 2 M norbornene in chlorobenzene (8 mmol), which had been previously combined under nitrogen, was added. After 10 minutes the copolymer was precipitated in methanol and dried at reduced pressure.

Comparison of 1-Octene and *cis*-2-Hexene as Chain Transfer Agents

(6-70) Chlorobenzene (5 mL), 2.0 mL of 2.5 M norbornene in chlorobenzene (5 mmol), 0.4 mL of 0.12M SnMe_4 in chlorobenzene (0.048 mmol), 0.01 mL of heptane and 0.2 mL of a 0.06 M chlorobenzene solution of *cis*-2-hexene or 1-octene (0.02 mmol) were added to a nitrogen-purged Schlenk tube which contained a stir bar. The reaction tube was placed in an 80 °C oil bath. After 5 minutes 0.4 mL of 0.06M WCl_6 in chlorobenzene (0.024 mmol) was then added. After 10 minutes the polymer was precipitated in methanol. The product was then dried at reduced pressure. Gas chromatography of the reaction mixtures indicated that all of the 1-octene and 40% of the *cis*-2-hexene reacted in 10 minutes. The molecular weight data (relative to polystyrene standards) is given in Table 2.1.

Table 2.1: 1-Octene versus *cis*-2-Hexene as Chain Transfer Agents, GPC Data

<u>Chain Transfer Agent</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
1-Octene	21000	43000	2.04
<i>cis</i> -2-hexene	69000	114000	1.65

Poly(norbornenamer-g-styrene) Synthesis

(6-90) The desired amount of ω -norbornenylpolystyrene and a Teflon coated stir bar were placed in a Schlenk tube which was then purged with nitrogen. Chlorobenzene (5 mL), 2.0 mL of 2.5 M norbornene in chlorobenzene (5 mmol), 0.4 mL of 0.12 M SnMe₄ in chlorobenzene (0.048 mmol) and the desired amount of 0.1 M 1-octene in chlorobenzene were added. The reaction tube was placed in an 80 °C oil bath. After 10 minutes 0.4 mL of 0.06M WCl₆ in chlorobenzene (0.024 mmol) was then added. After 10 minutes the product was precipitated in a 1:1 mixture of methanol and acetone, dissolved in toluene and reprecipitated in 1:1 methanol/acetone. The product was then dried at reduced pressure.

Poly(norbornenamer) synthesis

(6-90) The same procedure was used as in the graft copolymer synthesis except for omitting the macromonomer.

Casting of Polymer Films

(6-106) Films were cast on microscope slides by allowing 5 % (w/v) solutions to evaporate in air. A film of a mixture of 80 mole percent

poly(norbornenamer) with an average degree of polymerization of 500 and 20 mole percent ω -norbornenylpolystyrene (degree of polymerization of 29) was cloudy. A film cast of poly(norbornenamer-*g*-styrene) with approximately the same percentage of norbornene and styrene units was clear.

Block Copolymer Synthesis

Effect of Cyclohexene on Catalyst Activity

(4-63) A series of cyclooctene metathesis reactions were run with different catalyst aging times, with and without cyclohexene present during aging. The reactions without cyclohexene were run in the following manner: Chlorobenzene (9 mL) and 0.5 mL of 0.07 M SnMe_4 in chlorobenzene (0.04 mmol) were added to a Schlenk tube which contained a stir bar. The tube was then placed in an 80 °C oil bath. After 5 minutes 0.5 mL of 0.07 M WCl_6 in chlorobenzene (0.04 mmol) was added. After the desired catalyst aging time, 2 mL of a cyclooctene (11.5 mmol) and octane mixture was added. Thirty seconds later an aliquot of the reaction mixture was removed by cannula. This was then analyzed by gas chromatography.

In the reactions with cyclohexene the same procedure was followed except for the addition of 0.2 mL of cyclohexene before the tube was placed in the oil bath and the use of 8.8 mL of chlorobenzene instead of 9 mL.

Bicyclo[4.2.0]oct-7-ene Synthesis²

(5-30) The glass reaction tube with an internal heat exchanger used for this reaction is shown in Figure 2.1. After introducing a stir bar the tube

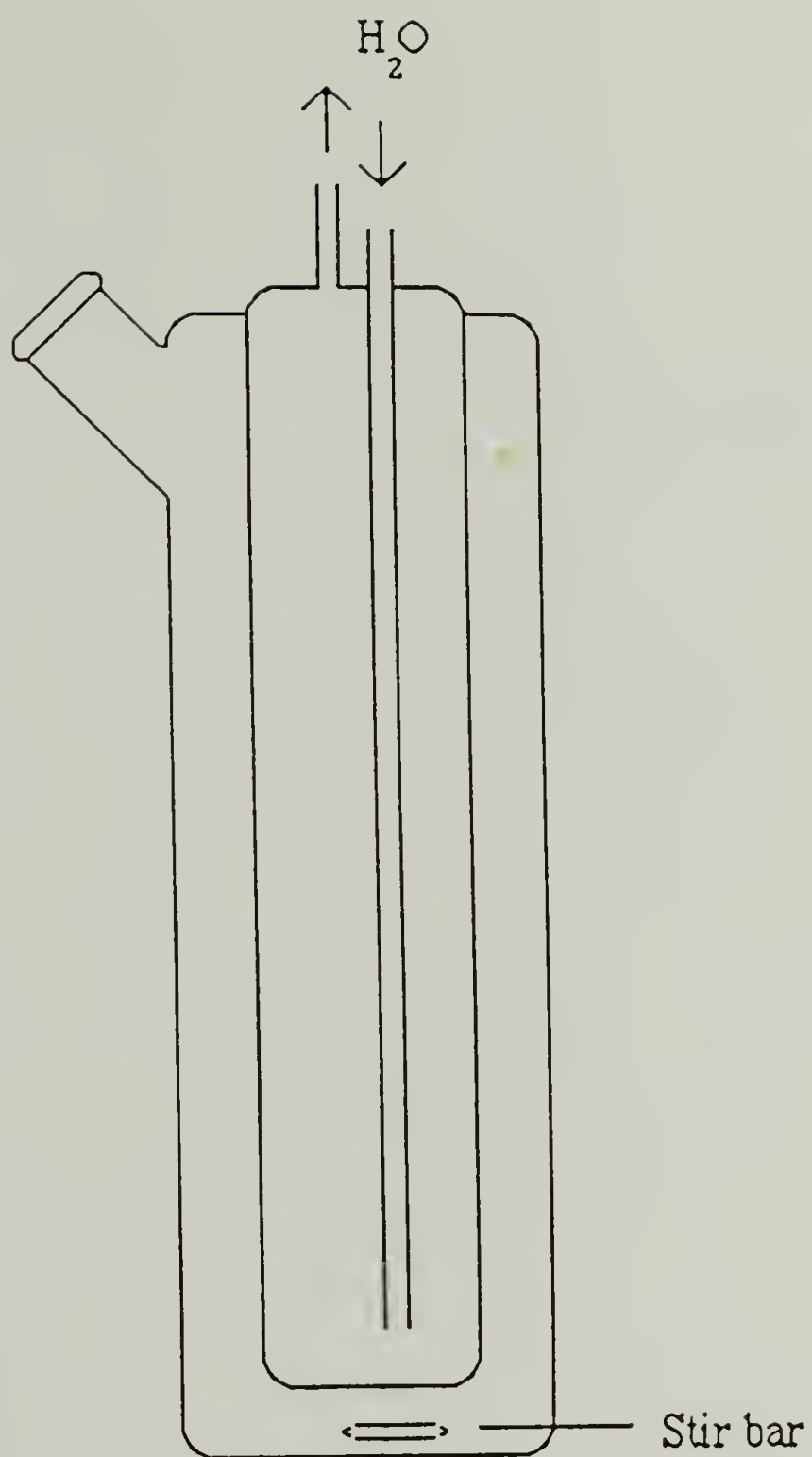


Figure 2.1 Reaction tube for UV photolysis.

was purged with nitrogen. Acetophenone (1 mL) and 1,3-cyclooctadiene (10 mL) were added to the tube. Enough heptane was then added to fill the tube to the bottom of the side arm (approximately 25 mL). An 85 °C mixture of water and ethylene glycol was circulated through the internal heat exchanger. A 100 watt Blak-Ray longwave ultraviolet lamp (Model B-100A) was used to irradiate the reaction mixture. The reaction apparatus was enclosed in a tent of aluminum foil for safety reasons. The reaction was stopped after 2 weeks. Bicyclo[4.2.0]oct-7-ene was isolated by distillation (130 mm) of the reaction mixture using a spinning band distillation apparatus. The fractions collected between 80 and 81 °C had a purity of 95% or greater by GC. The main impurity was heptane. These fractions were then used in further reactions after distillation from calcium hydride.

Concurrent Addition Copolymerization of Norbornene and Cyclooctene

(7-36) Four milliliters of 0.1 M 1-octene in chlorobenzene (0.4 mmol), 0.2 mL of 0.12 M SnMe_4 in chlorobenzene (0.24 mmol), 2 mL of 2 M norbornene in chlorobenzene (4 mmol) and 1 mL of a 3:1 (v/v) cyclooctene (6 mmol) and heptane mixture were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.2 mL of 0.06 M WCl_6 in chlorobenzene (0.12 mmol) was added to start the reaction. After 5 minutes the reaction mixture was poured into acetone, precipitating the copolymer. A sample of the product was dried at reduced pressure.

Sequential Addition Copolymerization of Norbornene and Cyclooctene

(7-32) Four milliliters of 0.1 M 1-octene in chlorobenzene (0.4 mmol), 0.2 mL of 0.12 M SnMe_4 in chlorobenzene (0.24 mmol) and 2 mL of 2 M norbornene in chlorobenzene (4 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.2 mL of 0.06 M WCl_6 in chlorobenzene (0.12 mmol) was added to start the reaction. Twenty seconds later an aliquot of the reaction mixture was removed. After another 20 seconds 1 mL of a 3:1 (v/v) cyclooctene (6 mmol) and heptane mixture was added. After 5 minutes the reaction mixture was poured into acetone, precipitating the copolymer. A sample of the product was dried at reduced pressure.

Concurrent Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene

(7-14) Chlorobenzene (4 mL), 0.1 mL of 0.1 M 1-octene in chlorobenzene (0.01 mmol), 0.4 mL of 0.12 M SnMe_4 in chlorobenzene (0.48 mmol), 1 mL of 2 M norbornene in chlorobenzene (2 mmol) and 1 mL of 2 M bicyclo[4.2.0]oct-7-ene in chlorobenzene (2 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.4 mL of 0.06 M WCl_6 in chlorobenzene (0.24 mmol) was added to start the reaction. After 5 minutes the reaction mixture was poured into acetone, precipitating the copolymer. A sample of the product was dried at reduced pressure.

Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene

(7-12) Chlorobenzene (4 mL), 1 mL of 0.01 M 1-octene in chlorobenzene (0.01 mmol), 0.1 mL of 0.12 M SnMe_4 in chlorobenzene (0.012 mmol) and 1 mL of 2 M norbornene in chlorobenzene (2 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.1 mL of 0.06 M WCl_6 in chlorobenzene (0.006 mmol) was added to start the reaction. Thirty seconds later an aliquot of the reaction mixture was removed. After another 20 seconds 1 mL of 2 M bicyclo[4.2.0]oct-7-ene in chlorobenzene (2 mmol) was added. After 5 minutes the product was precipitated in acetone. The product was dried at reduced pressure.

(7-48) The same general procedure as above was used again. Chlorobenzene (3 mL), 1 mL of 0.1 M 1-octene in chlorobenzene (0.1 mmol), 0.2 mL of 0.12 M SnMe_4 in chlorobenzene (0.24 mmol) and 0.5 mL of 2 M norbornene in chlorobenzene (1 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.4 mL of 0.06 M WCl_6 in chlorobenzene (0.24 mmol) was added to start the reaction. Twenty seconds later an aliquot of the reaction mixture was removed. After another 20 seconds 1 mL of 2 M bicyclo[4.2.0]oct-7-ene in chlorobenzene (2 mmol) was added. After 5 minutes roughly half the reaction mixture was poured into acetone, forming a white suspension. Only traces of solid precipitated. The solvent was removed from the rest of the reaction mixture at reduced pressure. The polymer isolated in this way was used for product analysis.

Polymerization of Bicyclo[2.2.2]oct-2-ene

(5-9) Chlorobenzene (2.6 mL) and 1.6 mL of 0.07 M SnMe_4 in chlorobenzene (0.11 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 5 minutes 0.4 mL of 0.06 M WCl_6 in chlorobenzene (0.24 mmol) was added. After 10 minutes 5 mL of 2 M bicyclo[2.2.2]oct-2-ene (10 mmol) was added. The reaction was run for 90 minutes. Then the reaction mixture was poured into methanol, precipitating a small amount of polymer. The polymerization was run a number of times; the yield was never greater than 15%.

Polymerization of Phenylacetylene

(5-31) Chlorobenzene (2.6 mL) and 1.6 mL of 0.07 M SnMe_4 in chlorobenzene (0.11 mmol) were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 5 minutes 0.4 mL of 0.06 M WCl_6 in chlorobenzene (0.24 mmol) was added. After 5 minutes 2 mL of phenylacetylene (18 mmol) was added. The reaction was run once for 1 minute and once for 10 minutes. The reaction mixture was then poured into methanol, precipitating a small amount of red polymer. The yield was 26 and 29% of the theoretical yield for the two reactions.

Polymerization of Phenylnorbornene

(7-50) Chlorobenzene (3 mL), 0.2 mL of 0.12 M SnMe_4 in chlorobenzene (0.24 mmol), 0.5 mL of 0.1 M 1-octene in chlorobenzene (0.05 mmol) and 0.5 mL of phenylnorbornene were added to a nitrogen-purged Schlenk tube containing a stir bar. The tube was placed in an 80 °C oil bath. After 10 minutes 0.2 mL of 0.06 M WCl_6 in chlorobenzene (0.12

mmol) was added to start the reaction. After 5 minutes the reaction mixture was poured into acetone, precipitating the polymer. A sample of the product was dried at reduced pressure.

Synthesis of ω -Vinylpolystyrene

(6-110) Benzene (40 mL) was added to a nitrogen-purged, crown-capped pressure bottle containing a Teflon stir bar. The appropriate amount (for the desired molecular weight) of *sec*-butyllithium was introduced. Styrene (3 mL) was then added dropwise at room temperature and the polymerization mixture was stirred for 30 minutes. Then 2 equivalents of allyl chloride (3-chloropropene) was added. Two samples were prepared: one low molecular weight sample for end group characterization, one high molecular weight sample for use in the polymerization.

The low molecular weight sample was isolated in the following manner: The reaction solution was transferred to a separatory funnel and washed with water (twice), and saturated sodium chloride solution. The solution was dried with magnesium sulfate. The benzene was then removed, first by rotary evaporation and then by drying on a vacuum line.

The high molecular weight sample was isolated and purified by precipitation in methanol, dissolution in tetrahydrofuran and reprecipitation in methanol. The sample was then dried at reduced pressure.

Polymerization of Norbornene with ω -Vinylpolystyrene

(6-118) A Teflon coated stir bar and 0.12 g of ω -vinylpolystyrene with a degree of polymerization of 24, (0.05 mmol) were placed in a Schlenk

tube which was then purged with nitrogen. Chlorobenzene (5 mL), 2.0 mL of 2.5 M norbornene in chlorobenzene (5 mmol) and 0.4 mL of 0.12 M SnMe_4 in chlorobenzene (0.048 mmol) were added. The reaction tube was placed in an 80 °C oil bath. After 10 minutes 0.4 mL of 0.06 M WCl_6 in chlorobenzene (0.024 mmol) was added. After 10 minutes, part of the reaction mixture was poured into methanol precipitating the crude product. The rest of the product was precipitated in a 1:1 mixture of methanol and acetone, dissolved in toluene and reprecipitated in 1:1 methanol/acetone. Not all of the polymer dissolved in toluene. Both samples were then dried at reduced pressure.

Reference and Note

- 1 The bold numbers in brackets are notebook references.
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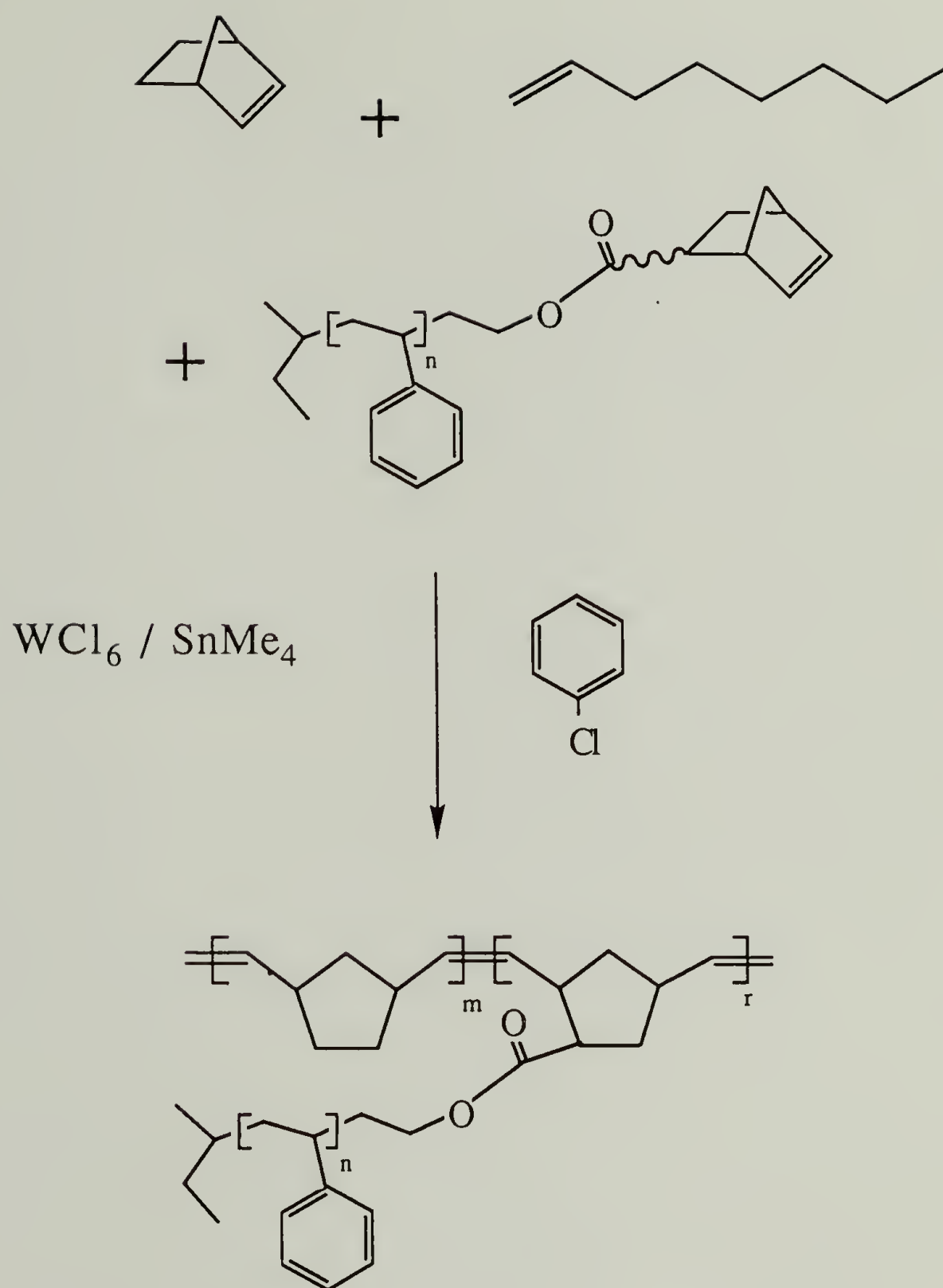
CHAPTER III

RESULTS AND DISCUSSION

Graft Copolymer Synthesis

The graft copolymer, poly(norbornenamer-*g*-styrene), was synthesized by the olefin metathesis copolymerization of ω -norbornenyl-polystyrene, a macromonomer, and norbornene as shown in Scheme 3.1. This reaction system was chosen for study for several reasons: Norbornene and a norbornene-terminated macromonomer were used because, due to the strain energy of the bicyclic ring, complete reaction was expected. The polystyrene macromonomer was used because it could be prepared with control of molecular weight since it is synthesized by a living anionic polymerization and the endcapping with an ester group had been previously demonstrated.¹ The chain transfer agent, 1-octene, was used to control the average backbone length. The $WCl_6/SnMe_4$ catalyst system was used because of its compatibility with ester functionality.²⁻⁵

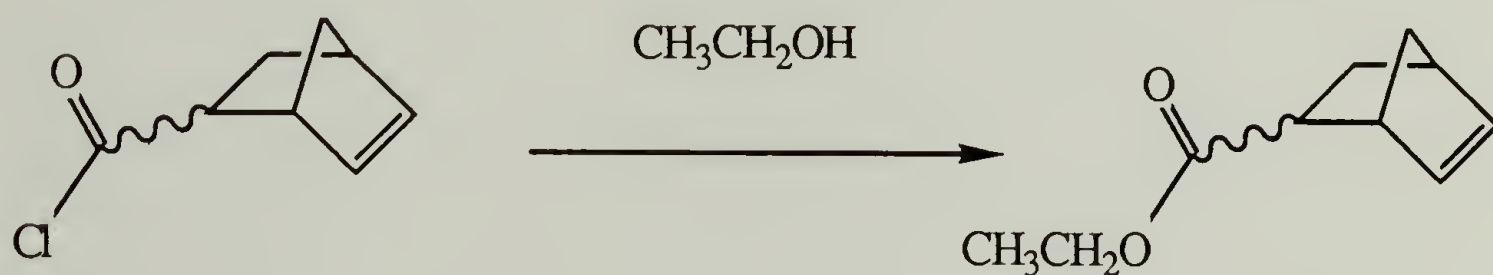
A great deal of control of the graft copolymer structure is theoretically possible in this copolymerization. This is indicated in Scheme 3.1. The degree of polymerization of the macromonomer can be controlled quite precisely in the living anionic macromonomer synthesis, this then determines the length of the grafts. The average degree of polymerization of the backbone is determined by the ratio of monomers to chain transfer agent. The average number of grafts per chain is determined by the ratio of macromonomer to chain transfer agent.



Scheme 3.1: Poly(norbornenamer-g-styrene) synthesis.

Model Compound Synthesis

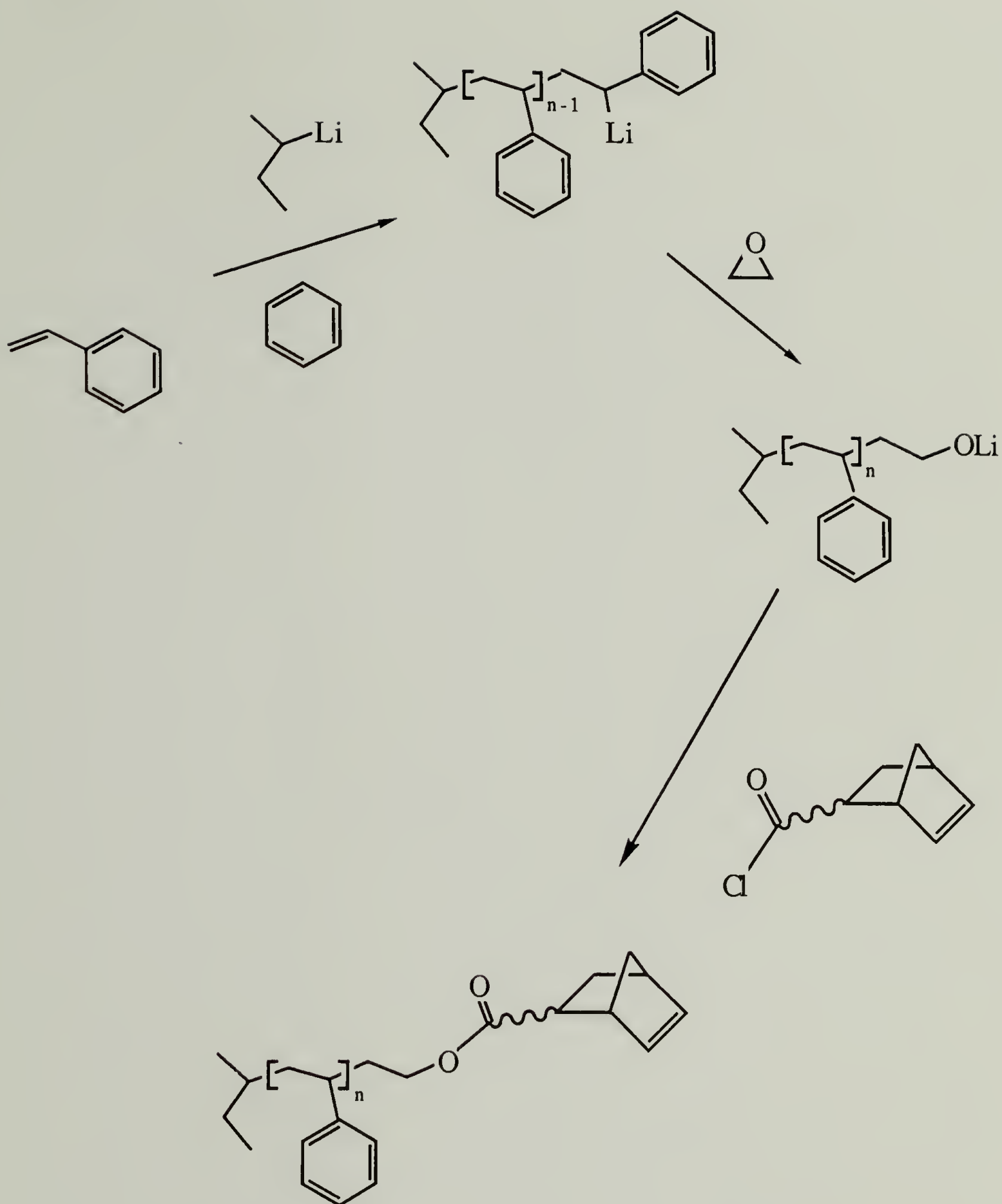
A model compound for the macromonomer was synthesized to aid in macromonomer characterization and to confirm that norbornenyl esters are reactive in this polymerization system. The ethyl ester of 5-norbornene-2-carboxylic acid was synthesized by the reaction of 5-norbornene-2-carbonyl chloride and ethanol as shown in Scheme 3.2.



Scheme 3.2: Synthesis of the ethyl ester of 5-norbornene-2-carboxylic acid.

Macromonomer Synthesis

The method used to synthesize the macromonomer, ω -norbornenyl-polystyrene, is outlined in Scheme 3.3. This is a variation of the procedure of Schulz and Milkovich for placing a methacrylic ester on the end of polystyrene.¹ Table 3.1 gives the GPC data for the samples that were prepared.



Scheme 3.3: Synthesis of ω -norbornenylpolystyrene

Table 3.1: Macromonomer GPC Data

<u>Sample</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
ω-NBPS-DP6	610	690	1.13
ω-NBPS-DP29	2900	3100	1.07
ω-NBPS-DP55	5500	5900	1.07
ω-NBPS-DP100	10000	11000	1.10

Characterization of ω-NBPS-DP6, outlined below, confirmed that the desired macromonomer structure was synthesized. This sample, a viscous oil, was isolated by rotary evaporation of the reaction mixture after several washings in a separatory funnel to remove impurities.

The IR spectra of the ethyl ester and the low molecular weight macromonomer are shown in Figure 3.1. The ester carbonyl stretch is seen at 1745 cm⁻¹ in the model compound and 1735 cm⁻¹ in the macromonomer. The broad absorbance from the stretch of the single bond between the carbonyl carbon and the other oxygen is seen at 1180 cm⁻¹ in both.

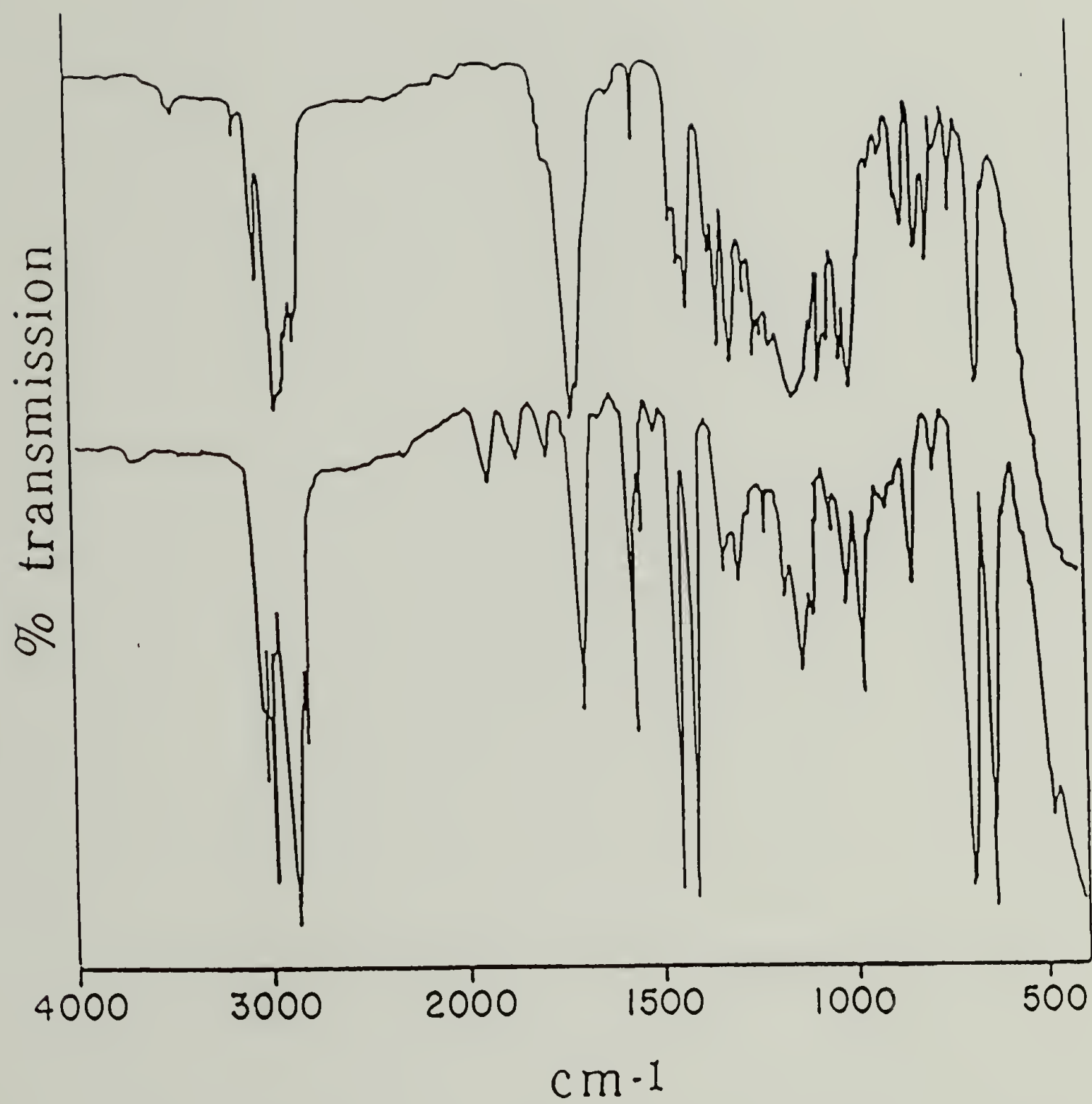


Figure 3.1: IR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).

Because the acid chloride used is a mixture of two isomers, one with the ester group *endo* to the ring and the other with it *exo*, the ethyl ester and the macromonomer are also mixtures of *endo* - and *exo*- isomers. This is evident in the ^{13}C NMR spectra shown in Figure 3.2; two resonances are seen for many carbons because of the presence of the two isomers. The following assignments can be made for both the macromonomer and the model compound: δ 174.6 and 176.0 (carbonyl carbon), δ 132.6 and 136.0 (olefin carbon, norbornenyl group carbon 5), δ 137.9 and 138.1 (olefin carbon, norbornenyl group carbon 6). The resonance of the methylene carbon that is bound to the alcohol oxygen is found at δ 59.0 in the ethyl ester and 62.0 in the macromonomer. The methyl carbon in the ethyl ester has a resonance at δ 13.0. The methylene carbon in the corresponding position in the macromonomer has a resonance at δ 11. The rest of the norbornenyl group resonances are between δ 30 and 50 and are overlapped by the resonances of the backbone and *sec*-butyl group resonances in the macromonomer. The aromatic carbons from polystyrene are at δ 126.1, 128.2 and 145.0.

The ^1H NMR spectra of the ethyl ester and the macromonomer are given in Figure 3.3. Both show olefinic resonances between δ 5.7 and 6.2 and the resonances of the bridgehead protons and the proton on the norbornenyl group carbon 2 between δ 2.7 and 3.1. The resonances of the methylene protons on the carbon alpha to the ester oxygen are two overlapped quartets at δ 4.0 in the ethyl ester and a broad peak at δ 3.8 in the macromonomer. The aromatic proton resonances from the styrene repeat units are found between δ 6.3 and 7.4. Integration of the aromatic and olefinic proton resonances and taking into account the 5 phenyl

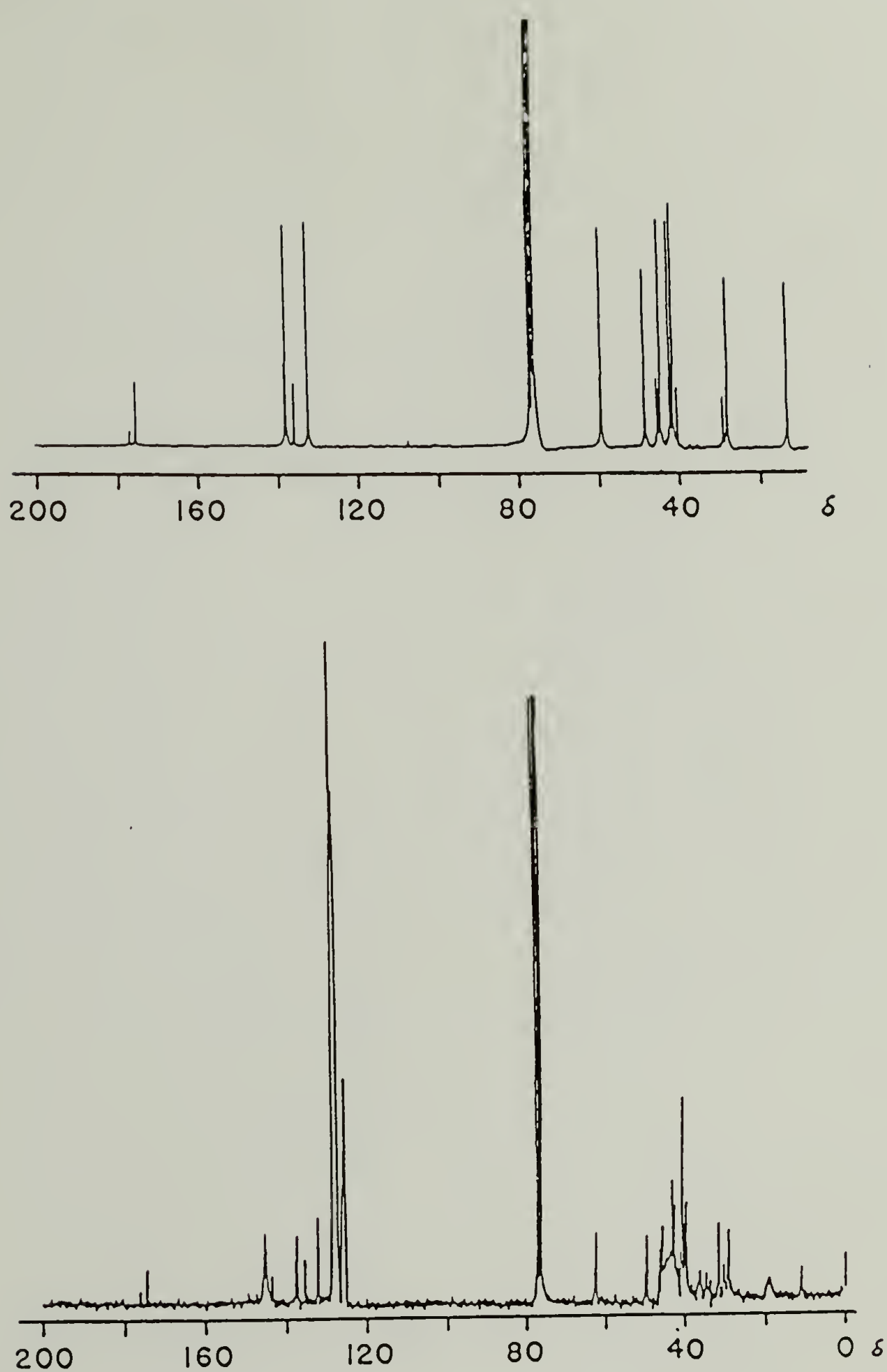


Figure 3-2: ^{13}C NMR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).

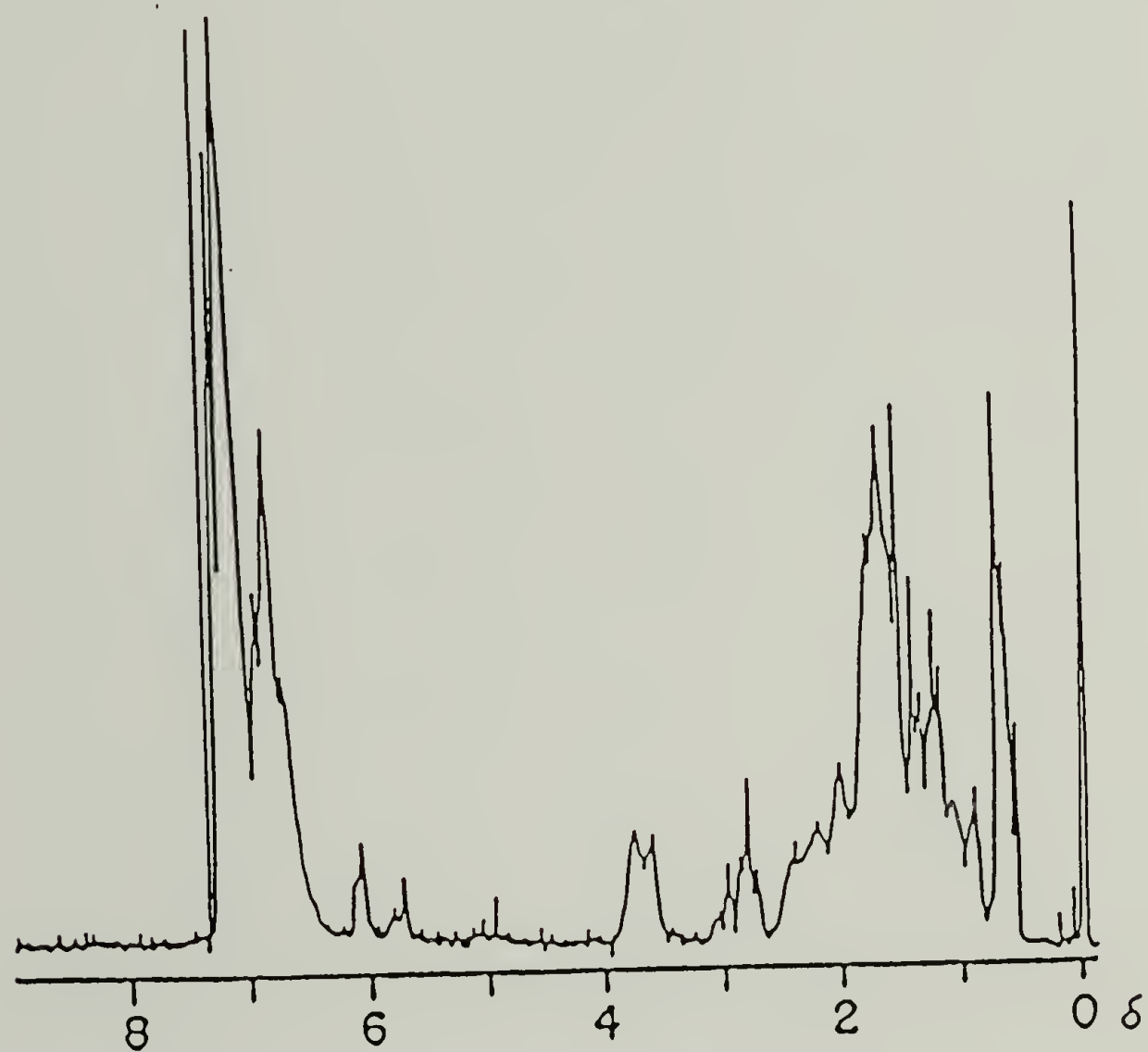
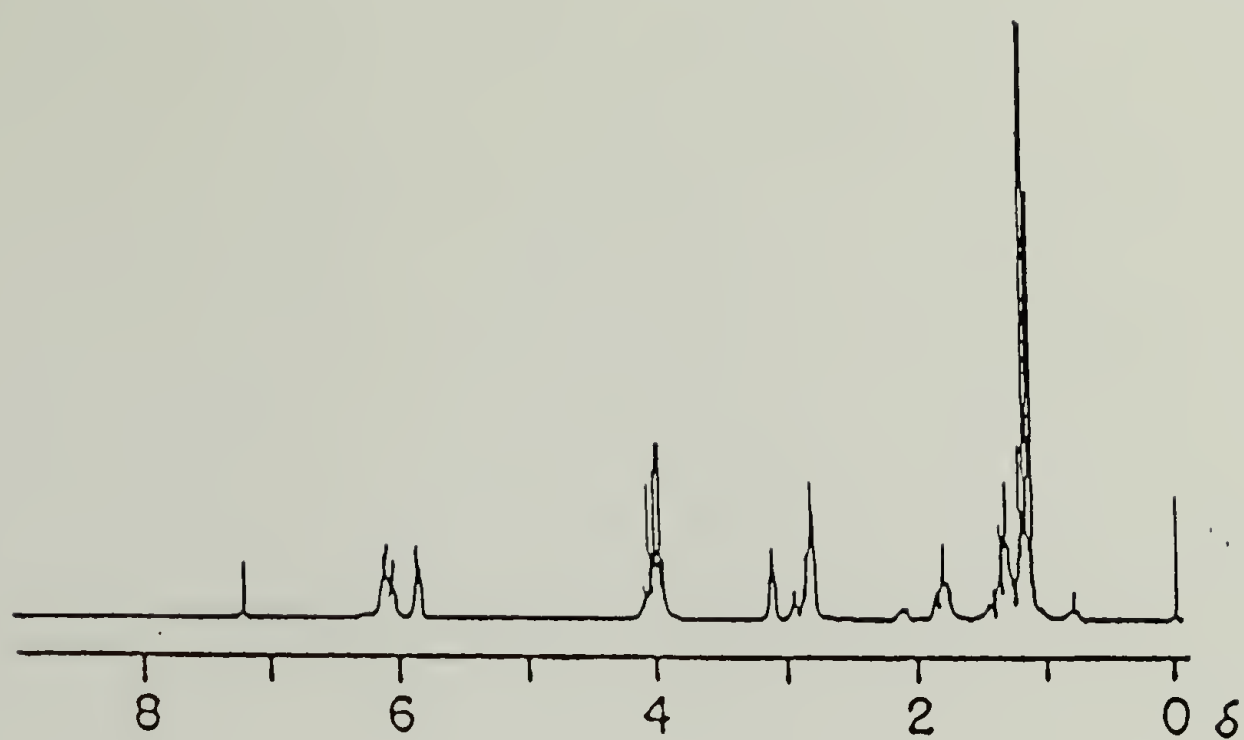


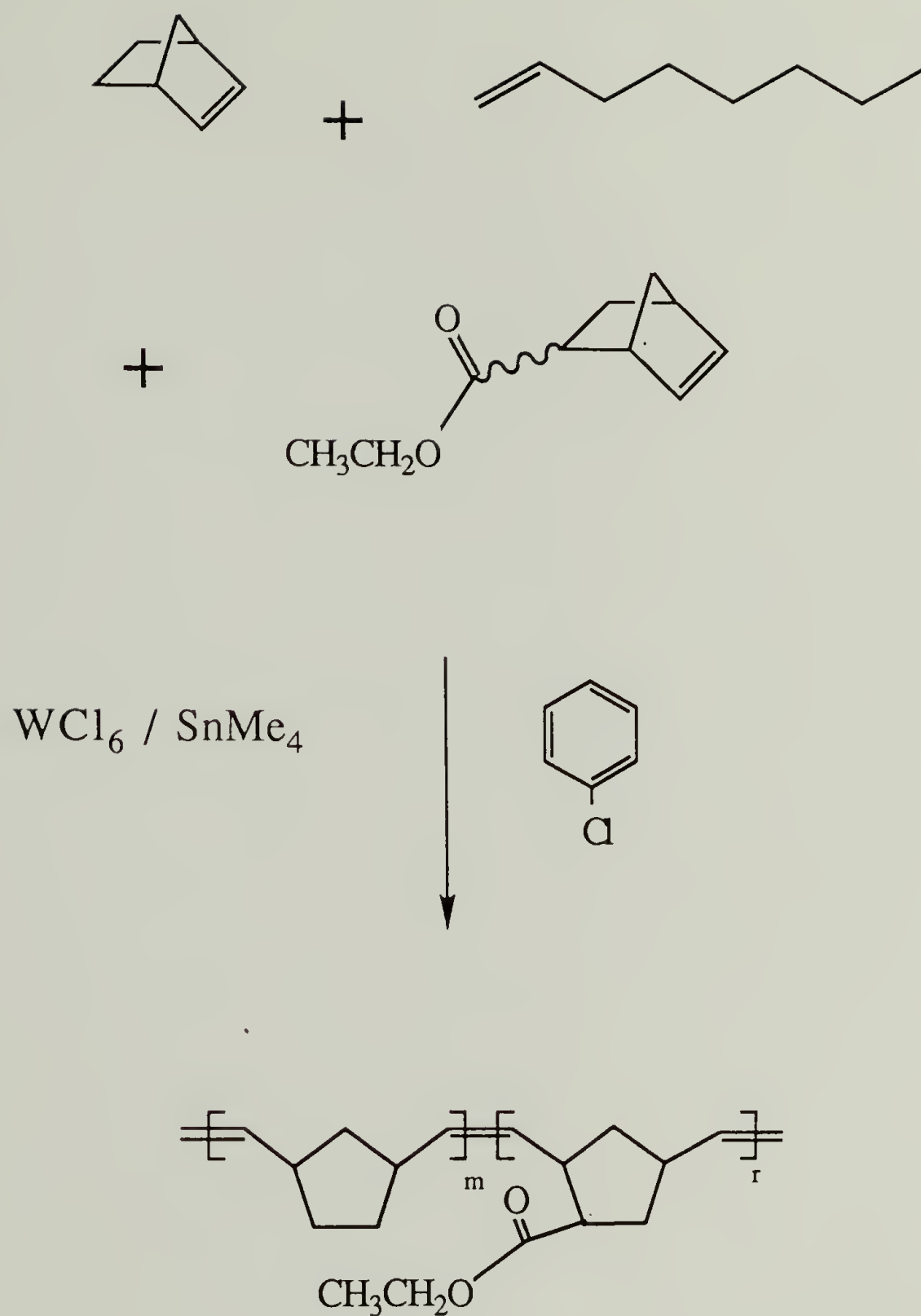
Figure 3.3: ^1H NMR spectra of the ethyl ester of 5-norbornene-2-carboxylic acid (upper) and ω -NBPS-DP6 (lower).

protons and the two olefin protons in the different units yields a number average degree of polymerization of 6.3. This is consistent with the GPC data for this sample indicating that the endcapping is effective.

The norbornenyl group is not seen spectroscopically in the higher molecular weight samples but should be present since the same reaction conditions were used. It is not clear if the endcapping is as effective in the higher molecular weight samples. Since the same weight of sample contains fewer chain ends in the higher molecular weight samples the same absolute amount of impurities causing side reactions could have a much larger effect on a percentage basis. These macromonomer samples were purified by precipitation of the reaction mixture in methanol, dissolution in THF and reprecipitation in methanol. The final product is a fine white powder for all of these samples.

Copolymerization of Model Compound and Norbornene

The ethyl ester of 5-norbornene-2-carboxylic acid was copolymerized with norbornene as shown in Scheme 3.4 as a model reaction for the graft copolymer synthesis. A gray rubbery mass was obtained by precipitation of the reaction mixture. The ^1H and ^{13}C NMR, shown in Figure 3.4, are as expected. The ratio of the integration of the methylene protons of the ethyl group in the ester (δ 4.1) and the olefin protons (δ 5.1 to 5.5) indicates that 18 percent of the repeat units in the polymer have the ester group attached. The feed was 20 percent ester.



Scheme 3.4: Copolymerization of norbornene and the ethyl ester of 5-norbornene-2-carboxylic acid.

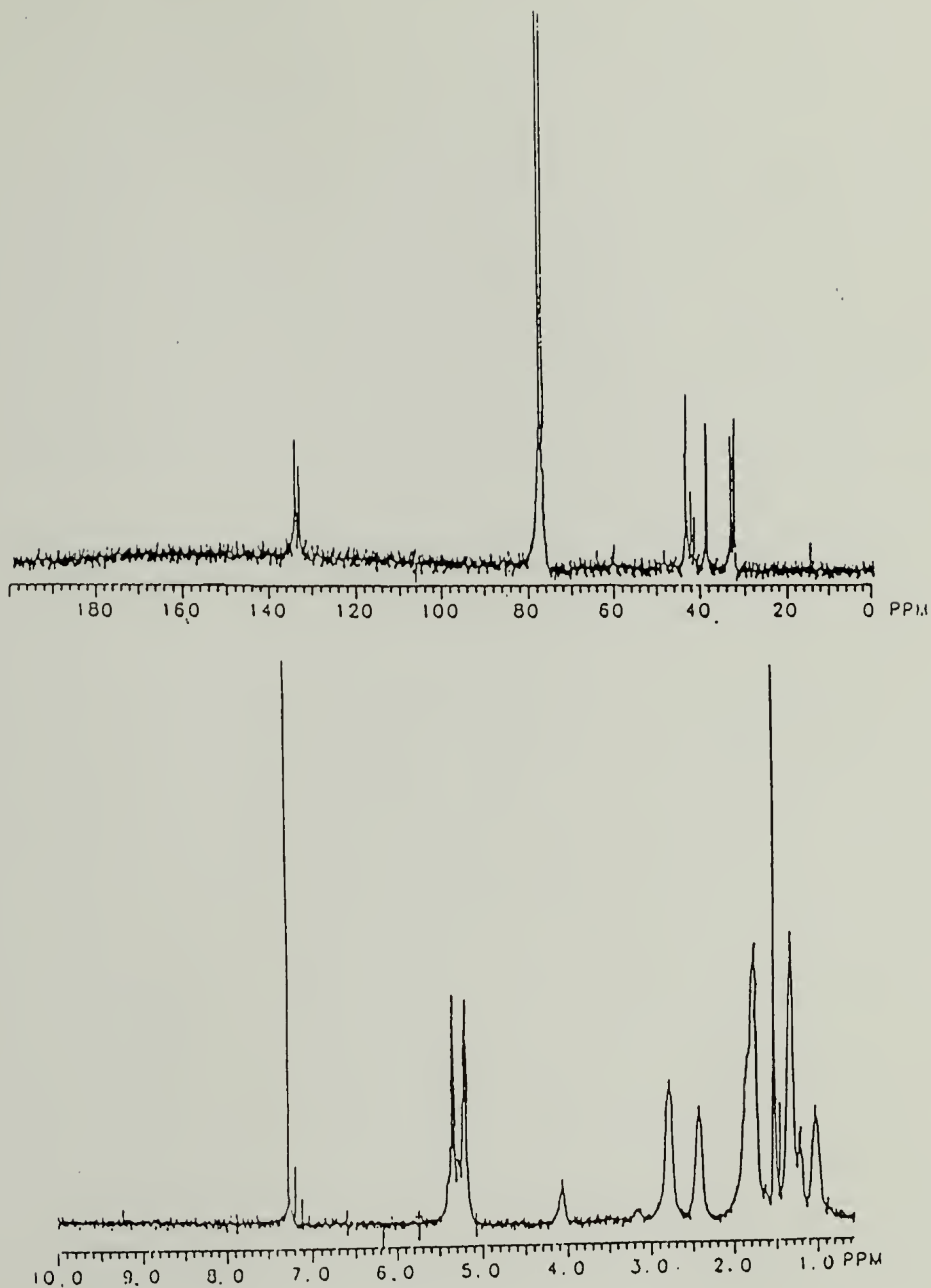


Figure 3.4: ^{13}C (upper) and ^1H NMR (lower) spectra of the copolymer of norbornene and the ethyl ester of 5-norbornene-2-carboxylic acid.

Copolymerization of the Macromonomer and Norbornene

The copolymerization of ω -norbornenylpolystyrene and norbornene is depicted in Scheme 3.1. The macromonomer, a white powder, is placed in the Schlenk tube. This is then purged with nitrogen. The solvent and solutions of reactants and catalyst precursors are then added by syringe. After 10 minutes the reaction is stopped by pouring the reaction mixture into a 1:1 mixture of methanol and acetone. The gray rubbery mass that precipitates is then dissolved in toluene and reprecipitated in a 1:1 mixture of methanol/acetone. The final product, a white rubbery mass, is then dried at reduced pressure before analysis.

A number of copolymerizations were performed. The analysis of a representative reaction (entry 2a in Table 3.2) will be outlined and then the data for the other reactions will be given in Table 3.2.

Figure 3.5 shows the GPC trace of ω -NBPS-DP29, the crude product of its copolymerization (isolated by precipitation in methanol), and the purified product (twice precipitated in 1:1 methanol/acetone). Some unreacted macromonomer is seen in the crude product but not the purified product. Other than the removal of the unreacted macromonomer there is apparently no substantial fractionation of the product.

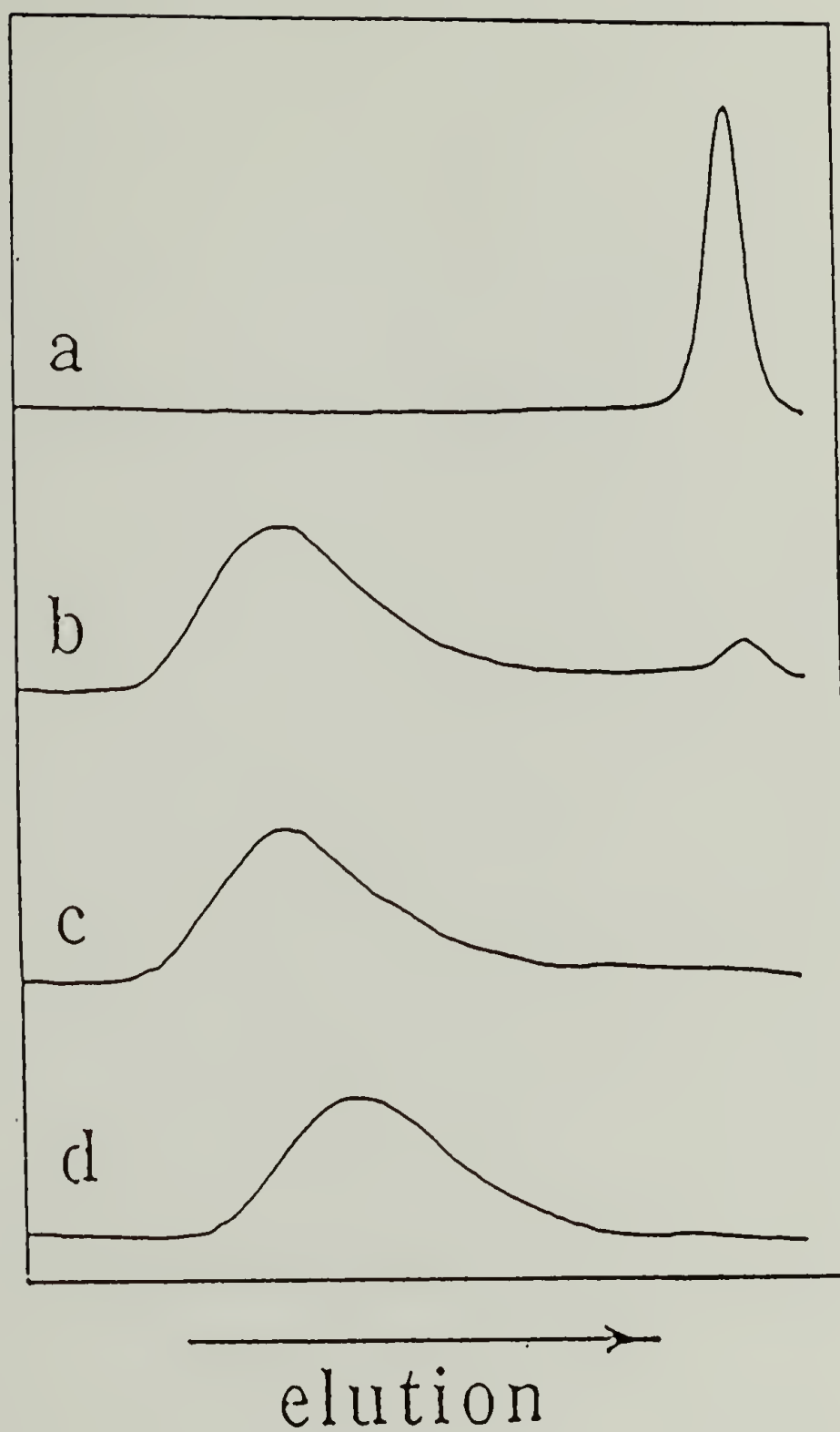


Figure 3.5: GPC of (a) ω -NBPS-DP29, (b) Methanol precipitated copolymerization product, (c) purified copolymerization product and (d) poly(norbornenamer) with a DP of 500.

Figure 3.6 shows the ^1H NMR spectrum of the purified product. The spectrum consists of the resonances of poly(norbornenamer) and polystyrene. Since the GPC shows that no unreacted macromonomer is present, this shows that graft copolymer is formed. The mole percent of styrene units in the product (M_s) is obtained from the integration of the phenyl protons (δ 6.4 - 7.7) and the olefin protons of the norbornene repeat units (δ 5.0- 5.5). Equation 3.1 is used to account for the number of protons in the repeat units and to express the result as a percentage.

$$M_s = \frac{0.2I_s}{0.2I_s + 0.5I_n} \times 100 \quad (3.1)$$

I_s = Integration of phenyl protons

I_n = Integration of norbornene protons

The average number of grafts per chain (g) can then be calculated by equation 3.2.

$$g = \frac{M_s/DP_s}{(100 - M_s)/DP_n} \quad (3.2)$$

DP_s = Macromonomer degree of polymerization

DP_n = Backbone degree of polymerization

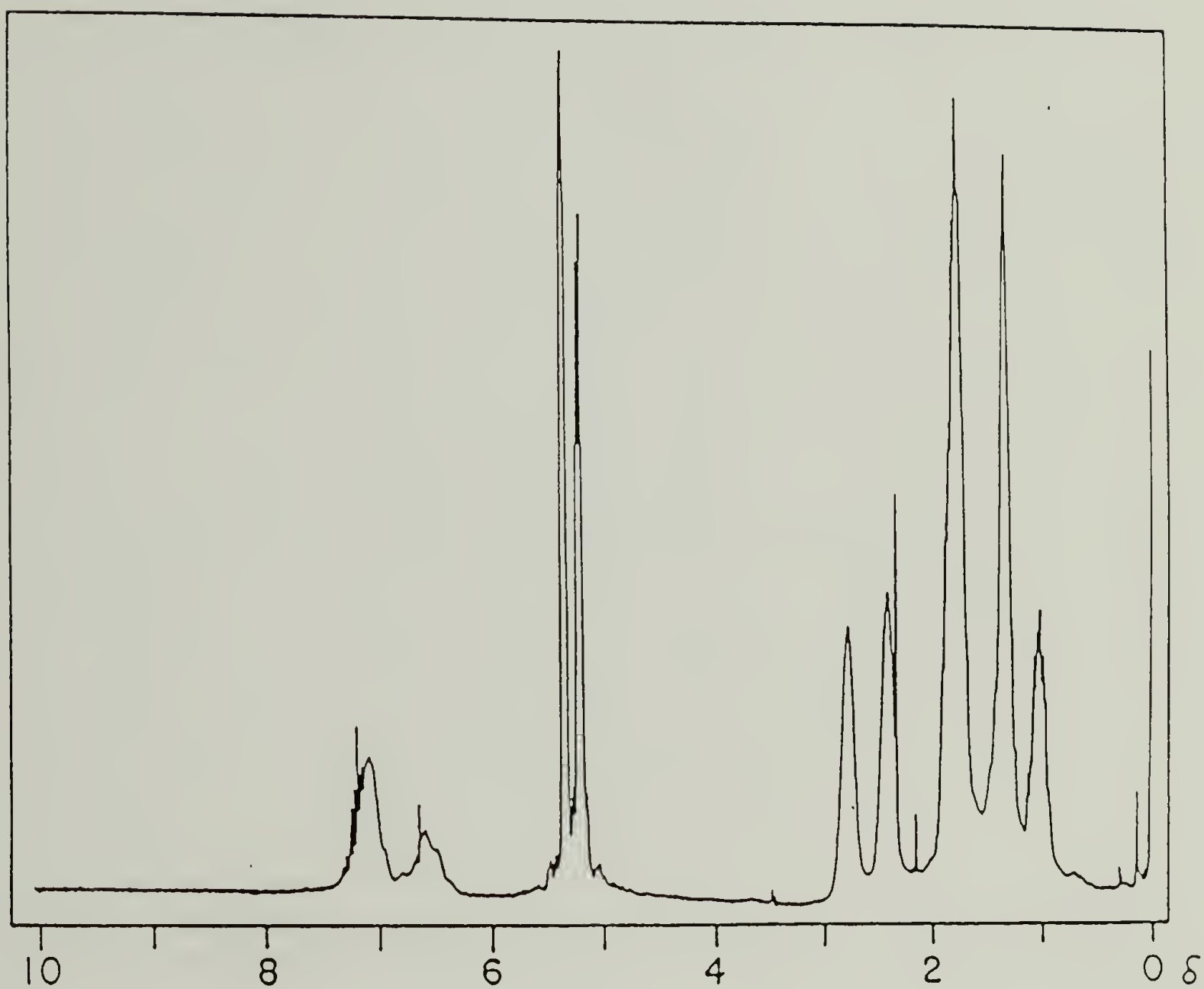


Figure 3.6: ^1H NMR spectrum of poly(norbornenamer-g-styrene).

The numerator in equation 3.2 is the number of grafted polystyrene chains per 100 total repeat units. The denominator is the number of backbones per 100 total repeat units. The degree of polymerization is known accurately for the macromonomer and therefore for the grafts. The degree of polymerization of the backbone is not measurable and there is certainly a broad distribution of chain lengths as in the poly(norbornenamer) homopolymer. (The GPC trace of a homopolymer made using the same reaction conditions is shown in Figure 3.5.) The backbone degree of polymerization is estimated by the the molar ratio of norbornene to 1-octene. Because both the monomer and the chain transfer agent react completely, as determined by gas chromatography, this is an accurate estimate of the number average degree of polymerization of the backbone chains formed. However, not all of the product is isolated. The final product yield is approximately 50 percent for most of these copolymerizations. Some fractionation may occur, particularly involving loss of low molecular weight material. Because of this uncertainty in the length of the backbones the average number of grafts per chain must be considered an estimate.

It is important to note that it is an *average* number of grafts per chain that is calculated. There is certainly a distribution in the number of grafts per chain and in the length of the backbones. The grafts should be randomly distributed but there is no way to determine if they are. Some poly(norbornenamer) homopolymer is expected in every sample even if the graft placement is totally random. Thin layer chromatography was investigated as a possible means of detecting the presence of poly(norbornenamer), but effective conditions were not found.

Table 3.2 contains data for a series of copolymerizations in which the amount of macromonomer, the backbone degree of polymerization and the macromonomer degree of polymerization were varied. The same amount of norbornene was used in all reactions. The data is for purified products which had no macromonomer present by GPC, except for entry 8. The mole percent of styrene units and the average number of grafts per chain were determined as described above. The predicted number of grafts per chain was calculated by using equation 3.2 and using the mole percent of styrene in the feed.

Table 3.2: Graft Copolymerization Data

Entry	Macro-Monomer	Main Chain	Mole % Styrene		Average Number Grafts/Chain	
<u>Number</u>	<u>DP</u>	<u>DP</u>	<u>Feed</u>	<u>Product</u>	<u>Predicted</u>	<u>Observed</u>
1	29	500	10	14	1.9	2.8
2a	29	500	19	18	4.0	3.8
2b	29	500	19	24	4.0	5.4
2c	29	500	19	23	4.0	5.2
2d	29	500	19	21	4.0	4.6
3	29	500	32	31	8.1	7.8
4	29	500	48	48	15.9	16.0
5	29	250	19	17	2.0	1.8
6	29	100	19	14	0.8	0.6
7	55	500	19	21	2.1	2.4
8	100	500	19	<10	1.2	<0.5

In entries 1 through 4 in Table 3.2 the amount of macromonomer ω -NBPS-DP29 was varied. In Figure 3.7 the mole percentage of styrene units observed is plotted versus the mole percentage in the feed. The diagonal line indicates where the product and feed mole percent are the same. It is clear with these reaction conditions the amount of polystyrene in the product is well predicted by the amount in the feed even up to a feed of almost half styrene repeat units.

Figure 3.8, is a plot of the average number of grafts per chain observed (actually calculated from the mole percent styrene and the monomer to chain transfer agent ratio) versus the predicted average. Assuming that the average backbone length in the purified product is as predicted from the feed, this shows that the average number of grafts per chain is controlled in this copolymerization.

For entries 5 and 6 in Table 3.2 the same conditions are used except for the lowering of the backbone molecular weight by increasing the amount of chain transfer agent added. In entry 5 the estimated backbone degree of polymerization is 250 and approximately the predicted amount of styrene and average number of grafts per chain are observed in the product. In entry 6 the backbone degree of polymerization is 100. Apparently, these short backbones are solubilized in the precipitation medium. The yield was very low and the product recovered had fewer styrene units than predicted. Precipitation of the product in a mixture richer in methanol would probably increase both the yield and styrene content of the product of this reaction. A

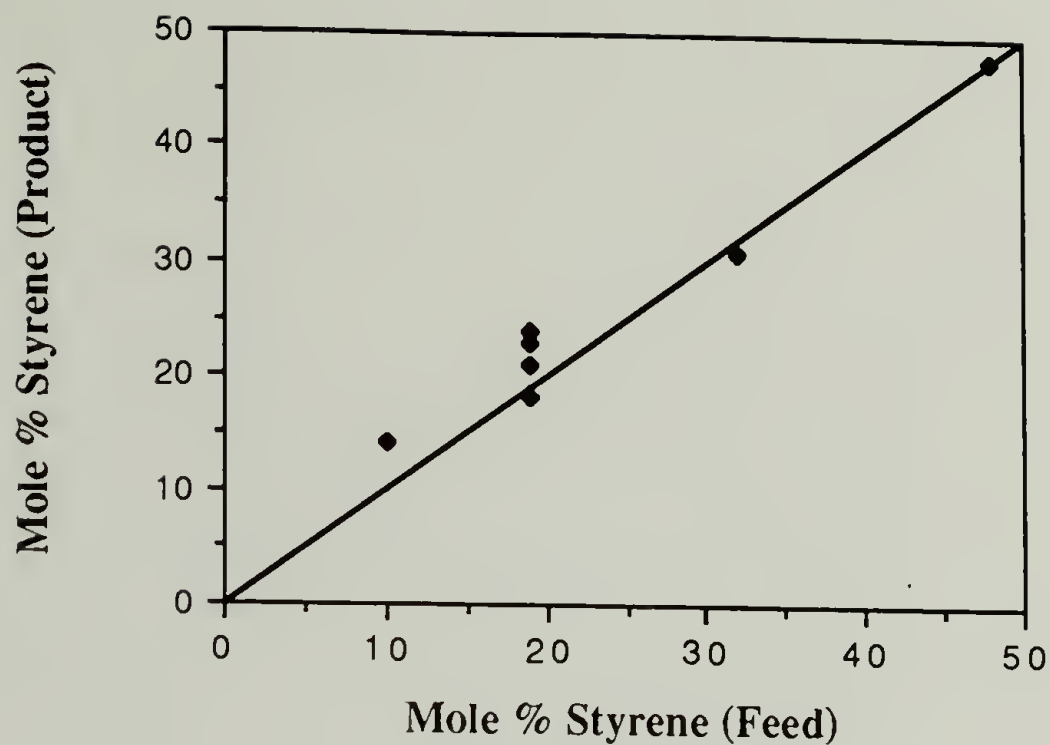


Figure 3.7: Mole percent styrene in product versus mole percent styrene in feed for graft copolymerization of norbornene and ω -NBPS-DP29.

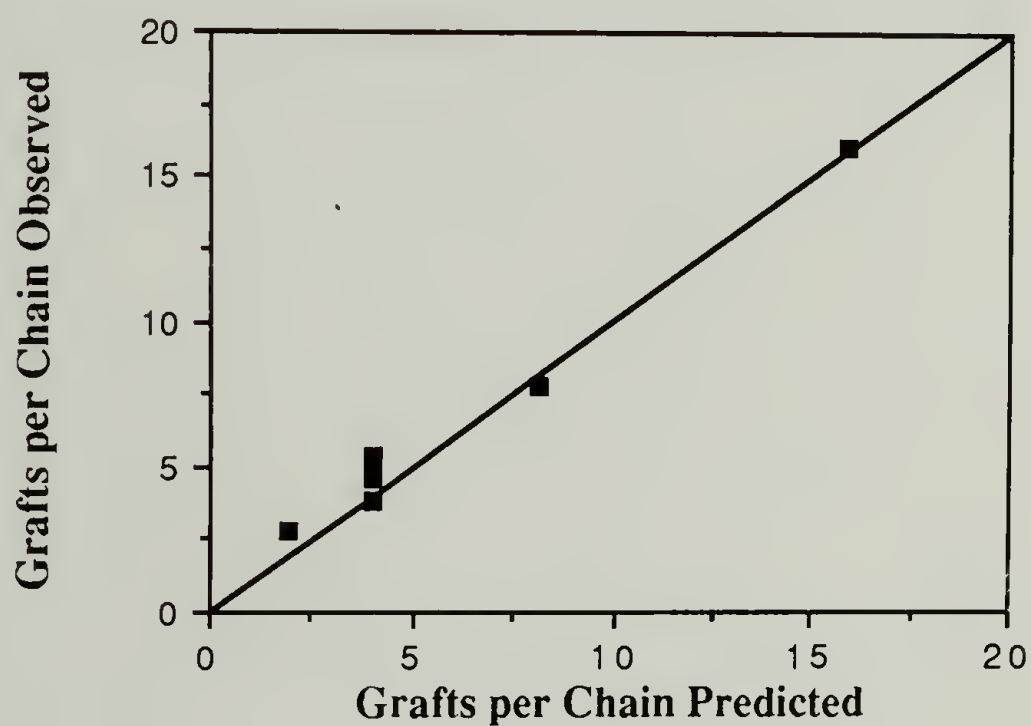


Figure 3.8: Observed average number of grafts per chain versus predicted number from feed for graft copolymerization of norbornene and ω -NBPS-DP29.

sample was prepared with a backbone degree of polymerization of 1000 but it was not soluble and therefore not analyzed. The lack of solubility could be due to the high molecular weight or to crosslinking, which may be occurring in all samples but is only effective enough to be noticeable in this high molecular weight sample (as molecular weight increases the total number of crosslinks needed to gel a sample decreases).

For entries 7 and 8 in Table 3.2 the same conditions as entry 2 are used except for changing the macromonomer molecular weight. The macromonomer with a degree of polymerization of 55 is incorporated into the product equally successfully as is the lower molecular weight sample. Both the mole percent of styrene and the average number of grafts per chain are well predicted by the feed. The macromonomer with a degree of polymerization of 100 was not incorporated into graft copolymer effectively. Only about half the predicted amount of styrene repeat units was detected in the NMR of the purified material. The data for this sample is only an upper limit since some unreacted macromonomer in this sample is detected by GPC. A lowering of reactivity with an increase in molecular weight has been observed in the copolymerization of macromonomers.⁶⁻⁸ This effect has been attributed to microphase separation of the macromonomer and the growing graft copolymer in solution which becomes more important as the molecular weight of the polymers increases. Another way to view this is that as the macromonomer becomes larger the reactive end can be more effectively buried in the polymer coil requiring greater interpenetration of the growing polymer and macromonomer chains for reaction to occur. Even with the lower molecular weight macromonomer,

the polymerizable end group of some chains remain effectively buried throughout the course of the polymerization. This is responsible for incomplete reaction of the macromonomer in all the copolymerizations. Another possible explanation the apparent low reactivity of the higher molecular weight sample is incomplete end functionalization.

The GPC data for the products of the reactions described above are given in Table 3.3. The entry numbers correspond to those in Table 3.2. The molecular weights reported are relative to polystyrene standards. There is no pattern to the GPC data; this is likely due to a complex dependence of hydrodynamic volume on graft density, graft location and backbone length.

These experiments demonstrate that poly(norbornenamer-*g*-styrene) can be synthesized by the macromonomer method with a great deal of control of the product structure: The length of the grafts is determined in the anionic macromonomer synthesis. The average number of grafts per chain can be controlled by the amount of macromonomer in the feed. The length of the backbone is controlled by the amount of chain transfer agent used. Unreacted macromonomer is easily removed from the product.

There are a number of aspects of the copolymerization that are not well controlled: Homopolymer of norbornene is formed and can not be removed from the product. There are broad distributions of backbone

molecular weight and number of grafts per chain. The reactivity of the macromonomer decreases with increasing molecular weight.

Table 3.3: Graft Copolymerization GPC Data.

<u>Entry Number</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
1	30000	12300	4.1
2a	85000	152000	1.8
2b	31000	111000	3.6
2c	35000	216000	6.2
2d	87000	182000	2.1
3	35000	120000	3.4
4	70000	153000	2.2
5	30000	79000	2.6
6	15000	37000	2.5
7	105000	122000	1.2
8	71000	128000	1.8

No physical studies of the graft copolymer were performed except a crude test of compatibility. A film cast from a toluene solution containing 80 mole percent poly(norbornenamer) with a degree of polymerization of 500 and 20 mole percent ω -NBPS-DP29 was cloudy. The two polymers are

incompatible and form domains large enough to scatter light. The film cast from a solution of poly(norbornenamer-*g*-styrene) with the same molar percentage of norbornene and styrene repeat units was clear. The two incompatible polymers can not separate sufficiently to form domains large enough to scatter light since they are covalently bound.

Block Copolymer Synthesis

The original goal of this research was to synthesize block copolymers via olefin metathesis. There was no known synthesis of well defined block copolymers when this program began. The living metathesis systems discussed in the introduction had not yet been developed.

Catalyst Activity Studies

The initial objective of this research was to develop a method to prepare a known and stable catalyst concentration using the $\text{WCl}_6/\text{SnMe}_4$ catalyst system. This was considered the first step in the control of the olefin metathesis reaction that would be required for block copolymer synthesis. The kinetics of the metathesis of cyclooctene were studied as a means of determining the activity of various catalyst preparations. The factors investigated were: the concentration of SnMe_4 and WCl_6 , the ratio of SnMe_4 to WCl_6 , the order and timing of addition of the catalyst precursors and monomer, and the temperature.

Under no conditions were a reproducible and measurable activity found. If a high concentration of active catalyst was formed the initial

reaction rate was too great to measure. At low concentration of active catalyst the system is very sensitive to impurities; the reactions generally did not continue to equilibrium and the initial reaction rates were irreproducible. The studies were abandoned as unworkable. No concrete conclusions could be reached from this investigation. Subsequent metathesis reactions were done at 80 °C, with a two to one ratio of SnMe_4 to WCl_6 and with WCl_6 added last. This appeared to yield the most active catalyst system.

The use of cyclohexene as a "hibernating agent" for the active catalysts was explored as part of the above kinetic studies. Cyclohexene does not undergo productive metathesis at 80 °C because of thermodynamics, but can participate in the catalytic cycle. The rate of cyclooctadiene metathesis is increased by the addition of cyclohexene because of the participation of the cyclohexene derived carbene.⁹ It was thought that cyclohexene undergoing nonproductive metathesis could serve as a hibernating agent for the active carbenes by preventing side reactions leading to catalyst destruction. This would be useful during catalyst aging (the time prior to monomer addition) and between monomer additions in block copolymerizations.

One series of experiments showed that the presence of cyclohexene during catalyst aging did increase the rate of cyclooctene metathesis. Equimolar amounts of WCl_6 and SnMe_4 were mixed and then a certain catalyst aging time was waited before addition of cyclooctene. The percentage of monomer remaining after 30 seconds of reaction was determined by gas chromatography of an aliquot of the reaction mixture. The first order reaction rate constant (k'), which contains the catalyst concentration as a factor, is defined by equation 3.3 and calculated by

equation 3.4. The results of the experiments with and without cyclohexene present during aging are presented in Table 3.4.

$$\frac{-d[\text{cyclooctene}]}{dt} = k [\text{catalyst}] [\text{cyclooctene}] = k' [\text{cyclooctene}] \quad (3.3)$$

$$k' = \frac{\ln(100) - \ln(M)}{0.5 \text{ min.}} \quad (3.4)$$

M = percentage of cyclooctene remaining after 0.5 minute reaction

Table 3.4: Cyclooctene Metathesis after Aging with or without Cyclohexene Kinetic Data.

Aging Time (min)	With Cyclohexene		Without Cyclohexene	
	M	k'(min ⁻¹)	M	k'(min ⁻¹)
10	31.2	2.33	92.7	0.15
10			88.7	0.24
23	53.4	1.25		
30	64.6	0.87		
150	71.7	0.67	94	0.12

The value of k' is many times greater when cyclohexene is present than when it is not. This greater activity can be explained by two factors.

Cyclohexene may be acting as theorized, stabilizing the carbenes formed so that more active carbenes are present when the monomer is added. Another

possibility is that cyclohexene acts as an alkylating agent for WCl_6 which simply increases the number of carbenes formed. Since only a one to one ratio of SnMe_4 to WCl_6 is used in these experiments the amount of alkylation may be limiting the number of carbenes formed. The mechanism for carbene formation involves two alkylations by SnMe_4 per WCl_6 and the catalyst system is generally more active when a two to one SnMe_4 to WCl_6 ratio is used. The substitution of cyclohexene for SnMe_4 as an alkylating agent may be the sole reason for the increased rate of cyclooctene metathesis. A minor factor influencing the reaction rate is the effect of cyclohexene derived carbenes as discussed before.

Block Copolymer Synthesis by Sequential Monomer Addition

Introduction

The limiting of chain transfer is critical for synthesis of block copolymers by olefin metathesis with sequential monomer addition. In the living metathesis polymerization systems any chain transfer causes loss of control of the product structure. In this research an alternate method of forming block copolymers by metathesis with sequential monomer addition relies on the occurrence of the proper amount of chain transfer.

In the living metathesis polymerizations chain transfer is avoided because of the selectivity of the initiator. Metathesis of only the monomer double bonds occur. The double bonds in the polymer do not react. This selectivity is apparently a function of the structure of the monomer and the double bonds in the polymer as well as the nature of the initiator. The reports of living metathesis systems all involve polymerization of monomers

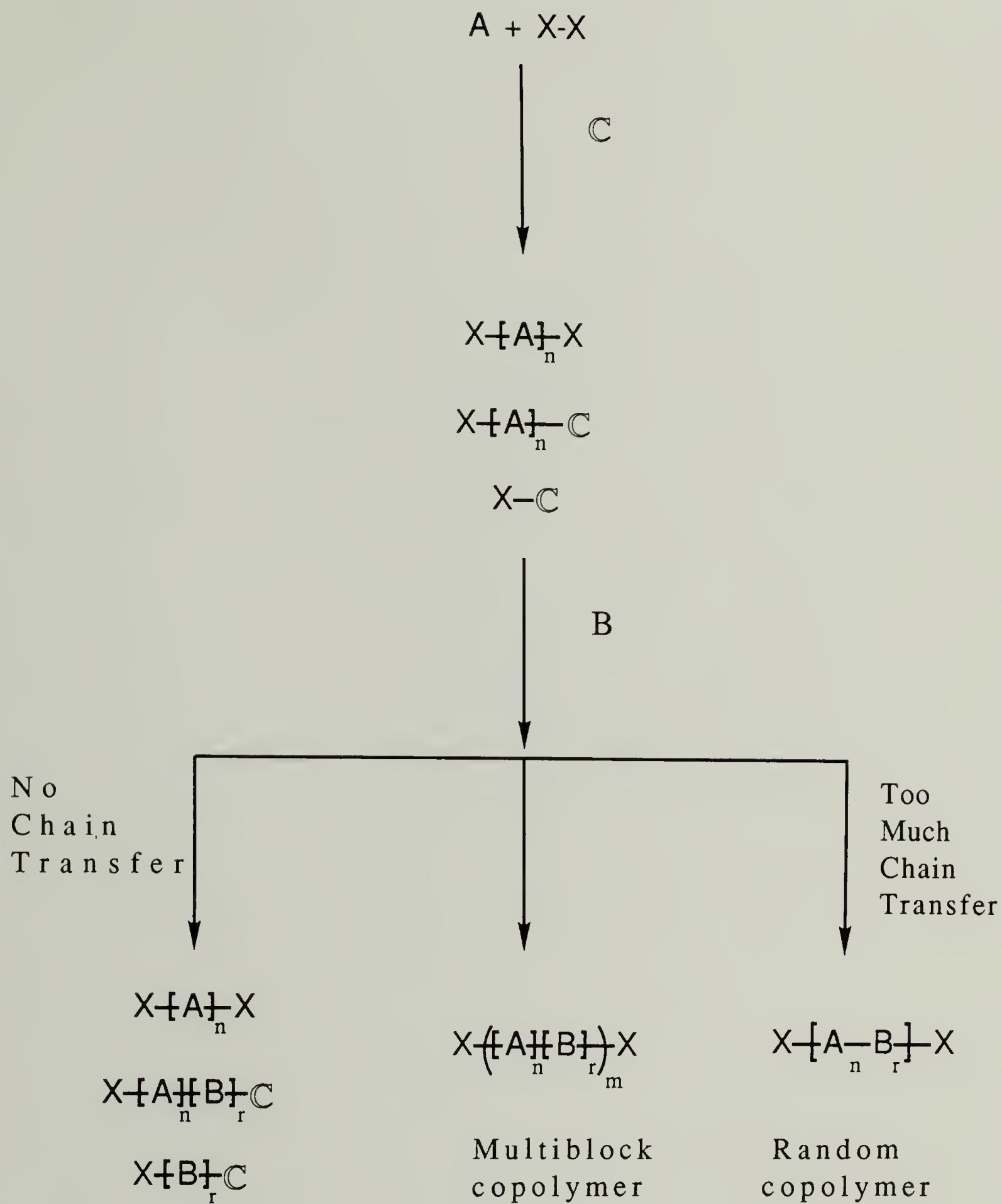
which yield sterically hindered double bonds on polymerization. There is one mention of the polymerization of cyclopentene with one of these systems resulting in a product with a broad molecular weight distribution.¹⁰ This could be due to chain transfer or possibly slower initiation than propagation.

The method explored in this research for synthesizing block copolymers by sequential monomer addition requires a limited amount of chain transfer. A standard ("non-living") catalyst system, $\text{WCl}_6/\text{SnMe}_4$, is used to completely polymerize one monomer with a chain transfer agent. The second monomer is then added. If the proper amount of chain transfer occurs block copolymers are formed.

This copolymerization method and its possible outcomes are illustrated by Scheme 3.5. The letters A and B represent the two monomers. The letter X represents the molecular fragment resulting from metathesis of the acyclic olefin represented by X-X. The letter C represents active carbenes.

The initial polymerization step yields a mixture of polymers with X units on both ends, polymers with an active carbene on one end and active carbenes bonded to a chain transfer agent fragment. Because there are far more chain transfer agents than active carbenes almost all of the product is polymer without a carbene.

On addition of monomer B there are three possible outcomes depending on the amount of intermolecular chain transfer that occurs.



Scheme 3.5: Sequential Addition copolymerization schematic.

If no chain transfer occurs only those few chains of monomer A which have an active carbene will add B units to form block copolymer. The polymerization of B initiated by carbenes attached to X units will result in formation of B homopolymer. Most of the product will be homopolymer of A which remains unchanged.

If a large amount of intermolecular chain transfer occurs random or only slightly blocky copolymer will be formed. The first chain transfer reactions will form block copolymer but subsequent reactions will result in the blocks being divided into smaller and smaller pieces.

Block or blocky copolymer will be formed effectively if enough chain transfer occurs to involve all the chains but not so much that the blocks are too finely divided. A wide range of block lengths and number of blocks per chain are to be expected. The block copolymers produced by this method could not be considered as well defined as those made by living metathesis systems, but could be useful in some applications..

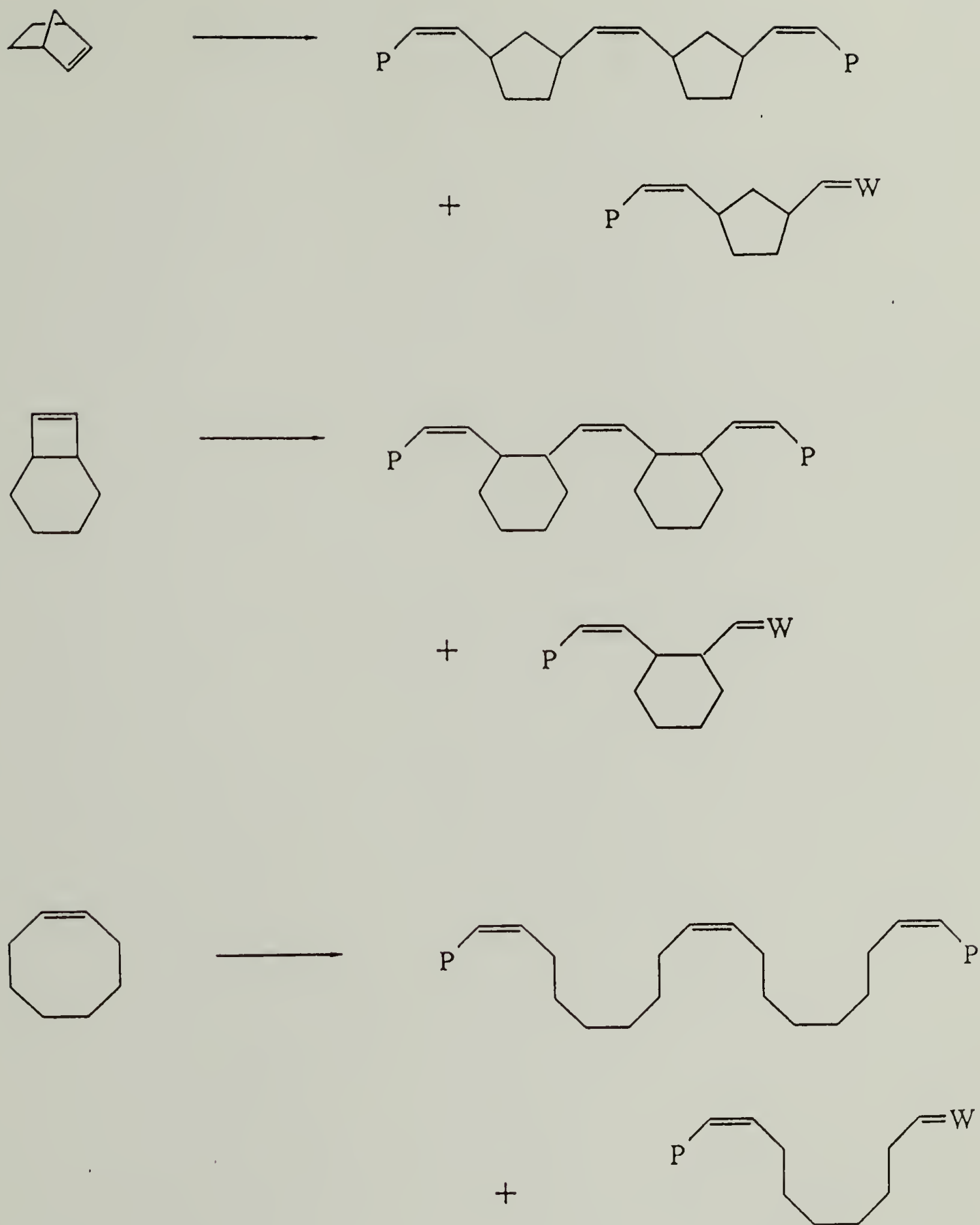
To test whether block copolymer can be formed by this method norbornene was used as the first monomer and either cyclooctene or bicyclo[4.2.0]oct-7-ene was used as the second monomer. The $\text{WCl}_6/\text{SnMe}_4$ catalyst system was used for these copolymerizations. The structures of the products were analyzed and compared to those of copolymerizations in which the monomers were polymerized concurrently.

A chain transfer agent, 1-octene, is used in these polymerizations to limit the molecular weight of the polymers formed. This aids mixing on both

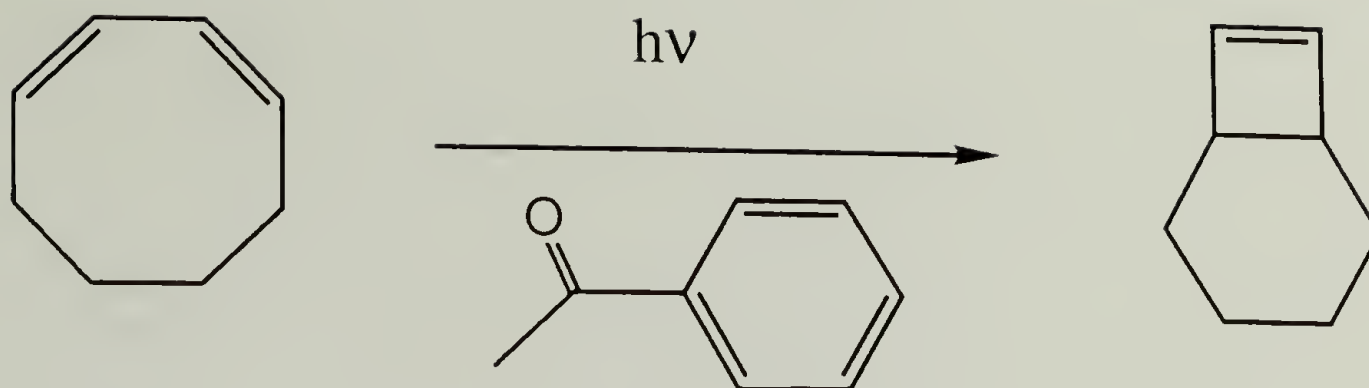
the macroscopic and molecular level. Norbornene polymerization without chain transfer agent results in very high molecular weight polymer which causes the viscosity of the reaction mixture to be far too high for the second monomer to mix into the reaction mixture effectively. Low molecular weight chains also interpenetrate more freely which should favor intermolecular chain transfer.

Norbornene was used as the first monomer because it polymerizes rapidly and completely with $\text{WCl}_6/\text{SnMe}_4$. Both the double bonds in poly(norbornenamer) and the carbene derived from norbornene are sterically crowded as shown in Scheme 3.6. Most of the living metathesis examples involve polymerization of norbornene or a norbornene derivative. This indicates that there is a definite difference in reactivity between the norbornene double bond and the double bonds of poly(norbornenamer). Intramolecular transfer can occur in norbornene polymerization with $\text{WCl}_6/\text{SnMe}_4$ catalysis. Cyclic oligomers of norbornene have been detected;¹¹ however they were not observed in the course of this work.

Bicyclo[4.2.0]oct-7-ene like norbornene is a rapidly polymerized monomer which yields sterically crowded double bonds and carbene on polymerization, as seen in Scheme 3.6. The polymerization of this monomer has been reported to be free of cyclic oligomers.¹² Bicyclo[4.2.0]oct-7-ene was synthesized by the UV photoisomerization of 1,3-cyclooctadiene using acetophenone as a sensitizer as shown in Scheme 3.7.¹³



Scheme 3.6: Polymer and carbene structures.



Scheme 3.7: Bicyclo[4.2.0]oct-7-ene synthesis.

Cyclooctene is an example of a monomer which forms a polymer that should easily undergo chain transfer. The flexibility of the polymer as well as the lack of steric crowding around the polymer double bonds and the cyclooctene derived carbene (as shown in Scheme 3.6) favor chain transfer.

The structure of the products of the copolymerizations was determined by ^{13}C NMR. Resonances due to dyad structures are seen in the olefin carbon region of the spectrum. The XL 300 spectrometer was used because of the resolution needed for these studies. In the measurement of the spectra (with one exception which is noted) a delay of 5 seconds was used between pulses so that the integration of these resonances could be considered quantitative.¹⁴

In the following discussion norbornene repeat units are represented by N, bicyclo[4.2.0]oct-7-ene repeat units are represented by B and cyclooctene repeat units are represented by C. The resonance due to the olefin carbon of a norbornene unit of a norbornene/cyclooctene dyad is represented by NC. The resonance due to the cyclooctene unit carbon in the same dyad is

represented by CN. The other dyads are represented in similar manner. Trans and cis double bond carbons are indicated by t and c respectively.

The integration of the different olefin carbon resonances can be used to calculate the mole fraction of the various dyads and repeat units present in a sample. The mole fraction of a dyad is calculated by dividing the integration of the resonances due to that dyad by the integration of all the olefin carbons and then normalizing to give a total mole fraction of one. The mole fraction of a repeat unit is equal to the sum of the mole fraction of its homodyad and one half of the mole fraction of the heterodyad.

The mole fraction of the dyads expected for a truly random copolymer can be calculated for comparison with the actual polymer structure. A variation of a Bernoullian statistical model ¹⁵ is used in which the mole fraction of a repeat unit detected in the polymer is used in place of the probability of adding a monomer unit. Equations 3.5, 3.6 and 3.7 are used in the calculations.

$$D_{AA} = (M_A)^2 \quad (3.5)$$

$$D_{BB} = (M_B)^2 \quad (3.6)$$

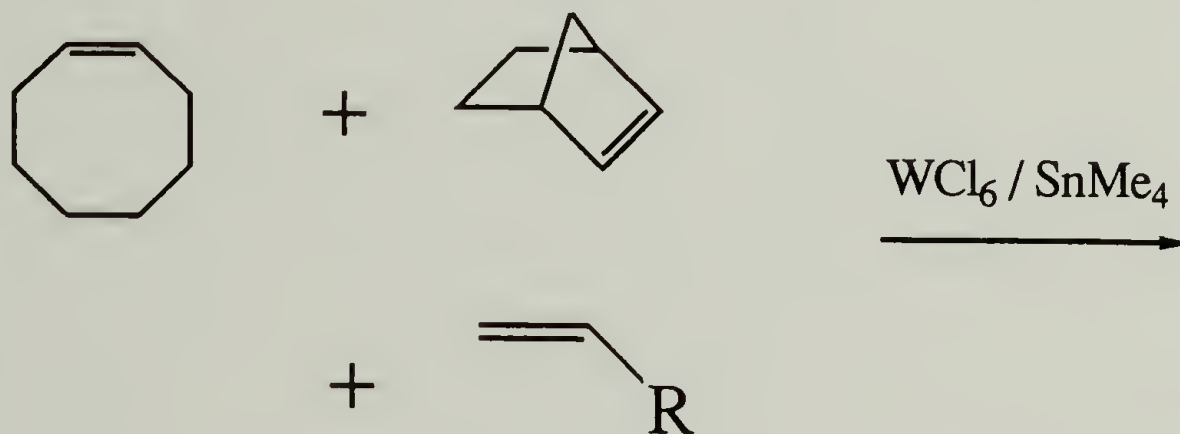
$$D_{AB} = 2M_A M_B \quad (3.7)$$

D_{XY} = Mole Fraction of dyad XY

M_X = Mole Fraction of Repeat unit X

Copolymerizations of Norbornene and Cyclooctene

Norbornene and cyclooctene were copolymerized with concurrent monomer addition as shown in Scheme 3.8. The product was isolated by precipitation in acetone. The olefin region of the ^{13}C NMR is shown in Figure 3.9. The peak assignments,¹⁶ integrations and mole fraction of dyads (observed and predicted for a random copolymer) are given in Table 3.5.



Scheme 3.8: Concurrent addition copolymerization of norbornene and cyclooctene.

The product of this copolymerization is a slightly blocky copolymer. This may be a result of norbornene polymerizing more rapidly than cyclooctene. The rate of disappearance of norbornene and cyclooctene in cometathesis with $\text{WCl}_6/\text{SnMe}_4$ catalysis are almost equal, but norbornene does react slightly faster than cyclooctene.⁹ This inequality in reactivity would cause norbornene rich copolymer to be formed at first and then cyclooctene rich copolymer. Apparently not enough chain transfer occurred to randomize the product. An alternate but unlikely explanation is that this slightly blocky copolymer is the thermodynamic product. Another possible explanation is that some fractionation occurs with

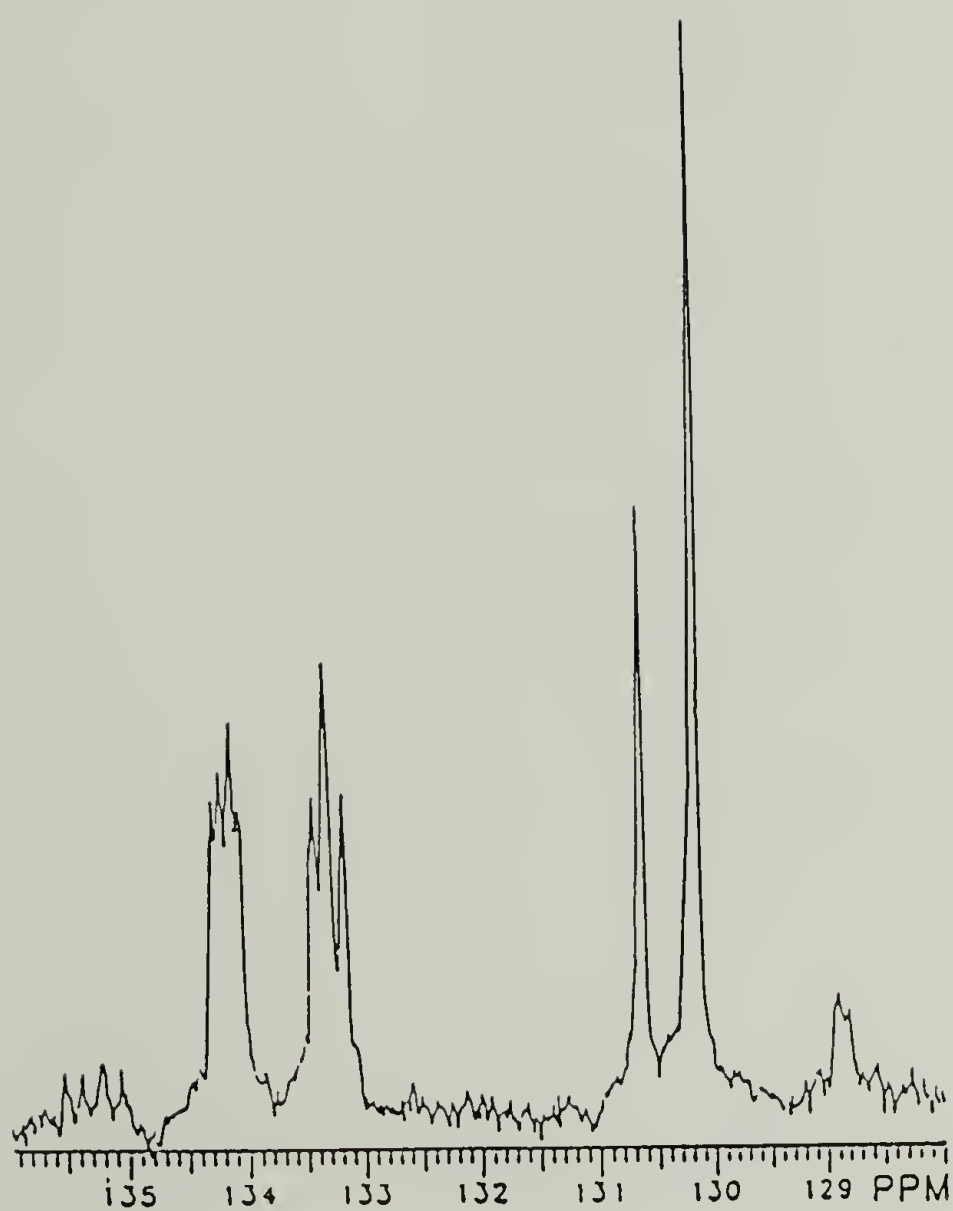


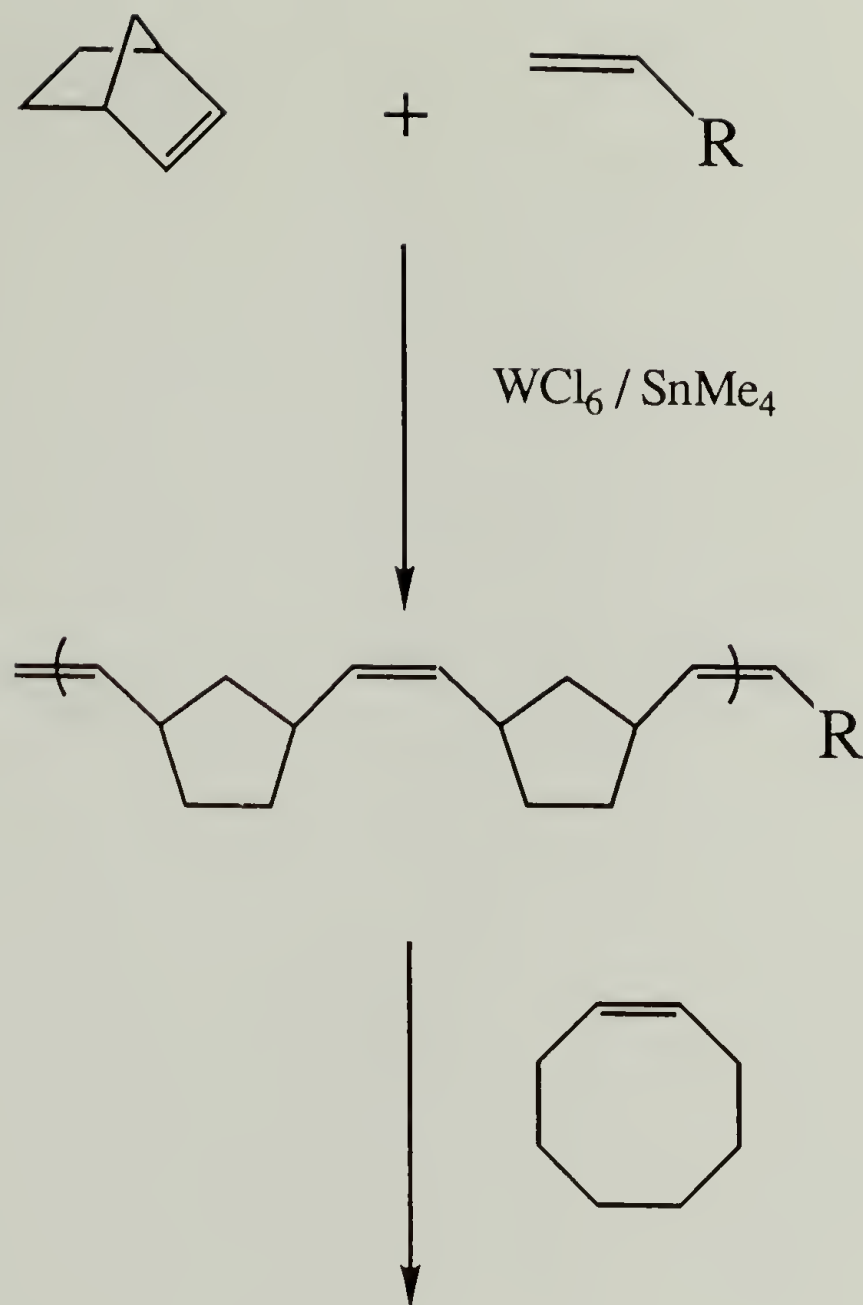
Figure 3.9: ^{13}C NMR spectrum of the product of concurrent addition copolymerization of norbornene and cyclooctene.

Table 3.5: Concurrent Copolymerization of Norbornene and Cyclooctene
NMR Data

<u>Dyad</u>	δ	<u>Integration</u>	<u>Dyad Mole Fraction</u>	
			<u>observed</u>	<u>predicted</u>
NC	135.0-135.7	5.2	0.23	0.42
(CN)	128.9			
NN	134.1,133.2(t,c)	12.5	0.58	0.49
CC	130.7,130.2(t,c)	4.0	0.19	0.09

precipitation with a fraction of more blocky material than average being isolated; it is unlikely that this is significant.

The sequential addition polymerization of norbornene and cyclooctene was done as shown in Scheme 3.9. First norbornene was polymerized with 1-octene as a chain transfer agent. The polymerization was complete after 20 seconds, there was no norbornene or 1-octene detected by gas chromatography of an aliquot of the reaction mixture taken at that time. Forty seconds after the start of the first polymerization, cyclooctene was added. The product was isolated by precipitation in acetone. The olefin region of the ^{13}C NMR is shown in Figure 3.10. The peak assignments, integrations and mole fraction of dyads(observed and predicted for a random copolymer) are given in Table 3.6.



Scheme 3.9: Sequential addition copolymerization of norbornene and cyclooctene.

The copolymer product of this reaction is only slightly blockier than that formed in the concurrent addition copolymerization. A significant amount of chain transfer must have occurred for this product to be formed. This is an example of too much chain transfer occurring leading to formation of a fairly random copolymer.

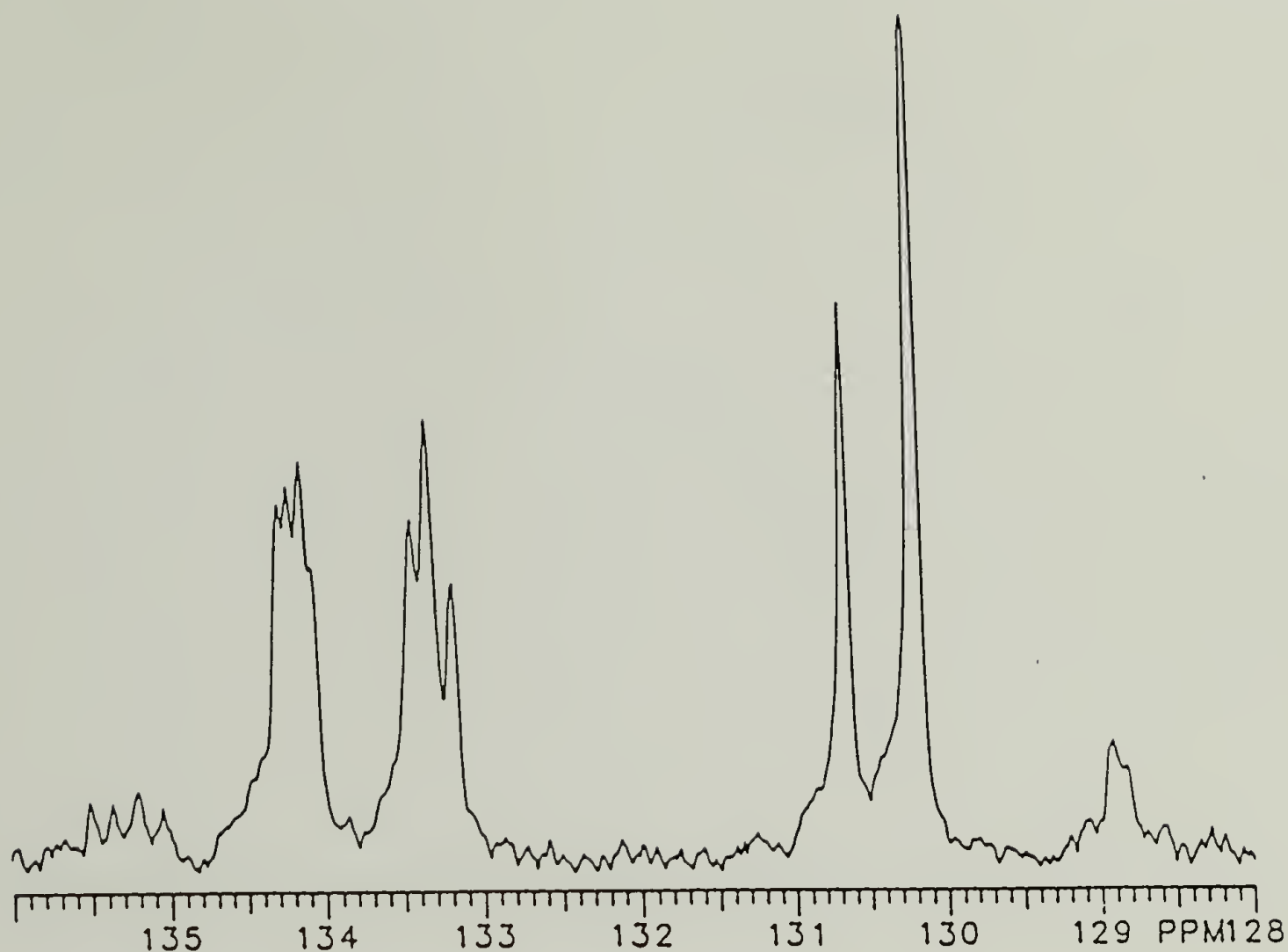


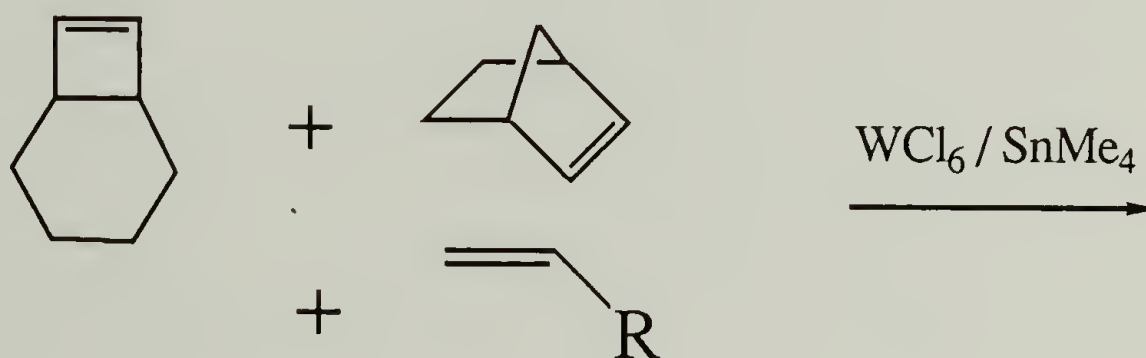
Figure 3.10: ^{13}C NMR spectrum of the product of sequential addition copolymerization of norbornene and cyclooctene.

Table 3.6: Sequential Addition Copolymerization of Norbornene and Cyclooctene NMR Data

<u>Dyad</u>	δ	<u>Integration</u>	Dyad Mole Fraction	
			<u>observed</u>	<u>predicted</u>
NC	134.9-135.6	1.6	0.13	0.49
(CN)	128.9			
NN	134.1,133.3(t,c)	6.2	0.49	0.31
CC	130.7,130.2(t,c)	4.8	0.38	0.17

Copolymerizations of Norbornene and Bicyclo[4.2.0]oct-7-ene

Norbornene and bicyclo[4.2.0]oct-7-ene were copolymerized with concurrent monomer addition as shown in Scheme 3.10. The product was isolated by precipitation in acetone. The olefin region of the ^{13}C NMR is shown in Figure 3.11. The peak assignments,^{12,17} integrations and mole fraction of dyads(observed and predicted for a random copolymer) are given in Table 3.7. Because of the overlap of the resonances of the bicyclo[4.2.0]oct-7-ene repeat units the integration for the BN and BB dyads were calculated by setting the integration of the BN resonance equal to that of the NB resonance and then subtracting that from that of total bicyclo[4.2.0]oct-7-ene repeat units resonance integration to determine the BB integration. The sharp resonances at 130 ppm and below are from chlorobenzene.



Scheme 3.10: Concurrent addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.

The product of this reaction is a truly random copolymer. The two bicyclic monomers are apparently of nearly equal reactivity in the copolymerization or sufficient chain transfer occurs to eliminate any initial blockiness in the copolymer.

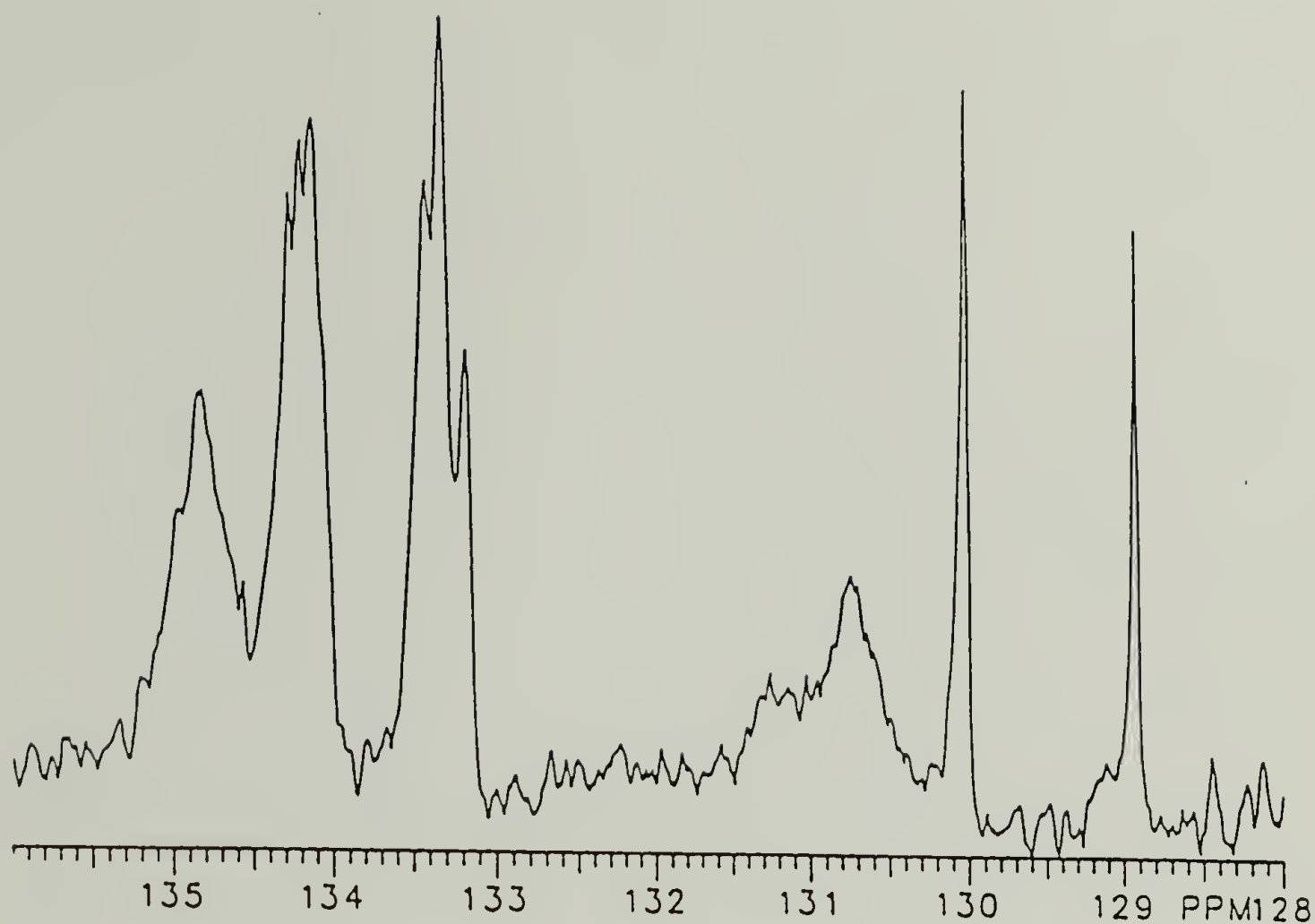
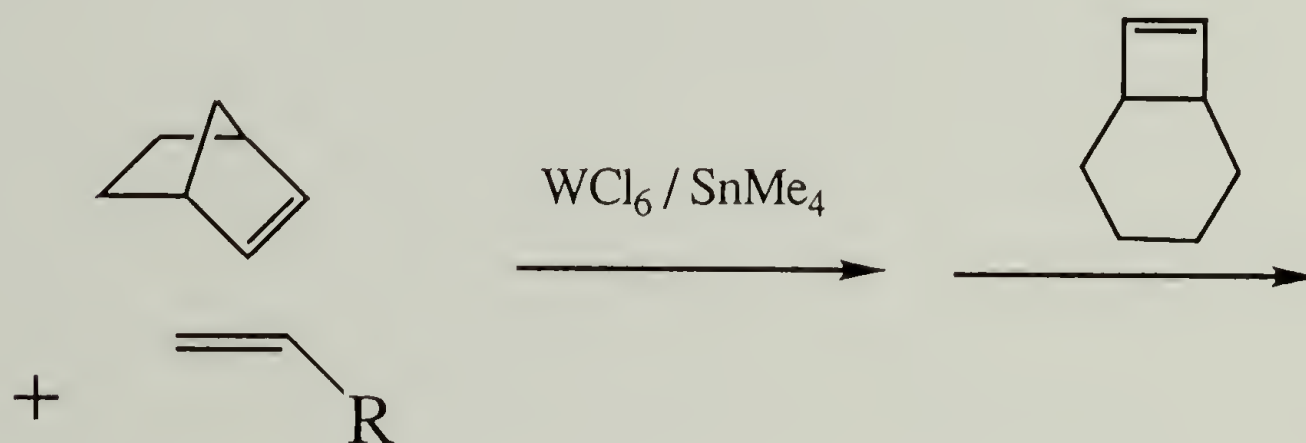


Figure 3.11: ^{13}C NMR spectrum of the product of concurrent addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.

Table 3.7: Concurrent Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene NMR Data.

<u>Dyad</u>	$\underline{\delta}$	<u>Integration</u>	Dyad Mole Fraction	
			<u>observed</u>	<u>predicted</u>
NB	134.6	4.0	0.40	0.39
(BN)	130.4			
NN	133.8,133.0(t,c)	5.3	0.53	0.53
BB	130.0-132.5	0.7	0.07	0.07

The sequential addition polymerization of norbornene and bicyclo[4.2.0]oct-7-ene was done as shown in Scheme 3.11. This is the same general procedure as the norbornene and cyclooctene experiment. The olefin region of the ^{13}C NMR is shown in Figure 3.12. This spectrum was obtained with a delay between pulses of one second. The resonances due to the heterodyads are present only as slight shoulders on the homodyad peaks if it all. This clearly shows that chain transfer is extremely limited when these two monomers which yield sterically hindered olefins on polymerization are copolymerized in this manner. Because the integration of the heterodyad resonances could not be measured no estimate of the amount of copolymer formed in this reaction was made.



Scheme 3.11: Sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.

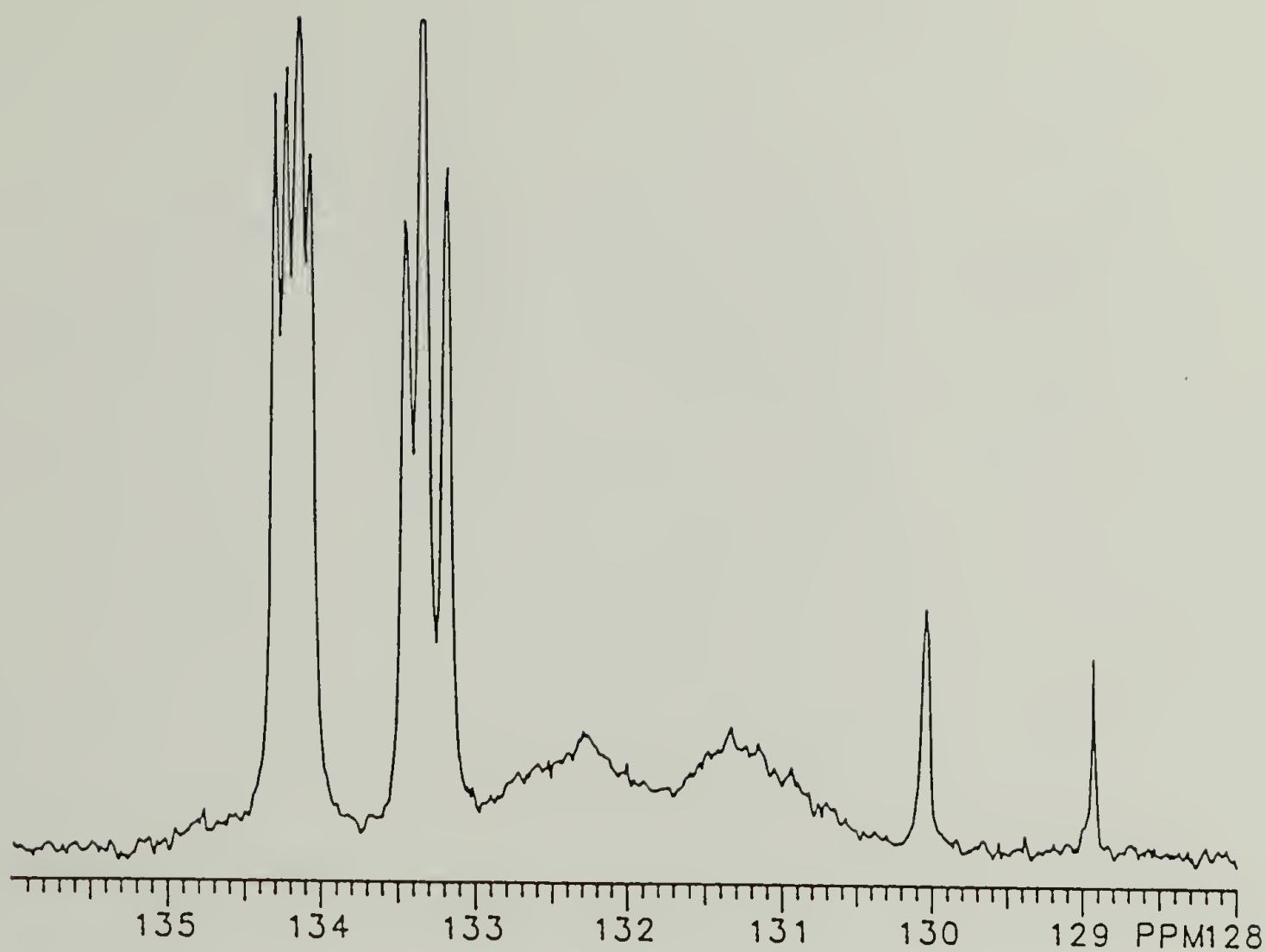


Figure 3.12: ^{13}C NMR spectrum of product of sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.

This same general procedure was used in another sequential addition copolymerization of these two monomers. A 10 to 1 ratio of norbornene to 1-octene was used. The product of this copolymerization did not precipitate in acetone. This indicates that some chain transfer and hence block copolymer formation occurred after the addition of the second monomer. The NMR and GPC discussed below are of a sample of the crude reaction mixture isolated by removing the reaction solvent under reduced pressure.

The olefin region of the ^{13}C NMR is shown in Figure 3.12. The peak assignments, integrations and mole fraction of dyads (observed and predicted for a random copolymer) are given in Table 3.8. The integrations were done by cutting and weighing. The same procedure as in the concurrent addition polymerization was used to determine the integration of the different bicyclo[4.2.0]oct-7-ene dyads.

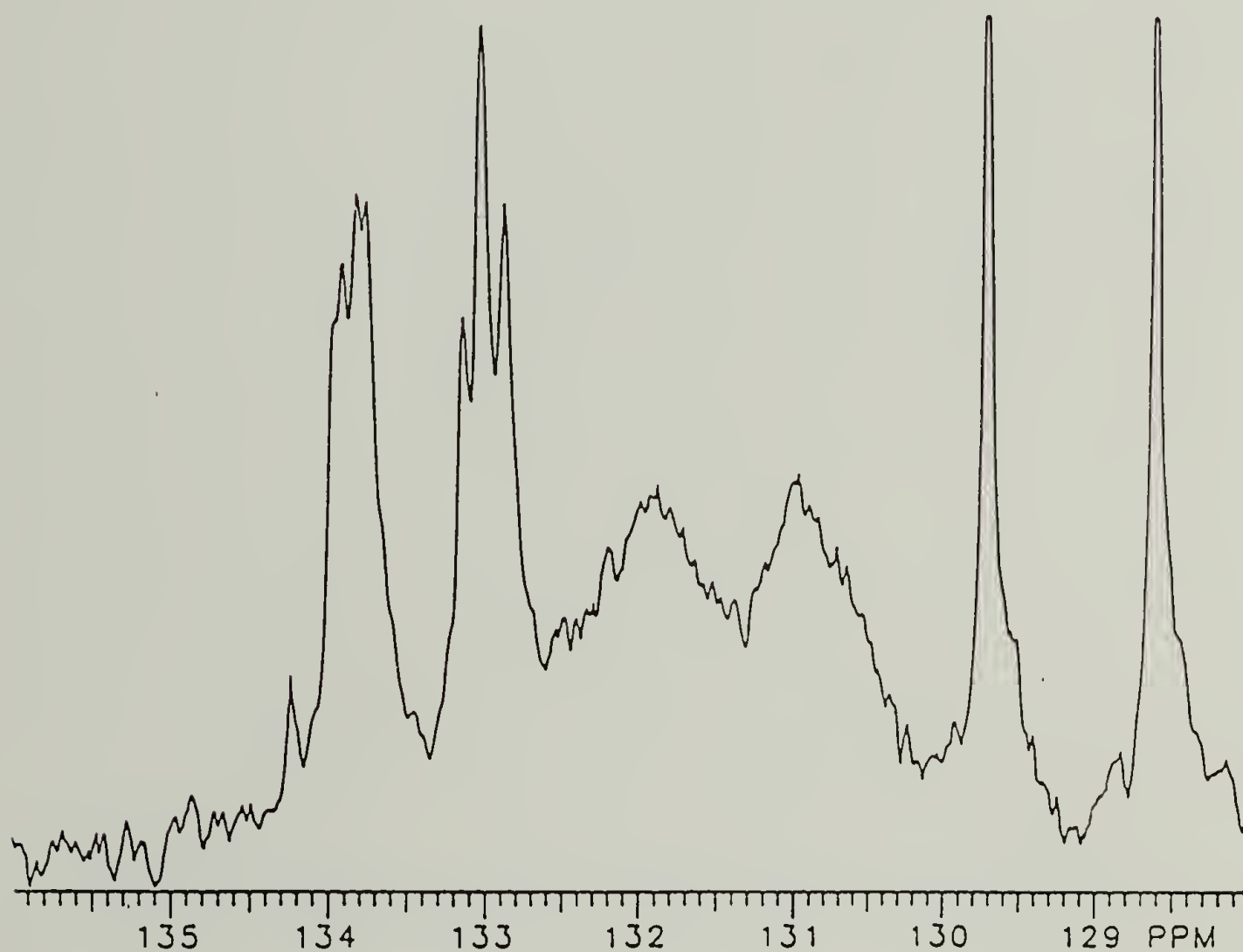


Figure 3.13: ^{13}C NMR spectrum of the product of sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene.

Table 3.8: Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene NMR Data

<u>Dyad</u>	<u>δ</u>	<u>Integration</u>	<u>Dyad Mole Fraction</u>	
			<u>observed</u>	<u>predicted</u>
NB	134.3	6.8	0.04	0.50
(BN)	not resolved			
NN	133.9,133.0(t,c)	104.9	0.51	0.28
BB	131.9, 131.0(t,c)	93.1	0.46	0.22

The definite presence of the NB dyad resonance is another indication that chain transfer and block copolymer formation has occurred. From the ratio of monomers to chain transfer agent the polymer chains average 19 repeat units and therefore 18 dyads. The heterodyad mole fraction of 0.04 corresponds to 0.7 heterodyads per chain. There is a significant amount of homopolymer in the product. Diblock copolymer is the predominant product of this reaction unless some chains undergo chain transfer

Chain transfer probably does not occur randomly along the polymer chain. The end double bonds of the polymer, between the 1-octene fragments and the monomer units are less sterically hindered than the internal double bonds of the polymer. After the initial polymerization in this experiment, the ratio of double bonds between norbornene units to these end double bonds is 9 to 2. This high percent of more readily reacted polymer double bonds explains why more heterodyads are formed in this experiment than in the previous one in which the norbornene to 1-octene ratio was 200 to 1.

The GPC of the poly(norbornenamer) formed in the first stage of this copolymerization and the final product are shown in Figure 3.14. Table 3.9 gives the molecular weights calculated (relative to polystyrene standards) for these two samples. The GPC data are consistent with a small amount of chain transfer having occurred. A portion of the initial product seems to have increased in molecular weight somewhat but much of it appears to be unchanged in molecular weight. Only part of the initial chains formed reacting further is responsible for the broadening of the molecular weight distribution with only a small change in the number average molecular weight.

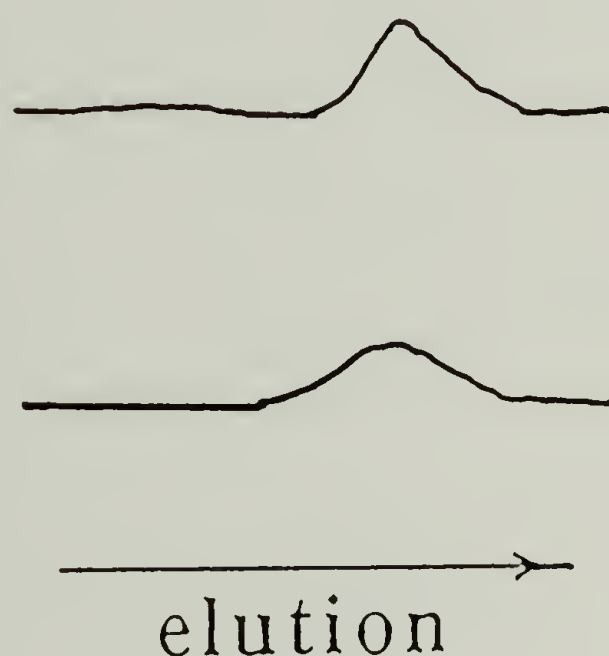


Figure 3.14: GPC of poly(norbornenamer) before addition of bicyclo[4.2.0]oct-7-ene (upper) and the product after the addition (lower).

Table 3.9: Sequential Addition Copolymerization of Norbornene and Bicyclo[4.2.0]oct-7-ene GPC Data

<u>Sample</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
poly(norbornenamer)	5500	13000	2.4
final product	7300	28000	3.9

The sequential addition copolymerization of norbornene and bicyclo[4.2.0]oct-7-ene demonstrates that block copolymer can be formed by the proper amount of chain transfer during a $\text{WCl}_6/\text{SnMe}_4$ catalyzed olefin metathesis polymerization. The sequential addition copolymerization of norbornene and cyclooctene is an example of enough chain transfer occurring to form an only slightly blocky copolymer.

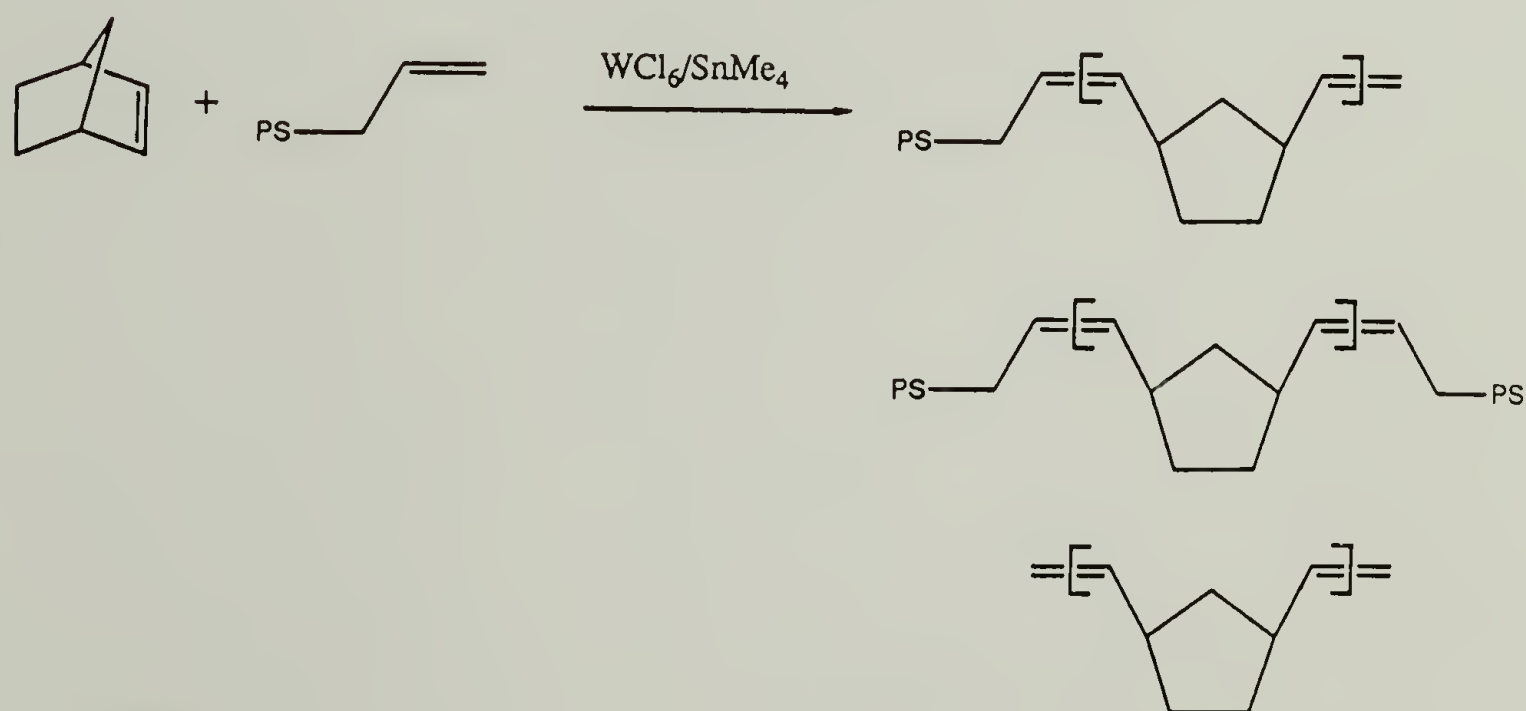
Other Monomers

Homopolymerizations of bicyclo[2.2.2]oct-2-ene, phenylacetylene and phenylnorbornene (2-phenylbicyclo[2.2.1]hept-5-ene) were done to determine if they would be appropriate monomers for sequential addition copolymerization experiments. The polymerizations of both bicyclo[2.2.2]-oct-2-ene and phenylacetylene gave poor yields of polymer with the $\text{WCl}_6/\text{SnMe}_4$ catalyst system. Phenylnorbornene did polymerize to a high yield, but was not used in copolymerization experiments because of the complicated olefin region in the ^{13}C NMR spectrum of the polymer. There are a large number of overlapped resonances from δ 125 to 136. This is due to the presence of phenyl as well as olefin carbons which have many different resonances because of the complicated structure of the polymer. The many

structural variations in the polymer structure are due to the presence of both the *exo*- and *endo*- isomers of the monomer and the possibility of head to head and head to tail linkages in the polymer as well as the presence of cis and trans double bonds.

Block Copolymer Synthesis by Reaction of a Polymeric Chain Transfer Agent Introduction

A preliminary investigation was done to see if block copolymers could be made with some control of product structure by reaction of a growing polymer chain and a polymeric chain transfer agent during an olefin metathesis polymerization. Norbornene was the monomer used and ω -vinylpolystyrene was the polymeric chain transfer agent used. As shown in Scheme 3.12, even if the reaction proceeds as expected the product will

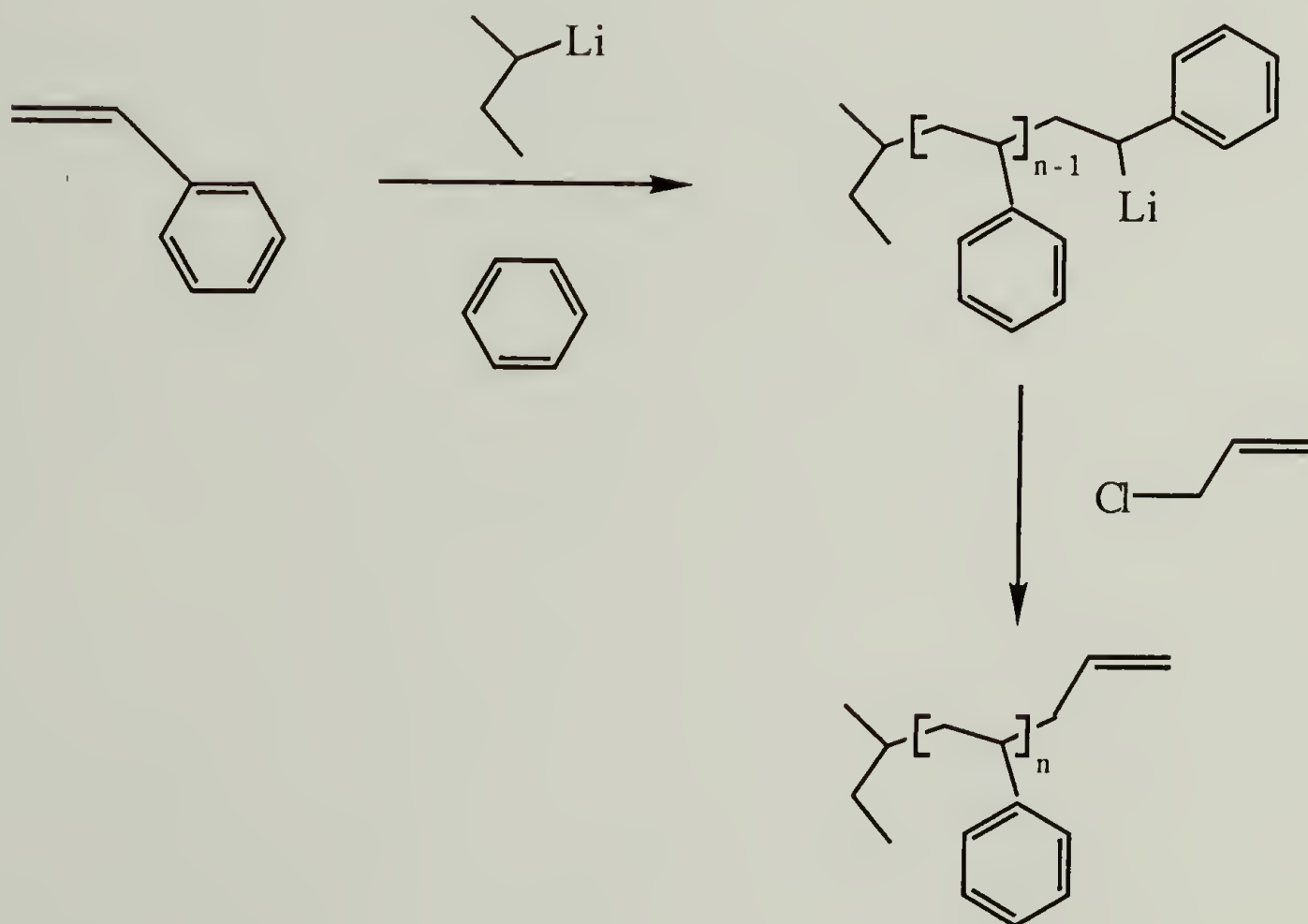


Scheme 3.12: Olefin metathesis of norbornene and ω -vinylpolystyrene.

contain norbornene homopolymer as well as diblock and triblock copolymers. The length of the styrene blocks will be easily controlled by the polystyrene synthesis. The amount of the polymeric chain transfer agent used should control the length of the norbornene blocks and the percentage of styrene units in the product.

Synthesis of ω -Vinylpolystyrene

ω -Vinylpolystyrene was synthesized by endcapping polystyryllithium with allyl chloride as shown in Scheme 3.13.¹⁸ Two samples were made, one low molecular weight for characterization purposes and one higher molecular weight for use in the metathesis reaction.



Scheme 3.13: Synthesis of ω -vinylpolystyrene.

The GPC data for the two samples is given in Table 3.10. There are two overlapped peaks in the GPC of the higher molecular weight sample. The data for this sample is reported both with the two peaks considered as one peak and as two peaks. The higher molecular weight peak, which is 13% of area of the two peaks, is clearly due to a "dimer" of the major product. The dimerization is due to oxidation of the anionic chain ends to radicals by the allyl chloride and the subsequent combination of these radicals. If allyl bromide is used in an attempted endcapping this radical combination is the predominant reaction.¹⁹

Table 3.10: ω -Vinylpolystyrene GPC Data

<u>Sample</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
ω -vinylPS-DP4	460	560	1.22
ω -vinylPS-DP24			
(both peaks)	2600	2870	1.10
(major peak)	2430	2520	1.04
(minor peak)	4950	5110	1.03

The ¹H NMR spectrum of ω -vinylPS-DP4 is shown in Figure 3.15. The styrene unit phenyl proton resonances are between δ 6.2 and 7.2. The resonance of the vinyl proton on the penultimate carbon is at δ 5.5. The resonance of the two vinyl protons on the terminal carbon is at δ 4.8. The integration of the 5 phenyl protons and the 3 vinyl group protons corresponds to a number average degree of polymerization of 5.5. This is

higher than the number average degree of polymerization of 4.5 calculated from the GPC data. This discrepancy is due to the presence of dimerized product and possibly to some chains which are unfunctionalized because of reaction of the anionic chain ends with proton sources. There is no separation of a dimerized product peak in the GPC of this sample, but the molecular weight distribution is relatively broad which is due to the presence of the dimerized product. Part of this discrepancy could also be attributed to inaccuracy of the GPC molecular weight determination.

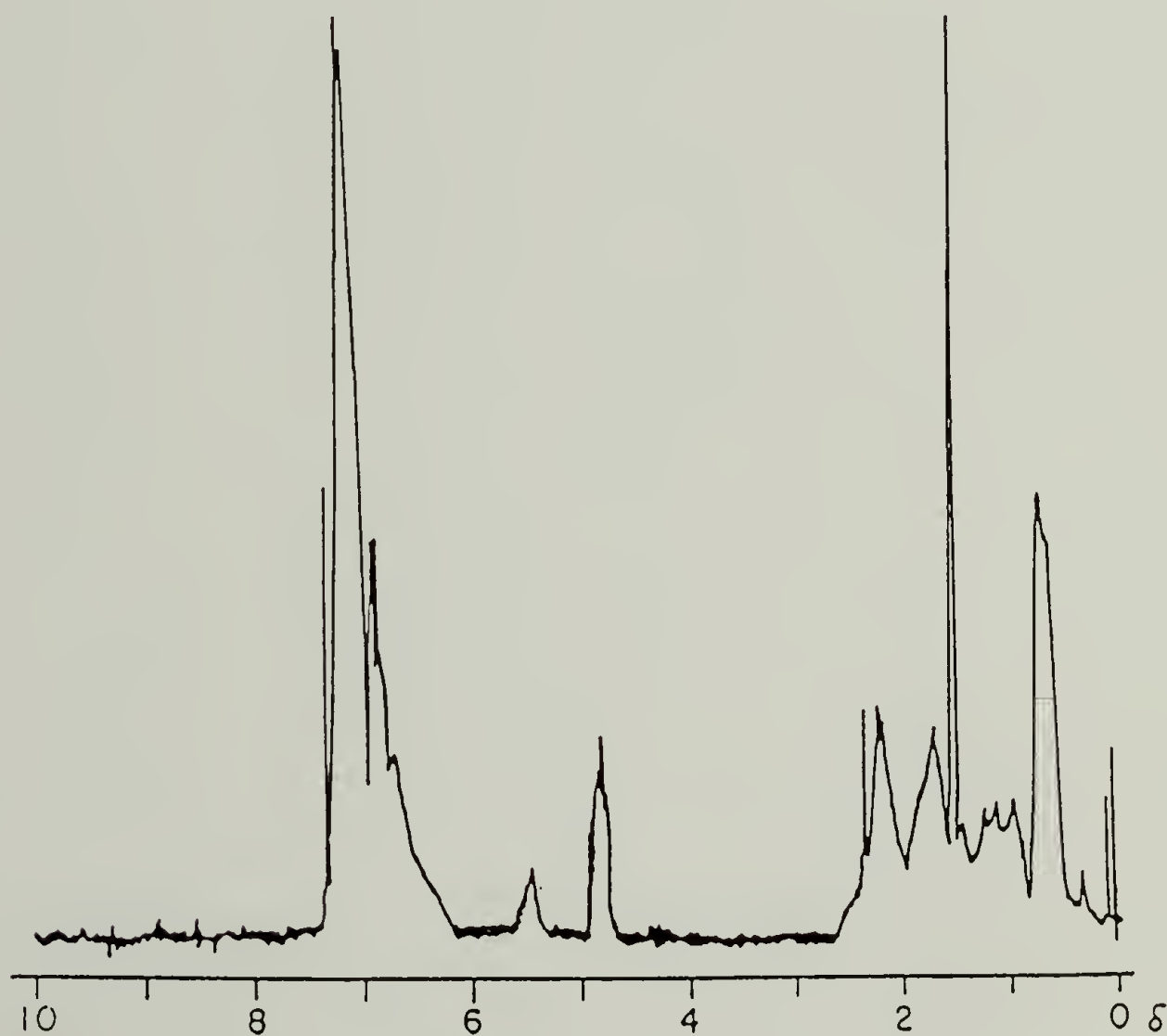


Figure 3.15: ^1H NMR spectrum of ω -vinylpolystyrene.

Polymerization Reaction

A norbornene to ω -vinylPS-DP24 ratio of 100:1 was used in the metathesis polymerization. The reaction mixture was very viscous. Part of the reaction mixture was precipitated in methanol. The remainder of the reaction mixture was purified as the poly(norbornenamer-*g*-styrene) had been: precipitated in a 1:1 methanol/acetone mixture, dissolved in toluene and reprecipitated in 1:1 methanol/acetone. Not all the product in either batch was soluble. The GPC of these two samples are shown in Figure 3.16. The molecular weight data (based on polystyrene standards) is given in Table 3.11. The fraction numbers in Table 3.11 correspond to the fraction numbers in Figure 3.16.

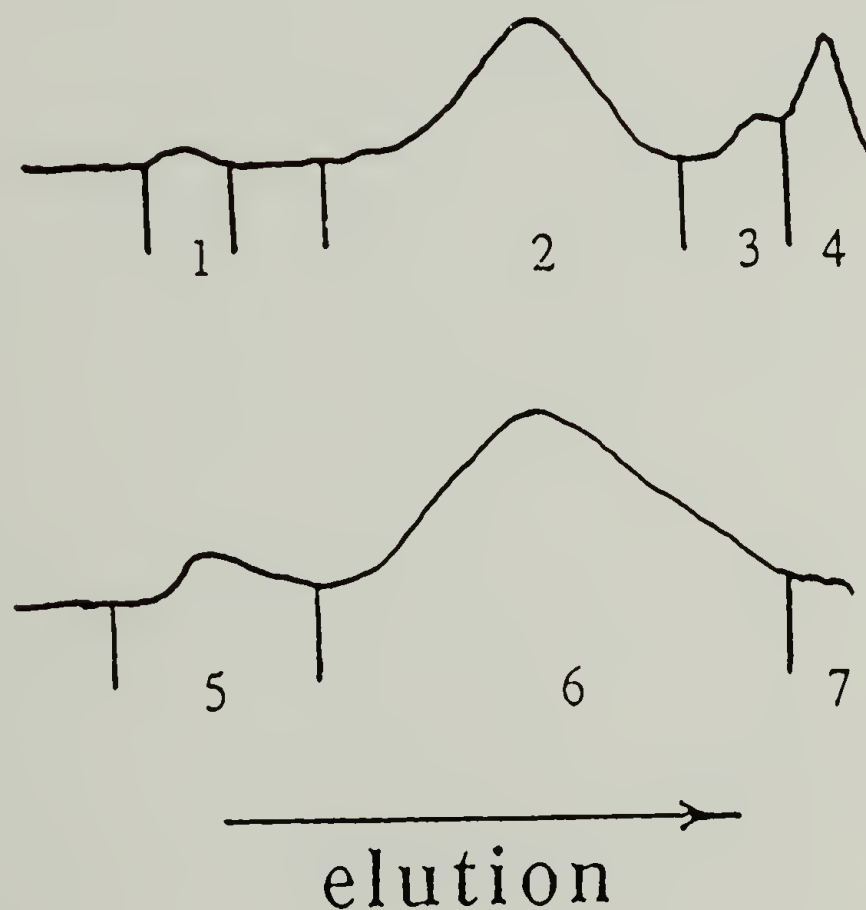


Figure 3.16: GPC of products of norbornene and ω -vinylpolystyrene metathesis.

Table 3.11: Norbornene and ω -Vinylpolystyrene Reaction GPC Data

<u>Fraction Number</u>	<u>M_n</u>	<u>M_w</u>	<u>M_w/M_n</u>
1	780000	810000	1.04
2	35000	47000	1.34
3	4600	4700	1.02
4	2500	2600	1.04
5	440000	500000	1.14
6	18000	37000	2.06
7	2300	2400	1.04

The GPC data indicate that there is a complex mixture of polymer structures in the product. There is some extremely high molecular weight material, some of which is insoluble and some of which makes up GPC peaks 1 and 5, which are the result of poly(norbornenamer) chains that grew quite long without reacting with the polymer chain transfer agent and are not affected by chain transfer after the polymerization is completed. The presence of this high molecular weight material is not surprising. Once a chain reaches high molecular weight, reaction with the polymeric chain agent is less likely because of the incompatibility of poly(norbornenamer) and polystyrene. The same factors as discussed in the lower reactivity of the high molecular weight macromonomer in the graft copolymerization are involved. Both samples have an intermediate molecular weight fraction, fractions 2 and 6, which is the result of the reaction of the polymeric chain transfer agent, as shown in Scheme 3.12. In the methanol precipitated sample there is a fraction due to dimers of ω -vinylPS-DP24, this may contain dimers

that are the result of a metathesis reaction as well as from the first synthesis. Unreacted ω -vinylPS-DP24 is seen in both samples, fractions 4 and 7.

The ^1H NMR spectrum of the sample precipitated twice in a methanol/acetone mixture is shown in Figure 3.17. The integration of the phenyl protons (δ 6.2-7.2) is greater than can be attributed to the unreacted ω -vinylPS-DP24 in this sample, indicating that there is block copolymer in this sample of the product. The ratio of the integration of the phenyl proton

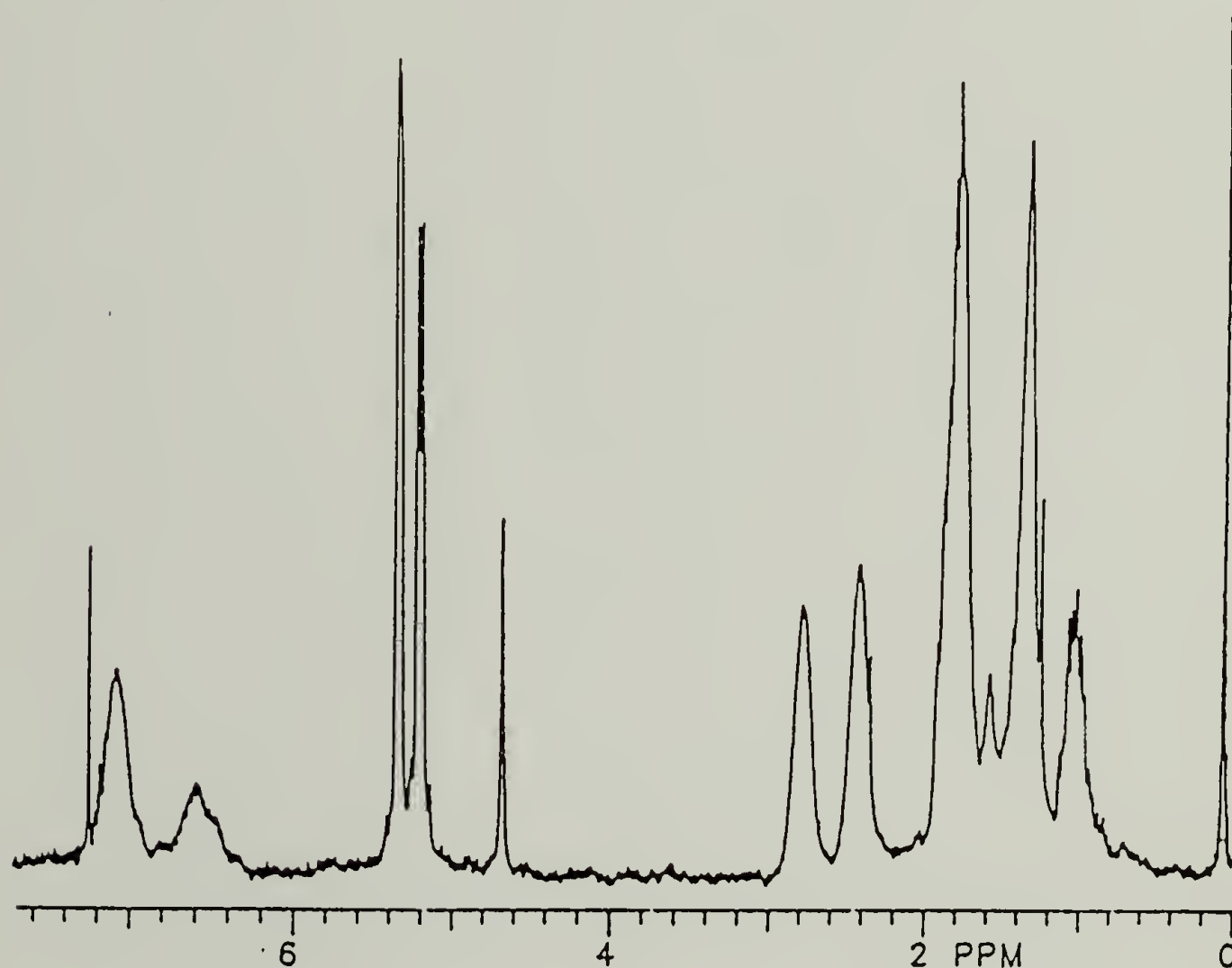


Figure 3.17: ^1H NMR spectrum of purified product of metathesis of norbornene and ω -vinylpolystyrene.

resonances of the styrene units and the double bond protons of the norbornene repeat units indicate that the mole fraction of styrene repeat units is 0.21. This corresponds to an "average" product of a diblock copolymer with the 24 styrene units from the ω -vinylPS-DP24 and 90 norbornene repeat units.

No further work was done with this reaction system. There are many possible routes to getting less complex product mixtures from this technique. Some will be discussed in the conclusion and suggestions chapter.

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CHAPTER IV

CONCLUSIONS AND SUGGESTIONS

Graft Copolymer Synthesis

Poly(norbornenamer-*g*-styrene) was synthesized by the olefin metathesis graft copolymerization of norbornene and ω -norbornenylpolystyrene. The length of the polystyrene grafts is determined by the molecular weight of the macromonomer, which is controlled in the anionic styrene polymerization. The length of the poly(norbornenamer) backbone is controlled by the amount of chain transfer agent used. The average number of grafts per chain is controlled by the amount of macromonomer in the feed. Repeated precipitation in a 1:1 methanol/acetone mixture gives a product free of unreacted macromonomer. The purified material does contain some norbornene homopolymer. Films of the graft copolymer are clear while a film cast from a mixture of the two homopolymers is hazy. This indicates that the two incompatible polymers are at least partially compatibilized by being covalently bound together.

Further research could continue along a number of lines. The influence of the length of the grafts, the length of the backbone and the number of grafts per chain might be studied. This synthetic method could also be used with different combinations of monomers and macromonomers to produce a range of graft copolymers by olefin metathesis.

Block Copolymer Synthesis

The formation of block copolymers by limited chain transfer in a $\text{WCl}_6/\text{SnMe}_4$ catalyzed olefin metathesis copolymerization with sequential monomer addition was shown to be possible. Block copolymer was formed in the sequential addition copolymerization of norbornene and bicyclo-[4.2.0]oct-7-ene. The sequential addition copolymerization of norbornene and cyclooctene resulted in formation of an only slightly blocky copolymer because too much chain transfer occurred.

Experimenting with different catalysts and monomers to find combinations that give the proper amount of chain transfer to form block copolymers would be a promising research direction. Monomer combinations in which the two monomers have different degrees of polarity would be useful in that determination of the amount of the two homopolymers present could be done by chromatography or fractionation. A variety of norbornene derivative could be synthesized by the Diels Alder reaction of cyclopentadiene and substituted ethylenes for this purpose.

Only the first experiment in the synthesis of block copolymer by the use of ω -vinylpolystyrene as a polymeric chain transfer agent during the metathesis polymerization of norbornene was done. Some block copolymer was formed. In addition to the range of structures expected for the polymerization because of the asymmetry of the chain transfer agent, there was a significant amount of very high molecular weight material. Decreasing the amount of very high molecular weight polymer formed requires increasing the efficiency of chain transfer. A different catalyst

system or monomer might cause chain transfer with the polymeric chain transfer agent to better compete with propagation or to occur more readily after the polymerization is complete. The use of some low molecular weight chain transfer agent could also lower the amount of high molecular weight polymer formed at the cost of increasing the amount of homopolymer formed.

Once a more effective method of reacting the polymeric chain transfer agent is found further research could take a number of directions: The effect of the ω -vinylpolystyrene molecular weight on the reactivity of the polymeric chain transfer agent and the properties of the product could be investigated. The distribution of homopolymer, diblock and triblock copolymer formed could also be studied. Other polymeric chain transfer agents and monomers could be used to synthesize a range of block copolymers. Utilization of a symmetric polymeric chain transfer agent could be investigated. A double bond in the middle of a polymer chain might be less reactive but the symmetry of the polymer would simplify the mixture of products obtained.

The two methods of block copolymer formation explored in this research with olefin metathesis could also be applied to other equilibrium polymerizations. The polymerization of cyclic siloxanes with many catalysts systems involves a competition of polymerization and chain transfer reactions that is similar to that seen in olefin metathesis.¹ The synthesis of block copolymers should be possible by the same general procedure as used with olefin metathesis in this work.

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PART II: SURFACE CHEMISTRY OF POLY(VINYLCHLORIDE)

CHAPTER V INTRODUCTION

In any polymer application, control of several polymer properties is desired. Many properties depend on the physical and chemical structure of the polymer bulk. Other properties such as wettability, adhesion, friction, gloss, electrostatic charging and biocompatibility depend on the structure of the polymer surface. Modification of the surface of a polymeric object after it is formed allows the structure, and hence the properties, of the bulk and the surface to be controlled independently.

What constitutes the surface of a polymer can not be rigorously defined. The surface properties listed above involve interaction of a polymer and its surroundings over different length scales. For example, when a polymer is in contact with a liquid the surface (or polymer/liquid interface) may be only a few angstroms thick, as in water and a hydrophobic polymer, or many microns thick, as when the liquid swells the polymer slightly. In this dissertation the surface is defined as that portion of a polymer which interacts with its environment in the situation discussed.

There are numerous polymer surface modification techniques. Most involve chemical modification of the surface, but many, such as plasma

treatment,¹ involve poorly defined chemistry. Obtaining the desired surface properties by such methods necessarily involves trial and error experimentation and reliance on empirical rules.

"Standard" chemical reactions can be used to modify polymer surfaces. This allows rational design of the chemical nature of a polymer surface and facilitates correlation of surface structure and properties. Typically the polymeric object is placed in a solution of a reagent. The reagent diffuses into the polymer/solvent interface and reacts with the polymer, chemically transforming the polymer surface. A wide range of reactions have been run on a number of polymer surfaces. Reports of chemical surface modifications include reduction of fluoropolymers,²⁻⁴ dehydrofluorination of poly(vinylidene fluoride),^{5,6} sulfonation of polystyrene^{7,8} and Friedels-Craft reaction of polycarbonate.⁹ The surface of polyethylene (PE) has been modified by a number of reactions: chemical oxidation,¹⁰⁻¹² ozonation,¹³ sulfonation,¹⁴ chlorination,¹⁵ fluorination,¹⁶ and reaction with carbenes.^{17,18}

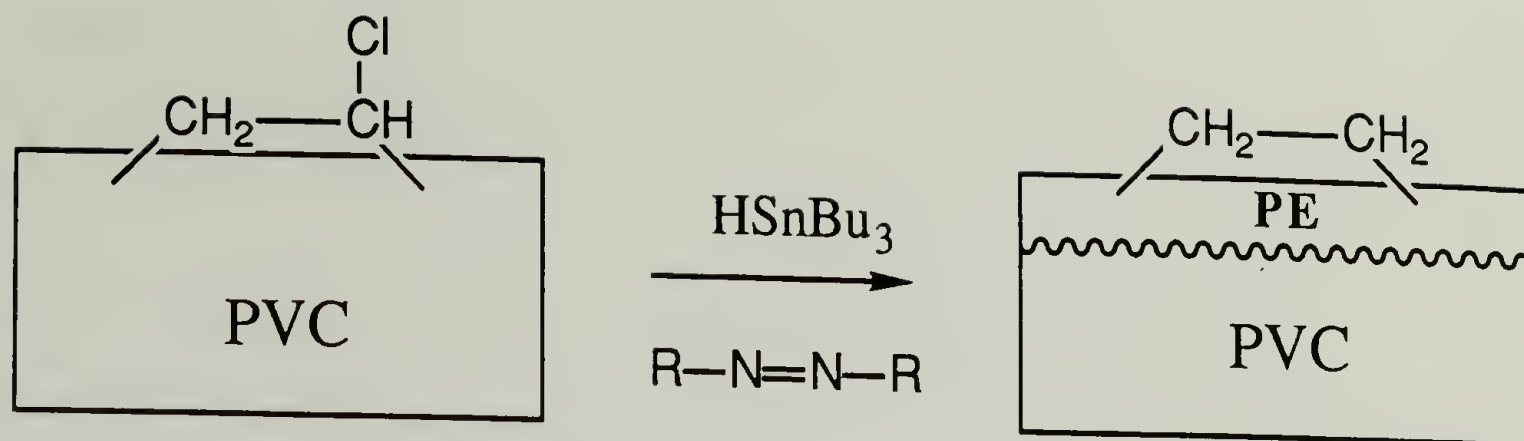
The work of the McCarthy research group has been involved primarily with the surface modification of fluoropolymers. Specific functional groups are placed at the surface by an initial reaction involving a reduction. Further surface modification is then carried out by subsequent reactions of these functional groups.¹⁹⁻²² This approach has allowed a wide range of functional groups to be placed at the surface of poly(tetrafluoroethylene),¹⁹ poly(chlorotrifluoroethylene),^{20,21} and poly(vinylidene-fluoride)²². The chemical and solvent resistance of these substrates has

allowed a wide range of reagents and solvents to be used to modify the more reactive surface region without affecting the polymer bulk.

Objectives of This Research

Poly(vinylchloride) (PVC) is much less solvent resistant and chemically inert than the aforementioned fluoropolymers and the methods used to modify these are inappropriate for PVC. The objective of the work described in this part of the dissertation was to modify the surface of PVC to increase solvent and chemical resistance, and to use this modified surface as a reactive handle for further modifications while also protecting the underlying PVC from attack by the reagents and solvents used. Increasing the solvent and chemical resistance of PVC would increase the number of environments in which PVC is useful. If this initially modified surface could be further reacted without affecting the PVC bulk, a wide range of functional groups could be placed at the surface of PVC. This would result in a great deal of control of the surface properties of PVC.

The approach taken was to chemically reduce the surface of PVC to polyethylene (PE) using tributyltin hydride (HSnBu_3) and a radical initiator as shown in Scheme 5.1.²³ The ability of this surface reduced material to resist attack by solvents and elimination by base was tested. This material was also chemically oxidized¹¹ (a standard PE surface modification which is the first step to a variety of surface structures¹²) to determine whether or not established PE surface modification methods could be applied for further modification of the PVC surface.



Scheme 5.1: Surface reduction of PVC.

Poly(vinylchloride) Background

The products made from PVC range from house siding to surgical gloves. PVC is versatile because many additives, particularly plasticizers, can be used to produce a wide range of properties. Unplasticized PVC has a glass transition temperature of approximately 80 °C and is typically less than 10 percent crystalline.²⁴ PVC film cast from tetrahydrofuran was used in the work described in this dissertation.

Chemical Modification of PVC

The chemical modification of PVC has been recently reviewed.²⁵ Modification reactions have been carried out in PVC solutions and suspensions. These modifications include chlorination, dehydrochlorination and graft copolymerization. Substitution of allylic and tertiary chlorides have been effected both for analytical purposes and to prevent degradation processes which start with these structures. A variety of substitution

reactions involving potentially all the chlorines in PVC have been studied. Dehydrochlorination is a major side reaction in most of these. PVC can be reduced quantitatively in solution with HSnBu_3 and a radical initiator to give PE which has been used for ^{13}C structural studies of PVC.^{23,26,27} Partial reductions yield random copolymers of ethylene and vinyl chloride.²⁸

Surface Modification of PVC

Chemical and physical modifications of the surface of PVC have been reported. These include various plasma treatments,²⁹⁻³¹ grafting of polymers to the surface of PVC³²⁻³⁴ fluorinating the surface with fluorine gas,³⁵ impregnating the polymer with dienes and peroxides to crosslink the surface on heating,³⁶ embedding another polymer in PVC by soaking PVC beads in a polymer solution³⁷ and coating PVC with a microns thick layer of another polymer.^{38,39} The objective of many of these modifications is to prevent plasticizer leaching. Some of the other objectives are to promote adhesion and increase blood compatibility. Most of the above examples are from the patent literature. Characterization of the modified surfaces is seldomly reported.

Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to study the products of some substitution and elimination/addition reactions carried out on the surface of PVC.⁴⁰ Hydroxy-carbamates were placed on the surface by reaction with potassium cyanate and ethylene glycol. The substitution of chlorine with cyanate gave isocyanates, which reacted with ethylene glycol to give 2-hydroxyethyl N-PVC carbamates. The films were highly colored because of the elimination which competed with the substitution. Treatment with chlorine gas removed the color by chlorinating

the double bonds. Isocyanate groups were placed on the surface of PVC by first eliminating the surface with sodium methoxide in a mixture of methanol and dimethyl sulfoxide and then reacting the eliminated material with isocyanic acid and t-butyl hypochlorite. This reaction places chlorine and isocyanate groups on the surface.

Reduction of Alkyl Chlorides with Tributyltin Hydride

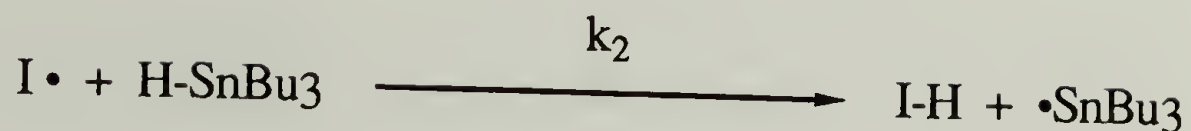
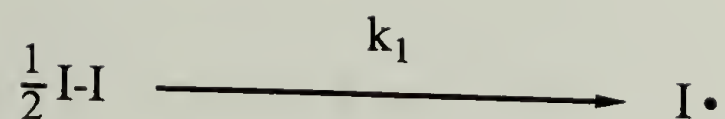
The surface reduction of PVC by HSnBu_3 was chosen for study because the solution reaction proceeds completely and cleanly.^{23,24} Lithium aluminum hydride has also been used to reduce PVC, but incomplete reduction and side products are reported.²³

The reduction of alkyl chlorides by HSnBu_3 is a synthetically versatile and well understood radical chain reaction.⁴¹⁻⁴³ The reaction steps are given in scheme 5.2. It has been shown in the reduction of a number of alkyl chlorides that alkyl radicals abstract hydrogen from HSnBu_3 more rapidly than the tributyltin radical abstracts chlorine and that the combination of tributyltin radicals is the predominant termination reaction.⁴⁴ The rate of the reaction is therefore given by Equation 5.1.

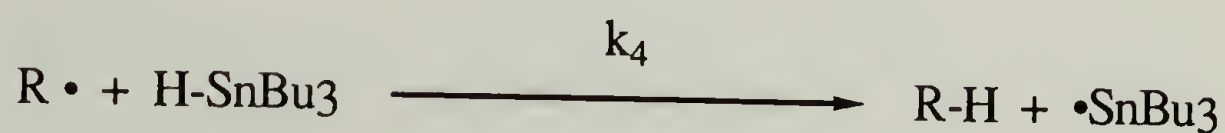
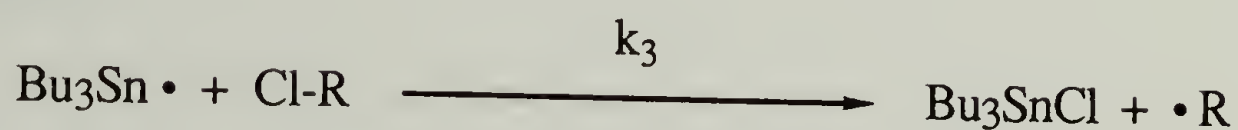
$$\frac{-d[\text{R-Cl}]}{dt} = k_3 [\cdot \text{SnBu}_3] [\text{R-Cl}] = k_3 \left(\frac{k_1 [\text{I-I}]}{2 k_5} \right)^{0.5} [\text{R-Cl}] \quad (5.1)$$

The kinetics of the surface reduction of PVC will certainly be influenced by the diffusion of reactants and solvent into the polymer. The

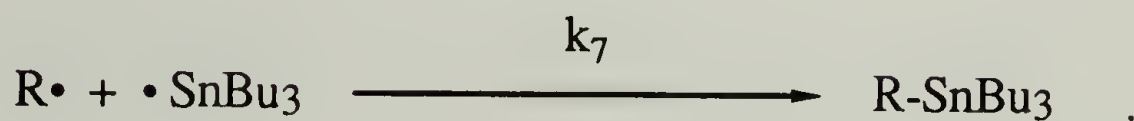
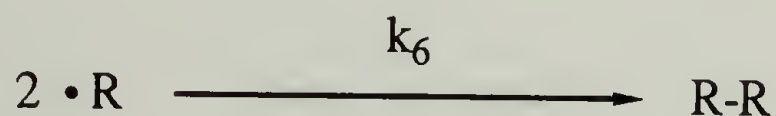
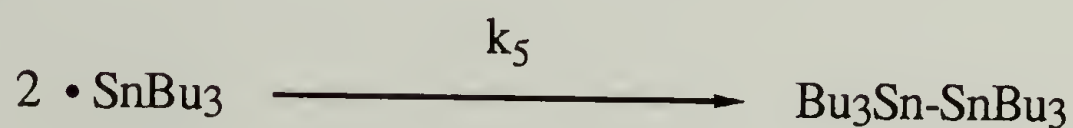
Initiation



Propagation



Termination



Scheme 5.2: Reaction Steps in Reduction of Alkyl Chlorides with HSnBu_3

other termination reactions may also be important leading to crosslinking and the covalent bonding of tributyltin groups to the polymer.

There is evidence that this reaction can be run heterogeneously. The complete reduction of poly(chlorotrifluoroethylene) to poly(trifluoroethylene) using HSnBu_3 has been performed.⁴⁵ The reaction begins heterogeneously but ends homogeneously. The starting material is not soluble in the reaction solvent (THF), but becomes soluble with reduction.

Polymer Surface Analytical Techniques

The complete chemical characterization of a polymer surface requires not only the detection of the identity and concentration of functional groups, but their position in the sample as well. Only techniques which can be used with solid samples and are very sensitive, since the surface is only a minute portion of the polymer, are useful. The techniques used in this research program are briefly described here in order of decreasing sampling depth, the thickness of the surface layer that is analyzed by a given technique.

UV-vis Spectroscopy

The transmission ultraviolet-visible (UV-vis) spectrum of a film sample was obtained by passing the sample beam through the film. The entire thickness of the film is assayed so it is not actually a surface sensitive technique. However, if a surface chromophore has a high enough extinction coefficient it can be detected above the background even if it is only present in a thin surface layer.

Attenuated Total Reflection Spectroscopy (ATR-IR)

In ATR-IR the IR spectrum of a polymer surface is obtained by placing the surface against two sides of an internal reflection element (IRE); infrared radiation is passed through the IRE so that multiple internal reflections occur as seen in Figure 5.1. The spectrum obtained is ratioed against a background spectrum of the IRE alone to give an IR spectrum of the surface region of the polymer film. The radiation striking the interface of the IRE and the film produces an evanescent (transient) electrical field in the film. The amplitude of this electrical field (E) falls off with distance from the interface as described in Equation 5.2.46

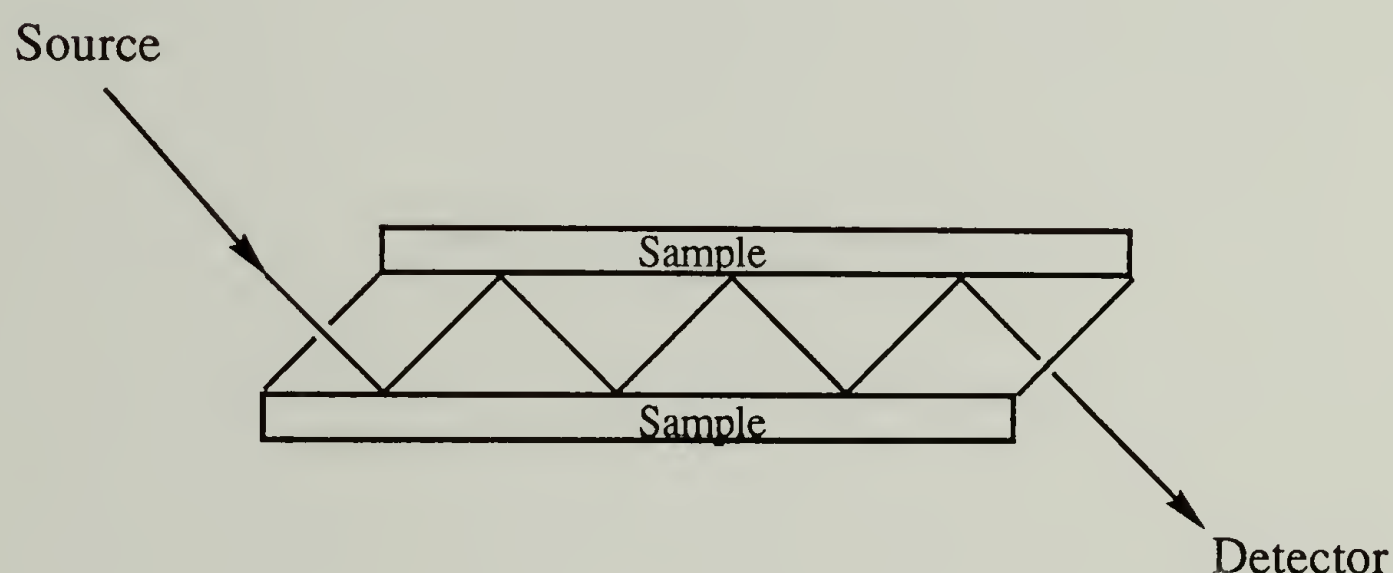


Figure 5.1: ATR-IR schematic.

$$E = E_0 \exp\left(\frac{-2\pi}{\lambda_1} \left(\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2\right)^{0.5} z\right) \quad (5.2)$$

E_0 = amplitude of electric field at the interface

n_1 = refractive index of the IRE

n_2 = refractive index of the sample

λ_1 = wavelength of the radiation in the IRE = λ/n_1

θ = angle of incidence

z = distance from the interface

The absorbance of energy by molecular vibrations, which occur in the same manner and at the same wavelength in ATR-IR as in transmission IR, is proportional to the intensity of the electric field which is E^2 . This means that the absorbance measured by ATR-IR for a particular vibration is a function of the depth at which the vibration occurs. The contribution (c) of the absorbance occurring in a surface layer of thickness t to the total absorbance is given by Equation 5.3.⁴⁷

$$c = \frac{\int_0^t E^2 dz}{\int_0^\infty E^2 dz} = 1 - \exp(-2t / dp) \quad (5.3)$$

dp = depth of penetration, the distance at which $E = E_0 \exp(-1)$

When the thickness of the surface layer (t) equals the depth of penetration (dp) the contribution of the surface layer (c) is 0.86. This means that for a homogeneous sample 86% of the absorbance seen at a given wavelength is

due to the material depth or less from the surface. This depth of penetration (which is a function of wavelength) will be used as the ATR-IR sampling depth even though some information is received from deeper in the film.

X-Ray Photoelectron Spectroscopy (XPS)

In X-Ray photoelectron spectroscopy (XPS), also known as electronic spectroscopy for chemical analysis (ESCA), monoenergetic X-rays are directed into a sample causing ionization of atoms by the photoelectric effect. A detector system counts the number of electrons which escape from the sample and measures their kinetic energy (KE). The kinetic energy of the photoelectron is related to the element that it came from by Equation 5.4.

$$KE = h\nu - BE - W \quad (5.4)$$

$h\nu$ = Energy of the X-ray photon

BE = binding energy of the atomic orbital losing the electron

W = spectrometer work function = energy lost by an electron in traveling through the spectrometer

XPS spectra are plotted as the intensity of signal, which is proportional to the electron count, versus binding energy. The surface selectivity of XPS derives from the mean free path length (λ) of the photoelectron in the sample. Only those electrons which escape the sample without loss of energy due to inelastic collisions and reach the detector are counted as part of a peak. The rest of the electrons reaching the detector make up the baseline noise. The fraction of the photoelectrons generated at a given point which escape

the sample without an inelastic collision (f) is a function of the distance that the photoelectron travels through the sample (x) as described in Equation 5.5.48

$$f = e^{-x/\lambda} \quad (5.5)$$

The contribution (c) of the photoelectrons which must travel a distance t or less to escape the sample to the total signal measured for a homogeneous sample is given by Equation 5.6.

$$c = \frac{\int_0^t e^{-x/\lambda} dx}{\int_0^\infty e^{-x/\lambda} dx} \quad (5.6)$$

Using this equation it can be determined that 85% of the signal from a homogeneous sample comes from electrons which travel 2λ or less to escape the sample. Before this can be used to determine the XPS sampling depth the geometry of the sample surface relative to the detector must be taken into account. In this work XPS spectra were taken at two take off (sample to detector) angles, (θ) 15° and 75° . The take off angle varies the distance that an electron must travel through the sample (x) from a given depth (d) to reach the detector as described in Equation 5.7 and Figure 5.2.

$$d = x \sin \theta \quad (5.7)$$

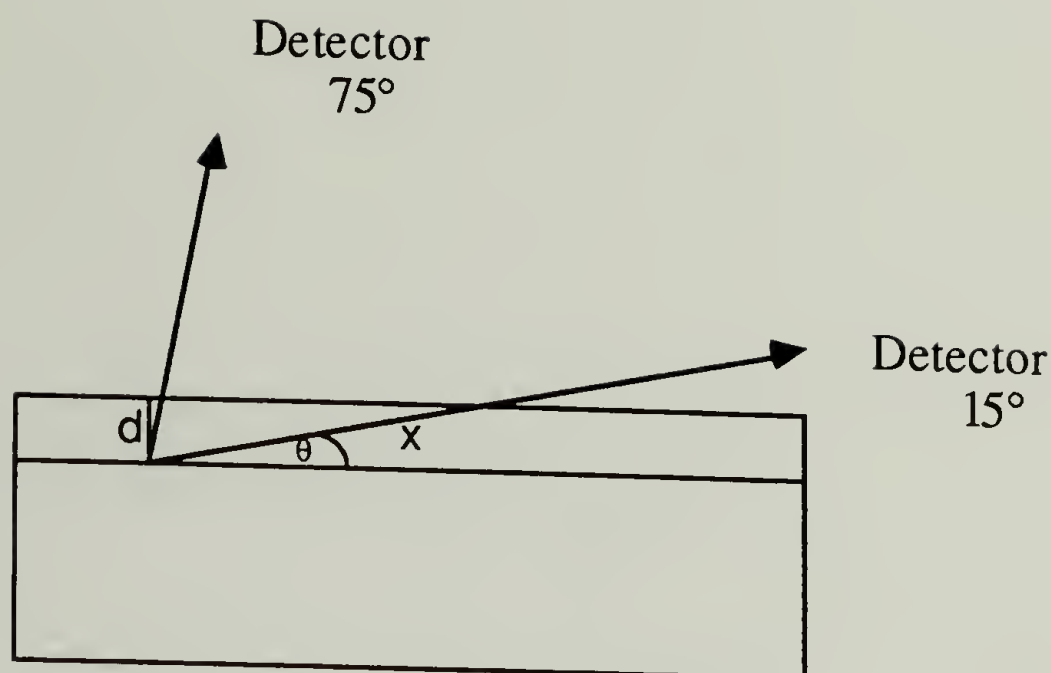


Figure 5.2: XPS schematic.

The mean free path of a photoelectron from the carbon 1s orbital has been measured to be 23 Å in poly(paraxylene).⁴⁹ Using two times this value as the distance (x) determining the sampling depth gives a sampling depth of 12 Å for spectra taken with a 15° take off angle and 45 Å for spectra taken with a 75° take off angle. Because this is a ballpark estimate (the mean free path length of an electron is dependent on the kinetic energy of the photoelectron and the nature of the sample) 10 Å and 40 Å will be used as estimates of the XPS sampling depths for the take off angles of 15° and 75°.

The intensity of a signal (I) from a particular atomic orbital is given by Equation 5.8.

$$I = nS \quad (5.8)$$

n = number of atoms of that element sampled

S = atomic sensitivity factor

The atomic sensitivity factor depends on a number of atomic and instrumental parameters. In this work relative atomic sensitivity factors determined from spectra of samples of known atomic composition were used. Atomic composition percentages are obtained by selecting one peak for each element and then calculating the molar percentage of each element by Equation 5.9.

$$\text{percentage of element A} = 100 \times \frac{n_A}{\sum n_i} = 100 \times \frac{I_A/S_A}{\sum I_i/S_i} \quad (5.9)$$

Atomic composition values determined in this manner are considered to have an error of 10 - 20 % if the sample is homogeneous in the XPS sampling depth.⁵⁰ If the atomic composition varies with depth this can introduce a large error, since sampling is a function of depth.

Contact Angle

Contact angles are measured by placing a drop of a probe liquid, usually water, onto a surface and measuring the angle at the surface/liquid/air interface as shown in Figure 5.3. The advancing contact angle (θ_A) is measured while the drop is growing larger because water is being added. The receding contact angle (θ_R) is measured while water is being removed, making the drop smaller. The water contact angles are an indication of the polarity of the outer few angstroms of a surface. The contact angles are also affected by such factors as: surface roughness and chemical heterogeneity, the ability of the surface to absorb the water and the pH of the water.⁵¹ Contact angle is a direct measure of the wettability of a surface by the probe liquid. This is an important surface characteristic for many applications.

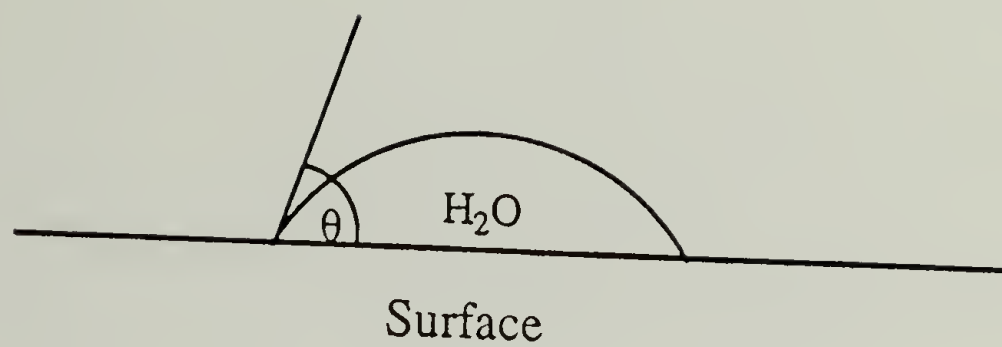


Figure 5.3: Contact Angle Measurement.

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CHAPTER VI

EXPERIMENTAL

Materials

2,2'-Azobis-(2-methylbutyronitrile), AMBN, (Polysciences) was used as received.

2,2'-Azobis-(methylpropionitrile), AIBN, (Polysciences) was recrystallized from methanol.

Benzophenone (Aldrich) was used as received.

Calcium hydride (Aldrich) was used as received.

Chromium (VI) oxide (Fisher) was used as received.

Chromium (II) Chloride was used as received.

Dichloromethane (Fisher) was used as received.

Ethylenediamine (Aldrich) was distilled trap to trap from molecular sieves.

Heptane (Fisher) was distilled from sodium/benzophenone dianion; a small amount of tetraglyme (Tetraethylene glycol dimethyl ether) was added to solubilize the dianion.

Isopropanol (Fisher) was used as received.

Methanol (Fisher) was used as received.

Pentane (Fisher) was used as received.

Polyethylene (Aldrich) high density polyethylene powder was pressed into films. The films were cut to size (1.4 cm. by 2 cm.) with a scalpel and washed by standing in dichloromethane for 30 minutes.

Poly(vinylchloride), PVC, (Polysciences) had a number average molecular weight of 93,000. Films were cast from 4% w/v solution in tetrahydrofuran in a nonstick baking pan. The films were dried

overnight in air and then in a vacuum oven. The films were cut to size (1.4 cm. by 2 cm.) with a scalpel.

Poly(vinylidene fluoride) film (Westlake Plastics) was used as received. The films were cut to size (1.4 cm. by 2 cm.) with a scalpel and washed in refluxing dichloromethane for 45 minutes.

Potassium hydroxide (Fisher) was used as received.

Sodium (Aldrich) was used as received.

Sulfuric acid (Fisher) was used as received.

Tetraglyme (tetraethylene glycol dimethyl ether) (Aldrich) was used as received.

Tetrahydrofuran (THF) (Fisher) was used as received for film casting and film washing. For use as a reaction solvent it was distilled from sodium/benzophenone dianion.

Toluene (Fisher) was distilled from calcium hydride trap to trap.

Tributyltin hydride (HSnBu_3) (Aldrich, Sure/SealTM bottle) was used as received.

Triethylsilane (Aldrich) was distilled trap to trap from molecular sieves.

Water was distilled trap to trap using a Teflon round bottom flask as the pot for use as a reaction solvent.

Material Handling

All distilled solvents and reagents were stored under nitrogen in flasks sealed with Teflon stopcocks. All transfers of these materials and tributyltin hydride were done under nitrogen using syringe and cannula techniques. All reactions were run in Schlenk tubes with o-ring joints and Teflon stopcocks to avoid contamination of the film surfaces with grease.

Methods

X-ray photoelectron spectra were obtained with a Perkin Elmer Physical Electronics 5100 with Mg K α excitation with a power of 200 watts. Spectra were recorded at two angles: the film surface 15° and 75° from the analyzer. Atomic composition values were obtained from the peak areas of spectra obtained in the multiplex mode, and corrected by a sensitivity factor. Infrared spectra were obtained with an IBM 38 FTIR. Attenuated total reflectance infrared (ATR-IR) spectra were recorded using a germanium 45° internal reflectance element. Contact angle measurements were recorded using a Rame-Hart telescopic goniometer. Water (doubly distilled) was the probe liquid. Dynamic contact angles were obtained by measuring the tangent of the drop at the air/water/surface intersection while adding (advancing) and withdrawing (receding) water to and from the drop. At least 3 drops were used and 5 measurements were made with each drop both of advancing and receding contact angle. Ultraviolet/visible light spectroscopy was performed using a Perkin Elmer Lambda 3A spectrophotometer. All measurements were done with a vacant reference cell. Spectra of film samples were obtained by placing the film in the sample beam using a film holding attachment. Gravimetric analysis was performed with a Cahn 29 electrobalance.

Reduction of PVC Film with Tributyltin Hydride

Initial Reductions Using AIBN

A number of experiments were run in an attempt to optimize the conditions for reduction. The atomic composition data from the XPS was

used to gauge the success of a reaction. In the tables of XPS data the letter g indicates that the spectrum was taken with a take off angle 15°. The letter n signifies a spectrum taken at takeoff angle of 75°. The number in the first column is the XPS file number.

(22A, 22 B)¹ AIBN (0.1 g., 0.6 mmols), and 3 PVC film samples were placed in a Schlenk tube which was then purged with nitrogen for 15 minutes. 30 mL of heptane was added by cannula. The desired amount of HSnBu₃ (see Table 6.1) was added by syringe. The tube was then placed in an oil bath which was heated to 65 °C. The AIBN only partially dissolved.

After 24 hours the reaction mixture, which included a small amount of white solid (unreacted AIBN?) was removed by cannula. The films, which had curled during the reaction, were washed in the reaction tube with four 10 mL portions of heptane. The films were then dried on a vacuum line at room temperature for three days. The reaction conditions and XPS results for these reactions are given in Table 6.1.

Table 6.1: Reaction Conditions and XPS Data for PVC Reduction

XPS _A_	Sample Number	Time (h)	mmoles			Atomic Composition Data				
			HSnBu ₃	AIBN		C	Cl	O	Si	Sn
615 614	PVC	--	--	--	g n	65.4 64.3	26.8 32.3	6.3 2.7	1.5 0.6	-- --
661 662	22 A	24	3	0.6	g n	90.9 95.7	1.2 1.9	6.8 1.9	0.9 0.3	0.3 0.3
659 660	22 B	24	6	0.6	g n	91.1 91.2	1.6 1.5	5.3 5.3	1.3 1.3	0.7 0.6

(36, 40 A, 40 C) The same general procedure as 22 A was used for the next set of reductions except that the reaction temperature was 60 °C and the AIBN and heptane were added as a solution. AIBN (0.025g, 0.15 mmoles) was dissolved in 15 mL of heptane before it was added to the purged tube. The reaction conditions and XPS results from these experiments are listed in Table 6.2.

(40B) One reaction was run in a mixture of 13 mL of heptane and 2 mL of toluene. All other conditions were the same as reaction 40C. The film samples were cloudy after reduction. The reaction conditions and XPS results from this experiment are also listed in Table 6.2.

Table 6.2: Reaction Conditions and XPS Data for PVC Reduction

XPS _D	Sample Number	Time (h)	mmoles		Atomic Composition Data					
			HSnBu ₃	AIBN		C	Cl	O	Si	Sn
9 11	36 A	2	1.5	0.15	g	66.8	2.7	7.7	1.7	2.8
					n	6.7	2.7	3.8	0.8	1.4
12 16 17	36B	2.5	1.5	0.15	g	74.1	7.4	11.4	2.3	4.8
					n	71.9	19.7	8.0	0.5	3.8
					g	73.5	9.8	10.4	1.5	4.8
18 19	36C	4.8	1.5	0.15	g	81.6	6.0	8.3	0.2	3.9
					n	7.9	1.1	6.6	0.5	2.8
E28 E30	40A	2.5	1.5	0.15	g	69.3	9.8	14.6	0.6	5.7
					n	6.9	14.5	11.2	0.5	4.7
E32 E34	40B	2.5	1.5	0.75	g	92.7	2.8	3.8	0.2	0.5
					n	92.0	2.6	4.0	0.8	0.6
E37 E38	40C	2.5	1.5	0.75	g	85.8	7.0	4.6	1.0	1.5
					n	84.2	11.0	3.0	0.9	1.0

(46) This general procedure was used for all subsequent reductions. Two PVC film samples and the desired weight of radical initiator (AMBN or AIBN) were placed in a Schlenk tube which was then purged with nitrogen for 15 minutes. Heptane (15 mL) was added by cannula and the desired volume of HSnBu₃ was added by syringe. The tube was then placed in a 60 °C oil bath and kept under a positive pressure of nitrogen. After the desired reaction time, the reaction solution was removed by cannula and the film samples were washed twice with 10 mL of heptane. The film samples were extracted (Soxhlet) for 24 hours with pentane and then dried on a vacuum line at room temperature for 3 days. The reaction conditions and the XPS results for these reactions are given in Table 6.3.

Table 6.3: Reaction Conditions and XPS Data for PVC Reduction

<u>XPS</u> <u>.E</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>		<u>Atomic Composition Data</u>					
			<u>HSnBu₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
144 145	46A	15	3	0.3	g n	83.9 80.1	10.6 15.3	3.8 3.6	1.2 1.0	0.5 0.4
146 147	46B	24	3	0.3	g n	90.4 87.9	6.9 6.9	1.9 1.7	0.6 0.0	0.3 0.5
148 149	46C	40	3	0.3	g n	94.5 91.1	4.4 6.9	0.6 1.7	0.3 0.0	0.2 0.3
F125 F126	86A	8	3	0.3	g n	77.5 74.0	10.4 17.9	8.1 5.2	1.5 0.5	2.5 2.3
F127 F128	86B	16	3	0.3	g n	84.3 84.0	5.0 8.7	6.5 4.6	2.9 1.2	1.4 1.6

The contact angles for PVC (washed in pentane and dried on the vacuum line) were 92/45 (92° advancing contact angle and 45° receding contact angle). Sample 46A had contact angles of 94/64. Sample 46C had contact angles of 98/72.

Reduction at 45 °C

(54) Table 6.4 gives the reaction conditions and XPS data for two reductions were run using the general procedure but with a reaction temperature of 45 °C.

Table 6.4: Reaction Conditions and XPS Data for PVC Reduction

<u>XPS</u> <u>.E</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>				
			<u>H</u> <u>Sn</u> <u>Bu</u> <u>3</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
275	54A	24	3	0.3	g	75.0	15.9	6.6	1.3	1.5
276					n	72.5	19.9	5.3	1.0	1.3
277	54B	24	3	0.9	g	73.7	15.0	8.4	1.2	1.8
278					n	72.7	18.8	6.0	1.0	1.5

Reductions with AMBN as Initiator

2,2'-Azobis-(2-methylbutyronitrile) (AMBN) was used as the initiator because it is more soluble in heptane than AIBN. (60) Table 6.5 lists the results of two reactions run using the same conditions as in Table 6.2 except for the substitution of AMBN for AIBN. The AMBN fully dissolved within a

few minutes after the reaction tube was placed in the oil bath. The reaction conditions and the XPS results for these reactions are given in Table 6.5.

Table 6.5: Reaction Conditions and XPS Data for PVC Reduction

<u>XPS</u> <u>.E</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>				
			<u>HSnBu₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
288	60 A	18	3	0.3	g	74.3	4.0	14.8	4.9	2.1
289					n	79.1	6.7	9.8	2.6	1.9
290					g	75.5	4.2	14.2	4.0	2.2
291	60 B	36	3	0.3	g	89.8	2.5	5.2	1.7	0.8
292					n	84	6.4	7.5	0.4	1.8
294					g	88.7	2.8	6.5	1.2	0.9

Kinetic Study of Reduction Using Tributyltin Hydride

A series of reductions were run which varied only in the time of reaction. All the samples were from the same piece of film which had been dried one week in a vacuum oven, cut into 2 cm by 1.4 cm samples, extracted with pentane in a Soxhlet extractor, and then dried 3 weeks under vacuum. The films samples were wrinkled and slightly curled after reaction.

The reaction conditions and the XPS results for these reactions are given in Table 6.6. The contact angle data is given in Table 6.7. The entry with a reaction time of zero hours is for a pentane washed PVC film. The contact angle data is missing for some samples which were too wrinkled for measurement.

Table 6.6: XPS Data for PVC Reduction Kinetic Study

<u>XPS</u> <u>.E</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>				
			<u>HSnBu₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
1557 1558 1559	76	0	---	---	g n g	69.6 67.1 69.5	27.8 31.6 29.0	2.5 1.5 1.5	-- -- --	-- -- --
1500 1501	76	1	3	0.3	g n	68.1 66.4	17.0 22.8	10.8 8.1	1.0 0.4	3.1 2.4
1502 1503	76	2	3	0.3	g n	69.4 66.6	16.3 22.4	11.1 8.6	0.7 --	2.4 2.4
1496 1497	76	4	3	0.3	g n	67.1 67.5	13.7 20.1	11.7 2.7	5.2 3.0	2.3 1.6
1498 1499	76	8	3	0.3	g n	79.5 75.8	13.0 16.7	5.6 5.7	0.3 --	1.6 1.9
1498 1499	76	16	3	0.3	g n	86.2 83.2	8.0 13.3	3.7 2.2	1.2 0.4	0.8 0.9
1740 1741	76	32	3	0.3	g n	76.2 75.6	7.5 11.3	9.1 7.9	5.0 5.4	2.1 1.8

Table 6.7: Contact Angle Data for PVC Reduction Kinetic Study

<u>Reaction</u> <u>Time (h)</u>	<u>θ_A</u>		<u>θ_R</u>	
	<u>Avg.</u>	<u>Std. Dev.</u>	<u>Avg.</u>	<u>Std. Dev.</u>
0 (Washed PVC)	87	3	53	11
1	88	5	51	6
2	88	1	44	4
4	85	3	54	14
16	86	4	62	4
Polyethylene	101	4	75	4

Reduction Control Experiments

Controls (76, 102 A, 102 B, 110 A, 110 B) were run for 32 hours using the same procedure as the kinetics experiments but not using all the reagents. One reduction (88) was run for 4 hours but the product was not extracted with pentane. The conditions used in these experiments and the XPS results are given in Table 6.8.

Table 6.8: Conditions and XPS Data for Reduction Control Experiments

<u>xps.</u>	<u>Sample</u>	<u>mmoles</u>				<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>	<u>N</u>
		<u>HSnBu₃</u>	<u>AMBN</u>								
E1561	76	0	0	g	68.4	29.6	1.7	0.4	--	--	--
E1562				n	66.6	32.4	1.0	--	--	--	--
R316	102 A	3	0	g	60.1	10.9	18.0	1.7	9.4	--	--
R317				n	60.8	20.5	12.1	0.5	6.1	--	--
R493	110 A	3	0	g	58.3	13.0	18.1	0.8	9.8	--	--
R494				n	59.6	21.6	11.9	0.7	6.3	--	--
R320	102 B	0	0.3	g	74.0	15.1	7.2	--	--	--	3.7
R321				n	68.9	17.0	11.1	--	--	--	2.9
R495	110 B	0	0.3	g	72.8	7.8	19.0	0.3	--	--	--
R496				n	72.1	10.5	17.3	0.2	--	--	--
F103	88	3	0.3	g	67.7	8.4	16.1	1.1	6.7	--	--
F104				n	65.2	17.6	11.4	0.5	5.3	--	--

Stronger Reduction Conditions

(88) The film samples were presoaked with HSnBu₃ for one reduction. The same procedure and reactant concentrations as in the kinetic

study were used, but the addition of the reactants was different. The HSnBu_3 and 5 mL of Heptane were added to the purged Schlenk tube containing the film samples. The tube was then placed in a 60 °C oil bath . After 6 hours the AMBN, which had been dissolved in 10 mL of heptane under nitrogen, was added. The reaction was run for 18 hours. (96) Reductions in which the concentration of HSnBu_3 or AMBN were doubled compared to the kinetic study reactions were also run. The reaction conditions and the XPS results for these reactions are given in Table 6.9.

Table 6.9: Reaction Conditions and XPS Data for PVC Reduction

XPS _F	Sample Number	Time (h)	mmoles			Atomic Composition Data				
			<u>HSnBu₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
170	88	18 ^a	3	0.3	g	85.2	2.9	8.5	0.5	2.9
171					n	83.4	5.6	8.2	--	2.8
179	94	16	6	0.3	g	89.9	6.3	2.1	1.7	--
180					n	88.7	8.4	1.8	1.1	--
181	94	16	3	0.6	g	84.7	1.7	7.3	6.3	0.1
182					n	87.5	1.8	7.3	3.3	--

a) Reaction time after addition of initiator (see text above).

Reductions Using UV Light to Dissociate AMBN

A series of reductions (84 A-C) were run under the same conditions as the kinetics study except that a reaction temperature of 0 °C and ultraviolet light, from a Spectronics B-100 lamp, was used to dissociate the AMBN. A mixture of ethylene glycol and water (-5 °C) was circulated through a water

jacket surrounding the Schlenk tube to control the reaction temperature. The PVC film was placed in the Schlenk tube which was then purged with nitrogen for 15 minutes. The AMBN was dissolved in the heptane at room temperature under nitrogen. This solution was transferred by cannula to the Schlenk tube, which had been cooled for 15 minutes. After another 10 minutes, the HSnBu_3 was added by syringe, the tube was shaken to mix the contents and the UV lamp was turned on. One reaction (**84 D**) was run at approximately 60 °C in the same manner. The reaction conditions and the XPS results for these reactions are given in Table 6.10.

Table 6.10: Reaction Conditions and XPS Data for PVC Reduction

<u>XPS</u> <u>.E</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>				
			<u>HSnBu₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
1716 1717	84A	1	3	0.3	g n	70.0 68.7	23.6 27.4	5.6 3.6	0.3 --	0.6 0.3
1738 1739	84B	8	3	0.3	g n	64.6 63.0	14.1 22.2	14.0 9.8	2.2 0.8	5.1 4.1
F66 F67	84C	24	3	0.3	g n	65.8 64.3	15.2 21.1	13.5 10.0	0.5 0.7	5.0 3.9
F76 F77	84D (60 °C)	1	3	0.3	g n	72.6 70.4	15.0 22.1	7.9 4.8	2.9 1.4	1.6 1.3

AMBN Dissociation Kinetics

(78) The kinetics of AMBN dissociation were determined using the same experimental set up as the reductions but with only AMBN and heptane

present. The reaction mixtures were sampled by cannula. The ultraviolet absorbance at 347 nm (the maximum of the azo group absorbance) was measured for each sample. The data from these experiments is given in Table 6.11.

Table 6.11 Kinetics of AMBN Dissociation Data

<u>Time (h)</u>	<u>60 °C Thermal Dissociation Absorbance(347 nm.)</u>	<u>0 °C UV Dissociation Absorbance(347 nm.)</u>
0	.357	.357
1	.322	.338
2	.319	----
4	.315	.224
8	.297	.130
32	.239	.048

Other Reductions of PVC

Reduction of PVC Film with Triethylsilane

(22 C, 22 D) The same procedure as 22 A was used but with triethylsilane instead of tributyltin hydride. The reaction conditions and XPS results for these reactions are given in Table 6.12.

Table 6.12: Reaction Conditions and XPS Data for PVC Reduction

<u>XPS .A</u>	<u>Sample Number</u>	<u>Time (h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>			
			<u>HSiEt₃</u>	<u>AIBN</u>		<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>
685	22 C	24	3	0.6	g	67.1	23.7	5.7	0.3
686					n	64.9	30.4	2.7	0
683	22 D	24	6	0.6	g	67.1	22.4	7.3	3.2
684					n	66.5	29.2	3.2	1.2

Reduction of PVC film with Chromium (II) Chloride

(50) A piece of PVC film was placed in a Schlenk tube. In a glove box, 0.37 g. (3 mmol) of CrCl_2 was added to the tube. 14.5 mL of water was added to give a greenish blue solution. 0.6 mL (9 mmol) of ethylenediamine was added by syringe. The solution turned purple instantly and a small amount of solid precipitated. After 24 hours the reddish purple reaction solution was removed by cannula. The film was washed with water 4 x 10 mL and heptane 2 x 10 mL. The wrinkled film was then dried on the vacuum line. The XPS results from this experiment are given in Table 6.13.

Table 6.13: XPS Data for PVC Reduction using Chromium (II) Chloride

XPS A	Sample Number	Time (h)		Atomic Composition Data					
				C	Cl	O	Si	Cr	N
224	50	24	g	54.5	8.6	28.3	0.0	4.5	4.1
226			n	55.3	13	24.2	0.0	4.0	3.5

Attempted Reduction of PVF₂ Film

(18) AIBN (0.1 g., 0.6 mmol), and 3 pieces (1.2 x 1 cm) of PVF₂ film were placed in a Schlenk tube (with condenser). The tube was purged with nitrogen for 15 minutes. THF (30 mL) was added by cannula. The desired amount of HSnBu_3 was added by syringe. The tube was then placed in an oil bath, connected to a nitrogen bubbler and heated to mild reflux. After 36 hours the reaction solution was removed by cannula. The films were washed in the reaction tube with four 10 mL portions of THF and then a

10 mL portion of CH_2Cl_2 . The films were then dried on a vacuum line. The contact angles of PVF₂ were 87/63. The contact angles of sample **18 B** were 97/45. The reaction conditions and XPS results are given in Table 6.14.

Table 6.14: Reaction Conditions and XPS Data for PVF₂ Reduction

<u>XPS</u> <u>.A</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>				
			<u>H</u> <u>Sn</u> <u>Bu</u> <u>3</u>	<u>AIBN</u>		<u>C</u>	<u>F</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>
654	18 A	36	3	0.6	g	57.6	30.7	4.7	0.7	2.2
655					n	60	33.6	4.7	0.3	1.6
647	18 B	36	6	0.6	g	57.7	27.4	11	0.9	3.1
650					n	59.8	30.3	6.8	0.5	2.2

(18) The above procedure was also done with triethylsilane instead of tributyltin hydride. The contact angles of sample **18 D** were 96/51. The reaction conditions and XPS results for these reactions are given in Table 6.15.

Table 6.15: Reaction Conditions and XPS Data for PVF₂ Reduction

<u>XPS</u> <u>.A</u>	<u>Sample</u> <u>Number</u>	<u>Time</u> <u>(h)</u>	<u>mmoles</u>			<u>Atomic Composition Data</u>			
			<u>H</u> <u>Si</u> <u>Et</u> <u>3</u>	<u>AIBN</u>		<u>C</u>	<u>F</u>	<u>O</u>	<u>Si</u>
681	18 C	36	3	0.6	g	50.4	47.1	2.5	0.0
682	18 D	36	6	0.6	g	48.2	48.7	2.5	0.5

Studies of the Properties of Reduced PVC

Base Treatment of PVC and Reduced PVC

(96) Samples of PVC film and reduced PVC film (4 hour reduction as in 76) were placed in a Schlenk tube which was then purged with nitrogen for 15 minutes. Then 10 mL of a 0.5 M solution of potassium hydroxide in isopropanol (prepared under nitrogen) was added. The tube was placed in a 60 °C oil bath and kept under a positive pressure of nitrogen. After one hour the films were rinsed with 3 x 10 mL of isopropanol (under nitrogen). The PVC film was stiffer and had a brownish tint. There was no visible change in the previously reduced sample. The films were dried on a vacuum line at room temperature for 3 days. Table 6.16 gives the XPS data for these samples. The PVC and reduced PVC data are given because a different batch of PVC was used.

Table 6.16: XPS Data for Base Treatment of PVC and Reduced PVC

XPS _R_	Sample		Atomic Composition Data					
			C	Cl	O	Si	Sn	K
381	PVC	g	66.5	31.1	1.8	0.6	--	--
382		n	67.4	31.6	0.8	0.2	--	--
387	Base treated PVC	g	74.0	17.0	7.5	1.4	--	--
388		n	73.2	22.1	4.2	0.5	--	--
383	Reduced PVC (76) 4 h	g	66.2	17.7	10.9	11.6	3.5	--
384		n	68.3	21.1	7.3	1.0	2.3	--
385	Base treated Reduced PVC	g	69.4	19.0	10.4	0.7	0.5	--
386		n	70.6	21.0	7.7	0.2	0.4	--

Solvent Resistance Tests of PVC and Reduced PVC

Samples of PVC, Reduced PVC (76 18 h) and Reduced PVC (94 16 h) were placed in 5 mL of THF or dichloromethane in vials. In THF all the samples dissolved almost immediately. After 10 minutes no solid was seen in the vial that had the PVC in it. Small pieces of material could be seen in the vials that contained the reduced samples. In dichloromethane all the samples appeared equally swollen after 10 minutes. None of the samples could be grasped with forceps without tearing the film.

Oxidation of PVC, Reduced PVC and PE

(84) Chromium (VI) oxide (29 g) was dissolved in 42 mL of water in a small crystallizing dish. Sulfuric acid was added dropwise, with swirling of the dish to redissolve the precipitate that formed. The precipitate did not dissolve after the addition of 20 mL of sulfuric acid even after heating to 65 °C. This heterogeneous mixture was used at 65 °C.

Each piece of film(PVC, reduced PVC (76 4 h), PE) was placed in the mixture for one minute. The films were immediately rinsed by swirling in a series of 3 beakers of water (300 mL), a beaker of methanol (200 mL) and a beaker of pentane (200 mL). The beakers of water were changed for each sample. The films were dried on a vacuum line at room temperature for 3 days. Table 6.17 gives the XPS data for these samples. The contact angle data is in Table 6.18.

Table 6.17: XPS Data for Oxidized Samples

XPS F	Sample		Atomic Composition Data			
			C	Cl	O	Si
130	PE (unreacted)	g	97.5	--	2.2	--
131		n	98.0	--	1.8	--
133	PE	g	85.5	--	14.5	--
131		n	86.6	--	13.4	--
136	PVC	g	89.0	6.5	3.1	1.4
137		n	78.7	17.5	3.0	0.8
139	Reduced PVC	g	79.6	9.2	10.0	1.2
140		n	74.0	15.8	10.2	0.0

Table 6.18: Contact Angle Data for Oxidations

Sample	Before		After	
	θ_A	θ_R	θ_A	θ_R
PE	101	75	59	<15
PVC	87	53	82	49
Reduced PVC	85	54	80	42

Note

- 1 Bold numbers indicate laboratory notebook references. All references in this part of the dissertation are to the surface reactions notebook.

CHAPTER VII

RESULTS AND DISCUSSION

Reduction of the Surface of PVC with Tributyltin hydride

Initial Reductions

The first goal of this work was to find a reduction system to convert the surface of poly(vinylchloride) (PVC) to polyethylene (PE). The radical chain reduction using tributyltin hydride (HSnBu_3) and 2,2' azobis-(methylpropionitrile) (AIBN) was tried first because it has been shown to convert PVC to PE in solution nearly quantitatively without side reactions.¹⁻³

Heptane was used as the solvent because it is a nonsolvent for PVC⁴ but a good solvent for HSnBu_3 . The solubility of AIBN in heptane is limited; solid AIBN is present for hours in most of the reactions described here.

A number of different reaction conditions were tried before making a detailed study of the reaction and its products. The chlorine to carbon atomic ratio was used as the measure of the success of a reaction. PVC should have a chlorine to carbon atomic ratio of 0.50, since each repeat unit has one chlorine and two carbons. The PVC film used in these initial experiments has a chlorine to carbon atomic ratio of 0.35 at a take off angle of 15° and 0.45 at a take off angle of 75° (after rinsing in heptane and drying on the vacuum line). This indicates that the very outer portion of the material is not entirely PVC. This is not surprising since the surface is most intimately in contact with the environment and can be eliminated or oxidized without the bulk being affected. Impurities from the bulk often migrate to the surface, an example of this is the blooming of plasticizers to the surface of polymers.⁵ It

is also possible that in the 15° measurement that the chlorine atoms are undercounted because they are oriented away from the surface.

The first attempts at this reaction (**22 A**, **22 B**) were very successful. The chlorine to carbon atomic ratios were less than 0.02 for both product samples at both take off angles. The carbon hydrogen stretching region in the ATR-IR of sample **22 B** shows only the two methylene stretches of PE. This indicates that the reduction is nearly complete throughout the ATR-IR sampling depth in this region of the spectrum (approximately 2300 Å). The remainder of the spectrum, which samples more deeply, is not significantly changed indicating that the reduction is not occurring throughout the film. A number of reactions were done to find milder reaction conditions which would reduce the PVC in the XPS sampling depth to PE. Table 7.1 gives the reaction conditions and the chlorine to carbon atomic ratio (Cl/C) determined by XPS for these initial experiments using HSnBu₃. The complete atomic composition data from the XPS is listed in tables in the experimental section.

2,2'-Azobis(2-methylbutyronitrile) (AMBN) was tried in place of AIBN in reactions **60 A** and **60 B** because of its greater solubility in heptane. This initiator dissolved within minutes of the reaction tube being placed in the 60 °C oil bath. Comparison of the chlorine to carbon ratios of the samples from these experiments and samples **46 A** and **46 C** which had been reacted under essentially the same conditions with AIBN show that the two initiators are equally effective for this reduction despite the longer half life of AMBN,^{6,7} perhaps because of its greater solubility. AMBN will be

used for further reactions. Using a readily soluble initiator avoids possible complications in investigating the kinetics of the reaction.

Table 7.1: Reaction Conditions and XPS Chlorine to Carbon Ratios for Initial Reductions

Sample	Time	Temp.	H ₂ SnBu ₃	Initiator		XPS Data	
<u>Number</u>	<u>(h)</u>	<u>°C</u>	<u>mmoles</u>	<u>Initiator</u>	<u>mmoles</u>	<u>Cl/C 15°</u>	<u>Cl/C 75°</u>
PVC	---	---	---	---	---	.35	.45
22 A	24	65	3.0	AIBN	0.6	.01	.02
22 B	24	65	6.0	AIBN	0.6	.02	.02
36 A	2	60	1.5	AIBN	0.15	.40	.40
36 B	25	60	1.5	AIBN	0.15	.10	.27
36 C	48	60	1.5	AIBN	0.15	.07	.14
40 A	25	60	1.5	AIBN	0.15	.14	.21
40 C	25	60	1.5	AIBN	0.75	.08	.13
46 A	15	60	3.0	AIBN	0.3	.14	.19
46 B	24	60	3.0	AIBN	0.3	.08	.08
46 C	40	60	3.0	AIBN	0.3	.05	.08
54 A	24	45	3.0	AIBN	0.3	.21	.28
54 B	24	45	3.0	AIBN	0.3	.20	.26
60 A	18	60	3.0	AMBN	0.3	.05	.08
60 B	36	60	3.0	AMBN	0.3	.03	.08

The chlorine to carbon atomic ratios of 0.05 at 15° take off angle and 0.09 at 75° take off angle for **60 A** indicates that there is 1 chlorine for every 10 to 20 carbons after 18 hours reaction. This was determined to be an effective reduction. The reaction conditions of **60 A** were used for further study of this reduction and its products.

Kinetic Study of Reduction

A series of reductions were performed with the same reaction conditions as in **60** but with different reaction times. All the film samples used in this study were cut from the same piece of film which was cast from tetrahydrofuran solution and dried for one week under vacuum. The samples were then cut, extracted with pentane in a Soxhlet extractor for 24 hours and dried under vacuum for three weeks. The samples produced were analyzed by XPS, ATR-IR and contact angle.

No change in contact angle with water was observed upon reduction. The advancing angle was between 85° and 88° for the starting material and the reduced films. The receding angle was between 44° and 53° for these samples. Some change was expected as PE has a somewhat higher contact angle (101/75). Incomplete reduction, side reactions which place oxygen on the surface and perhaps the physical roughness of the film could each or all be responsible for this change not being seen.

Table 7.2 gives the XPS atomic composition results from this series of experiments. Figure 7.1 is the XPS survey spectra of PVC and a sample reduced for 32 hours. Figure 7.2 is the C_{1s} region of the XPS spectrum acquired in the multiplex mode for these two samples. There is no separation

of the peak due to the chlorinated carbon from the methylene carbon but reduction does cause this composite peak to narrow.

Table 7.2 Reduction Kinetic Study XPS Data

Reaction	Take off	XPS Atomic Composition					
<u>Time (h)</u>	<u>Angle</u>	<u>C</u>	<u>Cl</u>	<u>O</u>	<u>Si</u>	<u>Sn</u>	<u>Cl/C</u>
0	15°	69.6	27.8	2.5	--	--	0.40
	75°	67.1	31.6	1.5	--	--	0.47
1	15°	68.1	17.0	10.8	1.0	3.1	0.25
	75°	66.4	22.8	8.1	0.4	2.4	0.34
2	15°	69.4	16.3	11.1	0.7	2.4	0.23
	75°	66.6	22.4	8.6	--	2.4	0.34
4	15°	67.1	13.7	11.7	5.2	2.3	0.20
	75°	67.5	20.1	2.7	3.0	1.6	0.30
8	15°	79.5	13.0	5.6	0.3	1.6	0.16
	75°	75.8	16.7	5.7	--	1.9	0.22
16	15°	86.2	8.0	3.7	1.2	0.8	0.09
	75°	83.2	13.3	2.2	0.4	0.9	0.16
32	15°	76.2	7.5	9.1	5.0	2.1	0.10
	75°	75.6	11.3	7.9	5.4	1.8	0.15

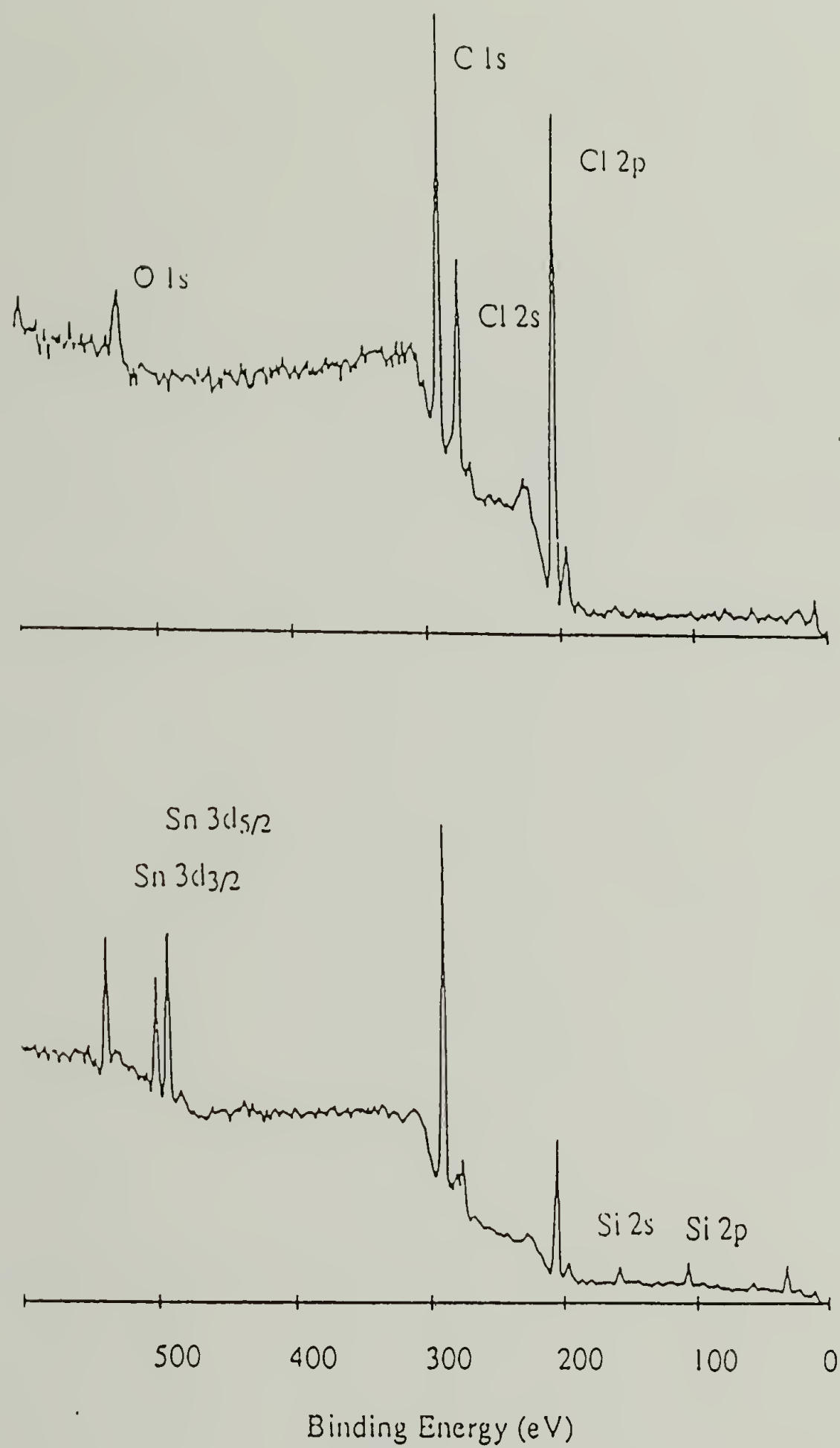


Figure 7.1: XPS survey spectra of PVC (upper) and 32 hour reduced PVC (lower) (take off angle = 75°)

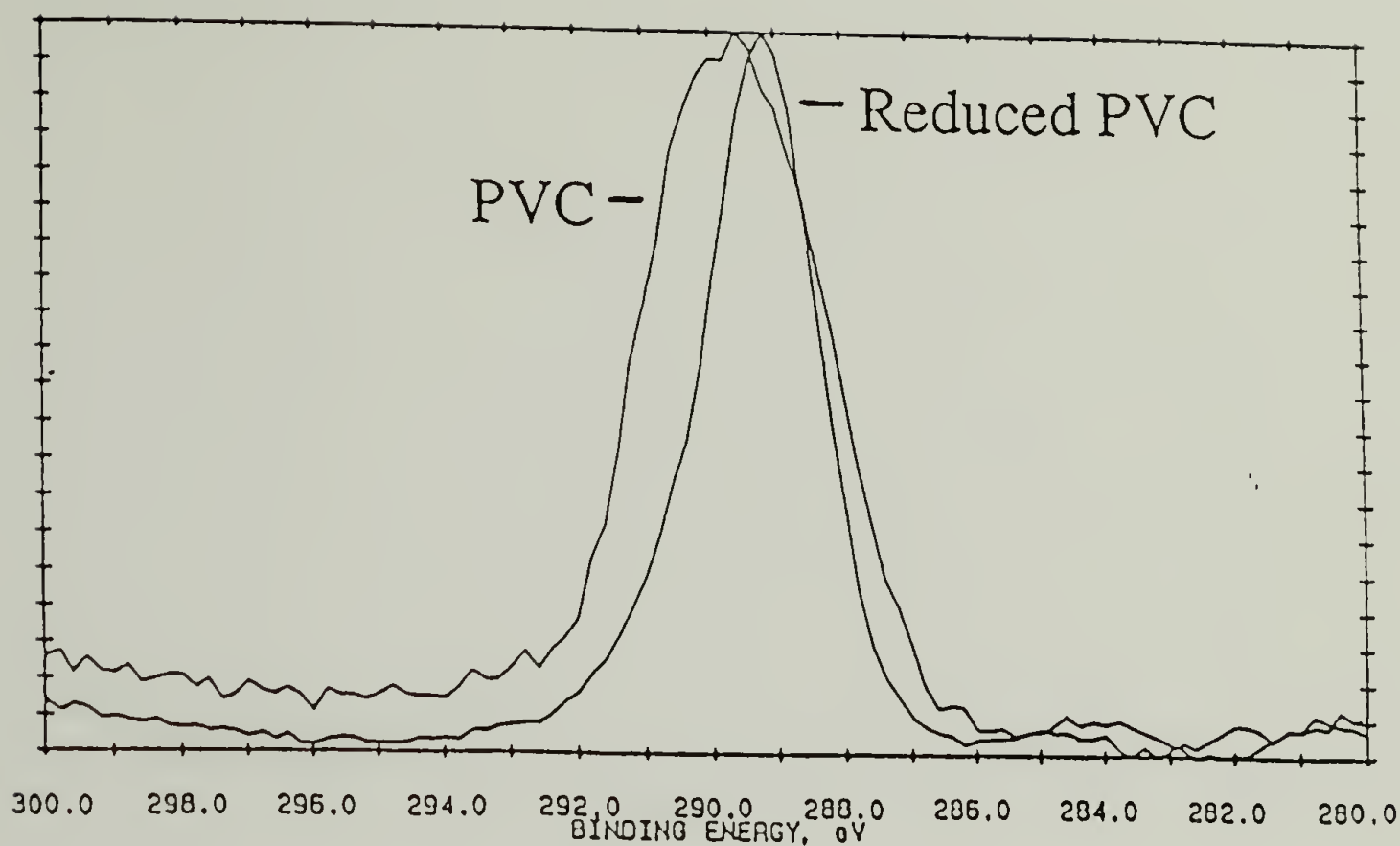


Figure 7.2 C_{1s} Region of the XPS Spectra (take off angle = 15°) of PVC and 32 hour reduced PVC

The chlorine to carbon ratio drops with time as expected. There is more oxygen in the reacted samples than in the starting material. This may be due to polymeric radicals reacting with adventitious oxygen during the reaction or with atmospheric oxygen during the reaction workup. Another source of the oxygen signal is the sample holder. Because the film samples do not lie flat on the sample holder some signal from the holder is observed. Silicon is present as surface contamination picked up from the atmosphere. Oxygen or carbon bound to this silicon will affect the amount of these atoms detected. The tin signal could be due to tributyltin hydride, tributyltin chloride or the dimer formed by combination of two tributyltin radicals

trapped in the film or the covalently bound product of the combination of a tributyltin radical and a polymer radical. The 12 carbons bound to each tin are a source of error in the percentage carbon observed. These samples were extracted with pentane in a Soxhlet extractor in order to limit the amount of tin detected.

Figure 7.3 is the ATR-IR spectra of PVC and a sample reduced for 32 hours. The only differences on reduction are changes in the carbon hydrogen stretching region (see below) and the appearance of a shoulder at 1464 cm^{-1} that may be due to methylene scissoring. The lack of change in the strong absorbances below 1500 cm^{-1} upon reduction indicates that the reduction is not substantial in the sampling depth of the ATR-IR in this region of the spectrum (4400 to 11000 Å). There is no change in the transmission IR of the film on reduction; this indicates that only the surface of the material is affected.

Figure 7.4 displays the carbon hydrogen stretching region of the ATR-IR spectra for the samples which were reacted for varying amounts of time. The methine stretching absorbance (2965 cm^{-1}) from the vinyl chloride repeat unit decreases with reaction time while absorbances due to methylene stretching increase and shift slightly (PVC 2913 asymmetric, 2855 symmetric; PE 2919 asymmetric, 2849 symmetric). These changes demonstrate that a significant reduction is occurring in the ATR-IR sampling depth for this region of the spectrum. The ratio of the heights of the methine peak and the symmetric methylene peak can be used to estimate the extent of reaction in the ATR-IR sampling depth.⁸

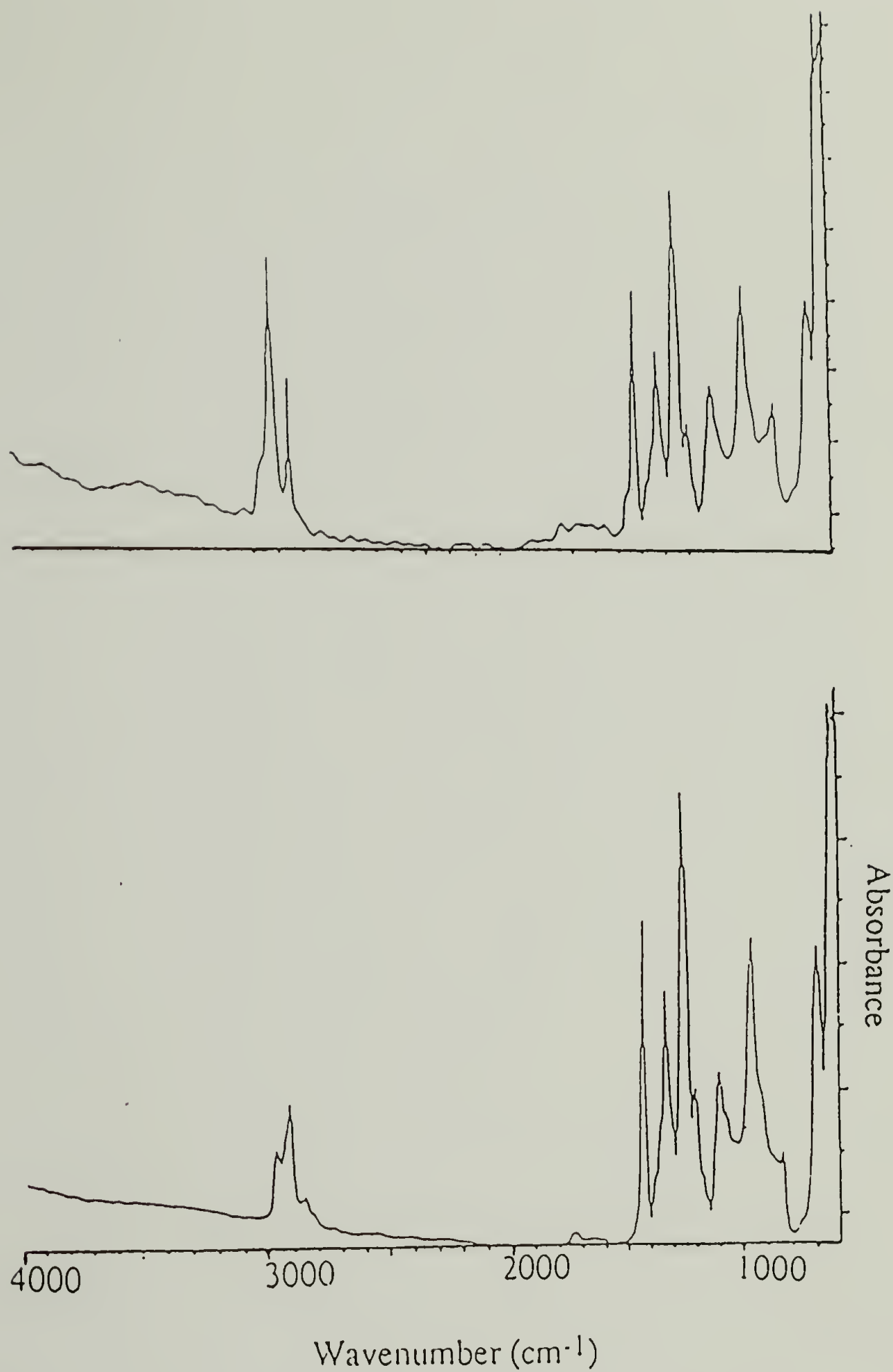


Figure: 7.3: ATR-IR spectra of 32 hour reduced PVC (upper) and PVC (lower).

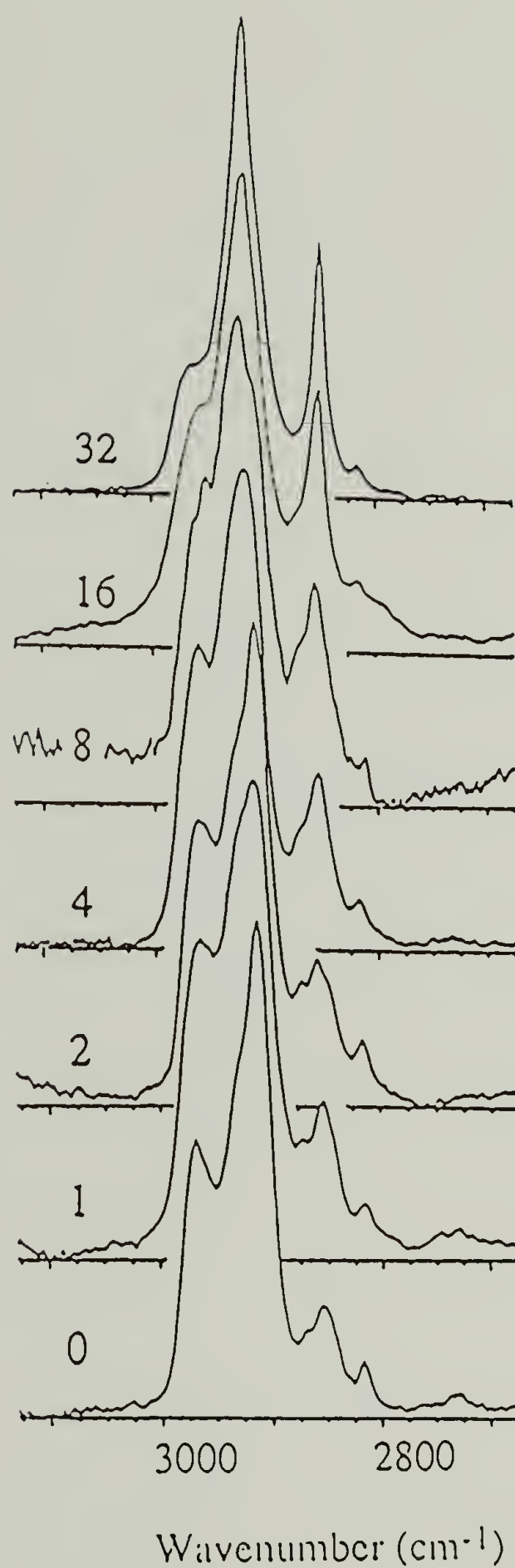


Figure: 7.4: ATR-IR spectra carbon hydrogen stretching region of samples reacted different times. (Time of reaction indicated in hours.)

If the spectra are treated as though the sample were a homogeneous mixture of PVC and PE in the ATR-IR sampling depth, (which is true only if the reaction occurs homogeneously through the ATR-IR sampling depth) the apparent PE fraction in the sampling depth can be calculated from the ratio of the methine and methylene absorbances (A_1 and A_2) using equations 7.1 and 7.2.

$$\frac{A_1}{A_2} = \left(\frac{\epsilon_1}{\epsilon_2} \right) \frac{[\text{CH}]}{[\text{CH}_2]} = \left(\frac{\epsilon_1}{\epsilon_2} \right) \frac{\text{PVC}}{[\text{PVC}] + 2[\text{PE}]} = \left(\frac{\epsilon_1}{\epsilon_2} \right) \frac{x}{x + 2(1-x)}$$

(7.1)

ϵ_1 = extinction coefficient of methine absorbance

ϵ_2 = extinction coefficient of methylene absorbance

x = apparent PVC fraction

$1-x$ = apparent PE fraction

The ratio ϵ_1 / ϵ_2 is 2.5, from the spectrum of PVC which has an equal number of methine and methylene units. Solving equation 7.1 for x gives equation 7.2.

$$x = \frac{2(A_1/A_2)}{2.5 + (A_1/A_2)} \tag{7.2}$$

This apparent PVC fraction is the fraction of PVC repeat units in a sample that has a uniform composition throughout the ATR-IR sampling depth that would have the same ATR-IR spectrum as the one that is observed. This is the lower bound for the amount of unreacted PVC in the ATR-IR

sampling depth. The sample could be less reacted than this indicates but with greater conversion near the surface and have the same spectrum.

The apparent PVC fraction in the XPS sampling depths is equal to two times the chlorine to carbon atomic composition ratios (found in Table 7.2). This assumes that the chlorines are distributed uniformly through the XPS sampling depth.

The ratio A_1/A_2 from the ATR-IR and the apparent PVC fraction in the ATR-IR, and XPS sampling depths for this series of reductions are given in table 7.3. The apparent PVC fractions are plotted versus reaction time in figure 7.5.

Table 7.3: Apparent PVC fraction data for kinetics experiments

<u>Reaction Time (h)</u>	<u>A_1/A_2</u>	<u>Apparent PVC fraction</u>		
		<u>ATR-IR</u>	<u>XPS 15°</u>	<u>XPS 75°</u>
0	2.5	1.00	0.80	0.94
1	2.1	0.91	0.50	0.68
2	2.1	0.91	0.46	0.68
4	1.7	0.81	0.40	0.60
8	1.4	0.72	0.32	0.44
16	0.9	0.53	0.18	0.32
32	0.5	0.33	0.20	0.30

After 32 hours reduction there is little difference in the apparent PVC fractions determined by XPS and ATR-IR indicating that the surface is uniformly reduced through the ATR-IR sampling depth of 2300 angstroms at 2850 cm^{-1} . In the less reacted samples there is a gradient in the apparent conversion through the ATR-IR sampling depth. The data from the two XPS angles is offset by roughly the same amount for all the samples. The 16 hour and 32 hour reduced samples from this series of experiments are not nearly as completely reduced in the XPS sampling depth as samples 60 A and 60 B. These samples were reduced 18 and 36 hours under the same reaction conditions as this last series of experiments. The XPS data for these samples corresponds to apparent PVC fractions of 0.16 or less. This difference in conversion may be due to a different batch of film being used. The amount of conversion observed may be dependent on morphology.

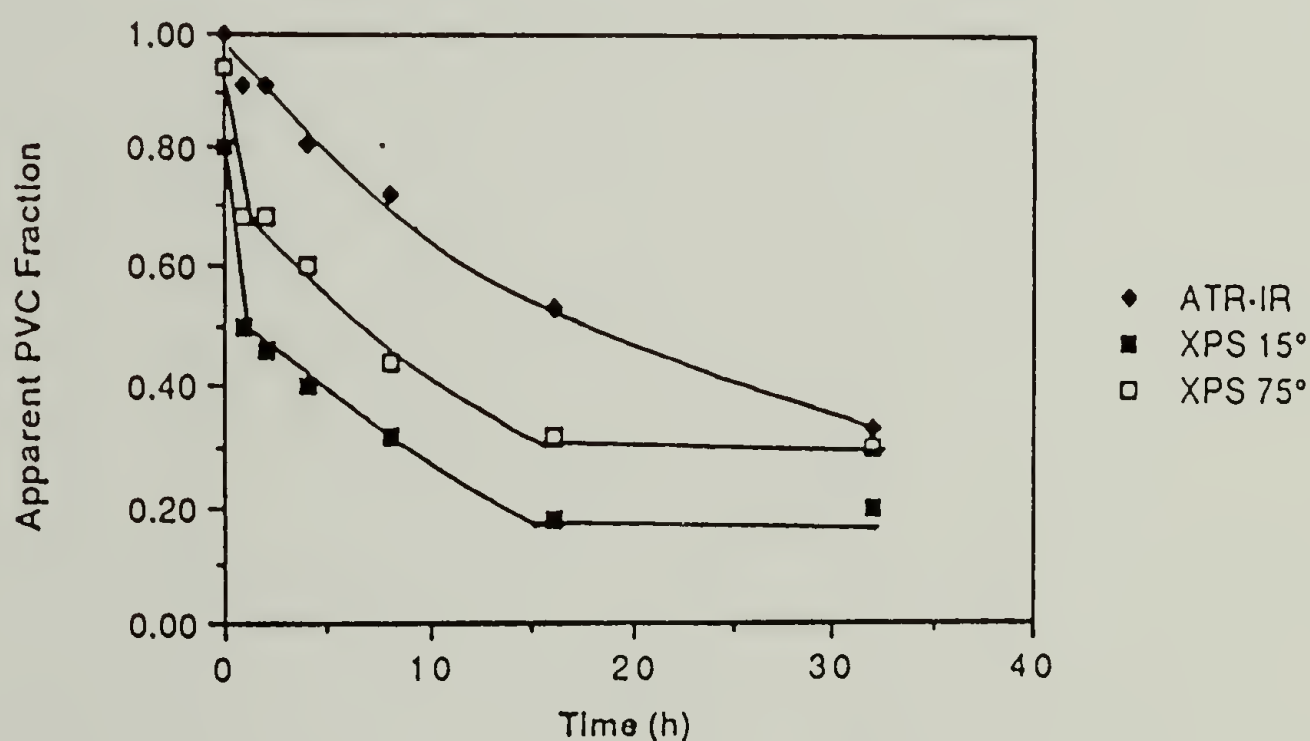


Figure 7.5: Apparent PVC fraction by ATR-IR and XPS plotted versus reaction time for reduction kinetic study.

The apparent PVC fraction in the XPS sampling depths falls very rapidly after one hour reaction, and then falls steadily until 16 hours after which it remains relatively constant. The apparent PVC fraction in the ATR-IR sampling depth falls fairly steadily.

There are both chemical and physical reasons that may be responsible for the complex kinetic results. The kinetics of the reduction of an alkyl chloride in solution is straightforward as described in the introduction. But a heterogeneous reaction involving a polymer introduces a number of complications.

The slightly polar transition state pictured in Figure 7.6 has been used to explain reactivity differences in reductions with HSnBu_3 .^{9,10} The rate of the reaction depends on the ability of the carbon to take on a partial negative charge. At the start of the reaction all the chlorinated carbons have two other chlorinated carbons two bonds away which would stabilize this transition state by inductive effects. As the reduction proceeds the chlorinated carbons become isolated so this inductive effect is lost. There may also be field effects that stabilize the transition state that diminish as the material reacts.

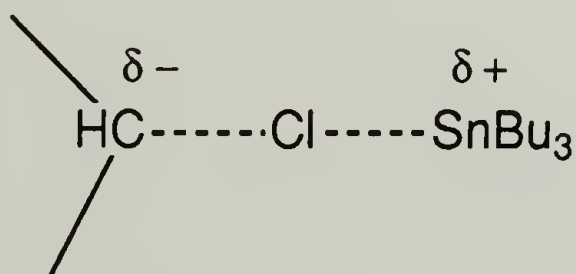


Figure 7.6: Transition State of Reduction.

The rate of diffusion of the initiator and HSnBu_3 into the film and throughout the film undoubtedly has a major effect on the course of the reaction. The concentration of the reactants in various portions of the film may also change during the course of the reduction. The reaction may proceed autocatalytically in some portions of the film if the solubility of the reactants increases with reduction. This is quite possible since with reduction the density of the film would go down and the swelling by solvent may increase. This would result in a corrosive reaction in which heavily reduced portions of the film could be surrounded by unreacted PVC. The benzoin dianion reduction of poly(tetrafluoroethylene) is an example of a corrosive reaction.¹¹

There are also physical changes that could occur during the reaction or the washing in pentane or while drying the film on the vacuum line before analysis. The surface may rearrange so that the surface observed in the analysis of the film is not the same as the surface during the reduction. The dissolving of reacted polymer chains out of a modified surface layer has been observed.^{12,13} There are some indications that this occurs during the reaction and/or the washing with pentane. A control sample for an attempted gravimetric study of the reaction lost weight. A sample of the same piece of film as used in the kinetic study was reacted 4 hours, rinsed with heptane but not extracted with pentane (82) has an apparent PVC fraction of 0.24 in the XPS 15° sampling depth and 0.54 in the 75° sampling depth. The 75° value is approximately that of the corresponding washed sample (0.60), while the 15° value is roughly half that of the washed sample (0.40). These values are somewhat suspect because of the higher amount of tin compounds in the unextracted sample, but the difference in the 15° and 75° values are larger

than can be explained by the difference in the amount of tin detected. Apparently the outer 10 Å is considerably more reduced than the outer 40 Å after 4 hours reaction but then loses more reduced material or is completely washed away in the extraction with pentane.

The dissolving of the more reduced material from the surface may be a major factor in the apparent PVC fraction determined by XPS. What appears to be a stoppage of the reaction may actually be the balancing of the reduction and the dissolving of the surface. The difference in the apparent conversion of these samples and the other samples reduced under the same reaction conditions could be explained by the different surface morphologies of the different batches of film affecting the dissolving of the reduced chains.

Reduction Control Experiments

Control experiments were run for 32 hours using the same conditions as the kinetics experiments (76) but not all the reactants. The reaction conditions and XPS results for these experiments are given in Table 7.4.

Table 7.4: Conditions and XPS Data for Reduction Control Experiments

<u>HSnBu₃</u> <u>mmoles</u>	<u>AMBN</u> <u>mmoles</u>	<u>XPS Cl/C</u> <u>15°</u>	<u>75°</u>	<u>XPS O/C</u> <u>15°</u>	<u>75°</u>
0	0	0.43	0.49	0.02	0.02
3	0	0.18	0.34	0.30	0.20
3	0	0.22	0.36	0.31	0.20
0	0.3	0.20	0.25	0.16	0.10
0	0.3	0.11	0.15	0.26	0.24

The XPS spectrum of the sample that had been placed in 60 °C heptane was no different than that of the starting film. The surface of PVC is thermally stable under the reaction conditions.

The samples treated with HSnBu_3 retained a large amount of tin compounds and show a decrease of chlorine and an increase in oxygen relative to carbon. It is more difficult to wash tin compounds out of PVC than the surface reduced PVC because pentane does not swell it. The decrease in the chlorine to carbon ratio is due to the carbons in the tin compounds lowering this ratio and partial reduction of the film initiated by adventitious free radicals. Roughly half of the oxygen increase can be attributed to tributyltin hydroxide, formed by decomposition of the tin hydride in air during the workup.¹⁴ Combination of polymeric radicals with oxygen is another source of oxygen in the film. The tin compounds may also act as Lewis acids to cause nucleophilic substitution of chlorine by water that is present during the reaction or workup.

The samples treated with AMBN alone also show a decrease in the chlorine to carbon ratio and an increase in the oxygen to carbon ratio in the XPS spectra. The ATR-IR spectrum of one of these samples, is shown in Figure 7.7. There is a definite hydroxyl absorbance and the 1500 to 1800 cm^{-1} region of the spectrum, where there is some absorbance in all the samples, has a strong broad absorbance. This implies that there is further formation of carbonyls and elimination during the control experiment. The ratio of the methylene and methine carbon hydrogen stretching absorbances is 1.9, which corresponds to an apparent PVC fraction of 0.86 by equation

7.2. This a higher apparent PVC ratio than in the sample reacted 4 hours in the presence of HSnBu_3 .

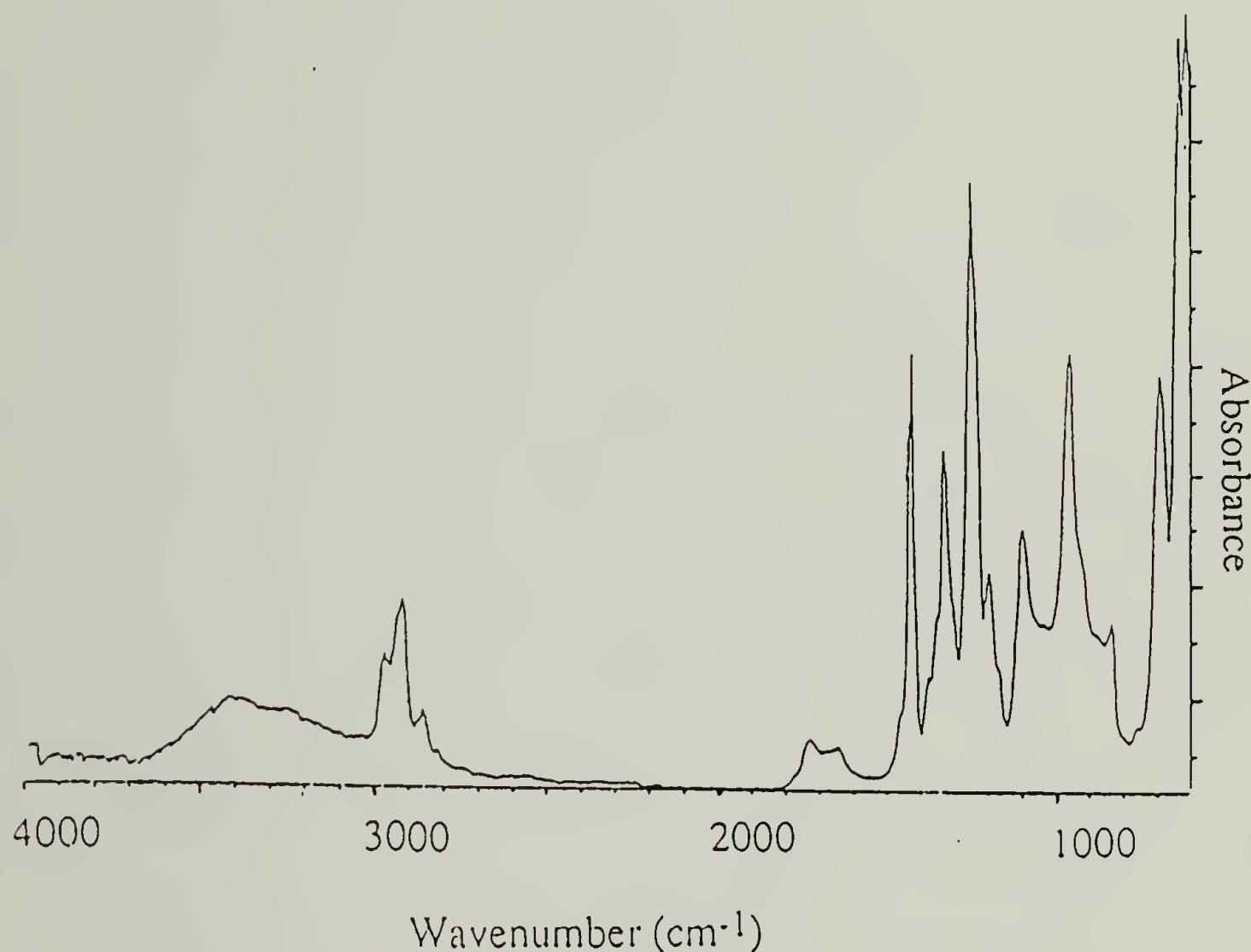


Figure 7.7: ATR-IR spectrum of AMBN control sample.

Chemistry does occur when PVC is treated with AMBN alone, but it is not the same chemistry that occurs in the presence of HSnBu_3 . Radicals derived from AMBN do abstract chlorine, particularly in the XPS sampling depth. Many of the polymeric radicals then react with oxygen either adventitious oxygen during the reaction or the oxygen in the air during the reaction

workup. Some radicals are perhaps involved in elimination. Some theories of PVC degradation involve radical reactions¹⁵ and impregnation of PVC with AIBN prior to heating has been shown to increase the rate of elimination of hydrogen chloride.¹⁶

Harsher Reduction Conditions

The XPS sampling depth was more completely reduced using harsher reaction conditions. In one experiment the film was placed in a solution of the 3.0 mmoles of HSnBu_3 for the reaction and 5 mL of heptane for 6 hours at 60 °C before the initiator and remaining solvent were added to start the 18 hour reaction. Two 16 hour reactions were run with the amount of either the HSnBu_3 or AMBN doubled compared to the kinetic experiments. The results of these experiments and of the kinetic study 16 hour reaction are given in Table 7.5.

Table 7.5: Reaction Conditions and Apparent PVC Fractions for Harsher Reductions

Reaction Time (h)	mmoles HSnBu_3	mmoles AMBN	Apparent XPS 15°	PVC Fraction XPS 75°	ATR-IR
18 ^a	3	0.3	0.06	0.14	0.44
16	6	0.3	0.14	0.20	0.48
16	3	0.6	0.04	0.04	0.28
16	3	0.3	0.18	0.32	0.53

a) After Presoaking film in HSnBu_3 (see text above).

The reaction with double the amount of AMBN used before converted the XPS and ATR-IR sampling depths much more completely. This supports the assumption that the rate of the reaction depends on the concentration of radicals and PVC repeat units. When the amount of HSnBu₃ in the film was increased, by presoaking or using more HSnBu₃, there was not a significant change in the conversion of the ATR-IR sampling depth but the XPS sampling depth was more thoroughly reduced. This is another indication of the complexity of the kinetics of the reaction.

Reductions Employing UV Initiation

Some reductions were run at 0 °C . The lower temperature was used in an attempt to limit the depth of reaction by limiting the diffusion of solvent and reactants into the film. Thermal initiation is too slow at this temperature so UV light was used to dissociate the AMBN. One reaction was done at 60 °C with UV initiation. Table 7.6 gives the reaction conditions used and the apparent PVC fraction determined by XPS.

Table 7.6: Reaction Conditions and Apparent PVC Fractions for Reductions with UV Initiation

<u>Reaction Time (h)</u>	<u>Temperature °C</u>	<u>mmoles</u>		<u>Apparent PVC Fraction</u>	
		<u>HSnBu₃</u>	<u>AMBN</u>	<u>XPS 15°</u>	<u>XPS 75°</u>
1	0	3	0.3	0.68	0.80
8	0	3	0.3	0.44	0.70
24	0	3	0.3	0.46	0.66
1	60	3	0.3	0.42	0.62

The ATR-IR spectrum of the sample reduced for 24 hours shows no reaction. This shows that the interface between the solution and the polymer is sharper at 0 °C than 60 °C. The conversion in the XPS sampling depth levels off more quickly under these conditions than at 60 °C. This is due partially to the sharpness of the interface but also to the dissociation rate of the AMBN. The half life at 0 °C with UV light is 5 hours, it is 69 hours for thermal initiation at 60 °C.¹⁷ The much shorter half life with UV initiation means the number of radicals is very high early in the reaction but falls off dramatically with time. This is certainly a factor in the leveling off of conversion in the UV initiated experiments. In the thermal reactions the radical concentration is relatively constant over the reaction times used.

The rate of radical generation is approximately the same for the UV reactions regardless of temperature. Therefore the lower extent of reduction of the film at 0 °C for the one hour reaction can be attributed to the sharpness of the polymer/solvent interface at that temperature. It is likely that a surface selective reduction of PVC with a significant conversion could be done with UV initiation at a low temperature if the initiator dissociation rate was lessened.

Other Reductions of PVC

Attempted Reduction of PVC Film with Triethylsilane

Two reductions were run using the same conditions as the first HSnBu_3 reactions but with triethylsilane as the hydride source. No reduction was evident in the XPS.

Reduction of PVC Film with Chromium (II) Chloride

Chromium (II) complexes have been used to reduce alkyl chlorides in two phase reactions.^{18,19} A reduction of PVC film was run with chromium (II) chloride and ethylenediamine in water. A surface selective reaction was expected because of a sharp interface between PVC and water. After 24 hours reaction the film was extremely wrinkled. The XPS shows that a partial reduction occurred. The apparent PVC fraction was 0.32 at 15° and 0.46 at 75°. No further reductions were tried since the reduction was less complete than the HSnBu₃ reductions and did not appear to be strongly surface selective.

Attempted Reduction of Poly(vinylidene fluoride)

The reduction of poly(vinylidene fluoride) (PVF₂) was tried using the same reactants and reactant amounts as first used for PVC. The reactions were run in refluxing THF because THF swells the polymer slightly. Even under these vigorous conditions the reduction of PVF₂ to PE did not occur. When HSnBu₃ was used the fluorine to carbon ratio in the XPS sampling depth was reduced to approximately 0.50 (from 1.0). What is probably occurring is the reduction of PVF₂ to poly(vinylfluoride) since gem-dihalides can be reduced stepwise.²⁰ The first fluorine can be removed because the slightly polar transition state is stabilized by the electron withdrawing ability of the other fluorine on the carbon. This remaining fluorine is then unreactive. Alkyl fluorides are considered unreactive with

HSnBu₃.^{21,22} There was no reaction when triethylsilane was used as the hydride source. No further reductions of PVF₂ were tried.

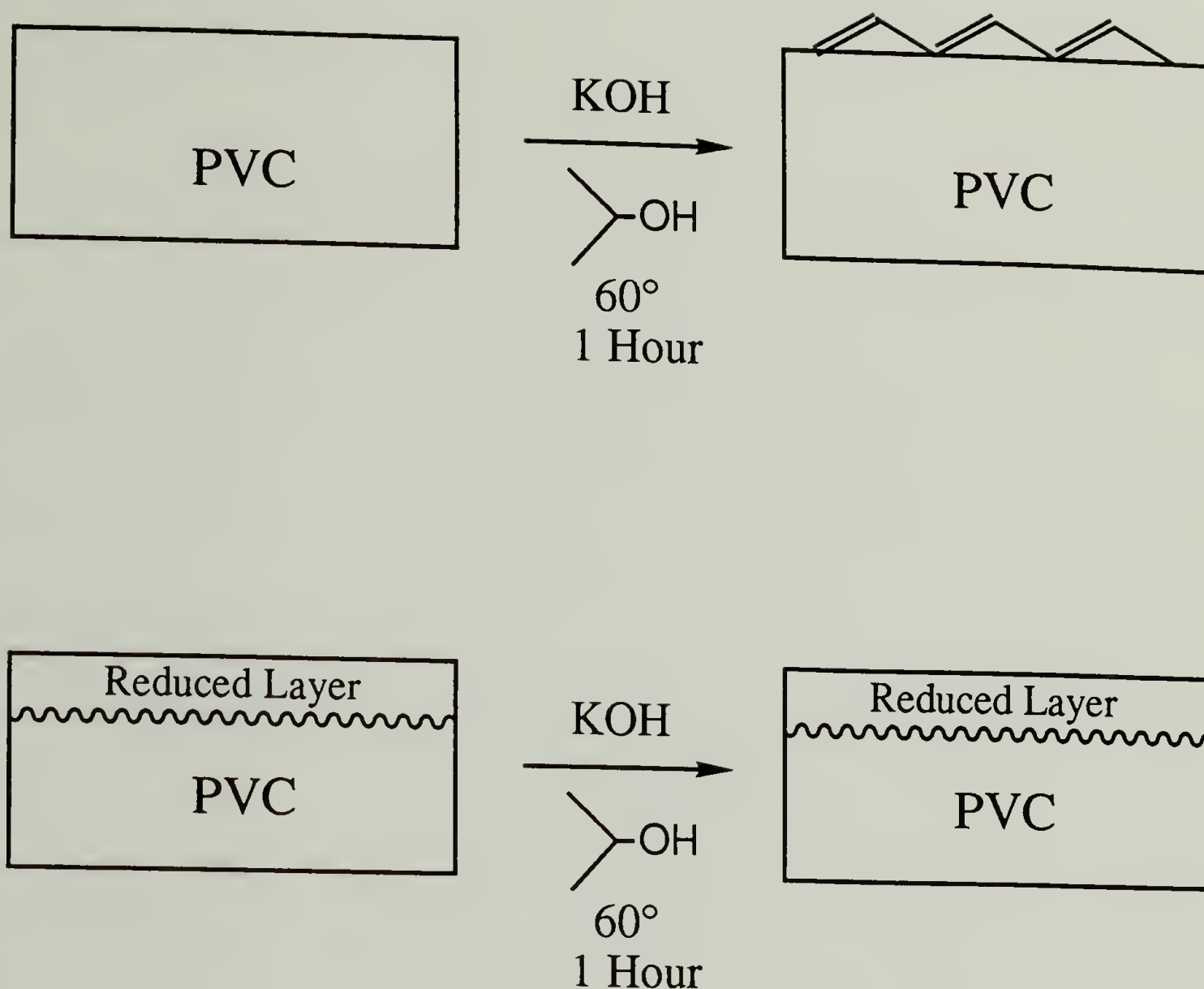
Studies of the Properties of Reduced PVC

The ability of the reduced surface of PVC to resist elimination and solvent attack were tested. The oxidation of the reduced surface was also done to determine if the reduced layer is an effective reactive handle for further PVC surface modification.

Base Treatment of PVC and Reduced PVC

PVC can be eliminated by a variety of bases to give conjugated polyenes.²³ Samples of PVC and reduced PVC (76 4 h)²⁴ were treated with potassium hydroxide in isopropanol as shown in Scheme 7.1 to determine if the reduced surface can prevent elimination.

After being exposed to the hot base solution, the PVC was stiffer and had a slight brownish tint. The XPS reveals a significant loss of chlorine and an increase in oxygen. This indicates that elimination and substitution by hydroxide ion are competing as expected. Oxidation of elimination products may also be occurring. A broad absorbance with a maximum about 420 nm. is expected in the UV-vis spectrum of eliminated PVC.²³ There is a very weak and broad absorbance from 300 to 700 nm in the spectrum of the base treated PVC. Elimination is not very extensive and appears to be limited to the surface.



Scheme 7.1: Base treatment of PVC and reduced PVC.

A different batch of PVC film (from that used for the kinetic and later studies) was used in these experiments. Table 7.7 gives the XPS chlorine to carbon and oxygen to carbon ratios for the starting materials and the base treated samples.

Table 7.7 XPS Data for Base Treatment of PVC and Reduced PVC

<u>Sample</u>	XPS Cl/C		XPS O/C	
	<u>15°</u>	<u>75°</u>	<u>15°</u>	<u>75°</u>
new PVC	0.47	0.47	0.03	0.01
Base treated new PVC	0.23	0.30	0.10	0.06
Reduced PVC (76) 4 h	0.27	0.31	0.16	0.11
Base treated Reduced PVC	0.27	0.30	0.15	0.11

There is no change in the flexibility or appearance of the reduced PVC sample after base treatment. There is also no change in the XPS or UV-vis spectra. The reduced surface layer protects the underlying PVC from elimination and is unaffected by the base treatment. The reduced layer is not permeable to the hot alcoholic base. The lack of elimination in the reduced layer can also be attributed to isolation of the chlorinated units. The elimination is not autocatalytic as it is in PVC where elimination forms allylic structures which are more easily reacted.

Solvent Resistance of Reduced PVC

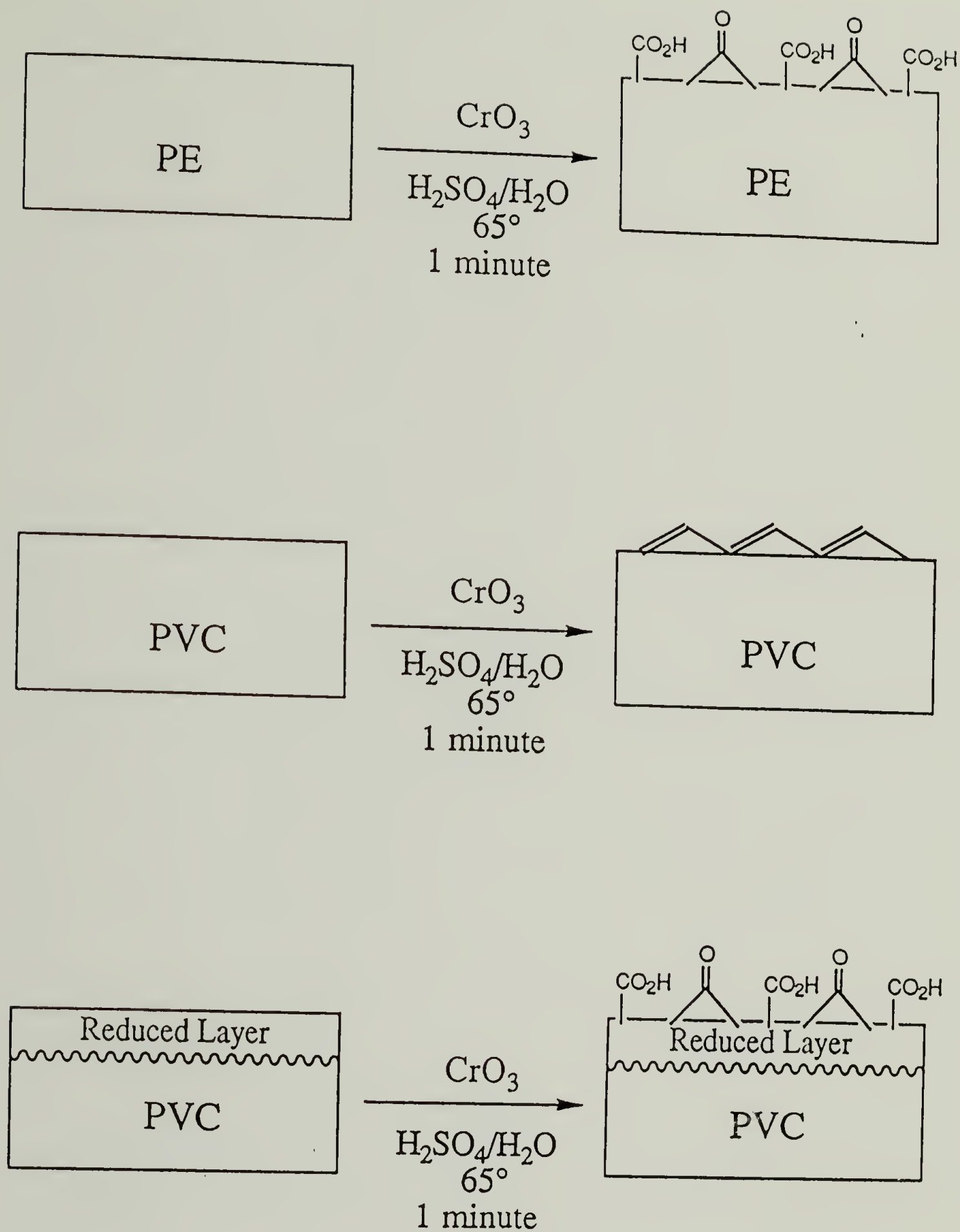
Samples of PVC, reduced PVC (76 18 h) and reduced PVC (94 B 16 h) were placed in THF and dichloromethane to determine if reducing the surface imparts any of the solvent resistance of PE to PVC. This second reduced PVC sample (94 B 16 h) was reduced with twice the amount of AMBN used in the kinetics experiments. The chlorine to carbon ratios were

0.02 in the XPS for a similarly reduced sample. In THF all the samples dissolved almost immediately. After 10 minutes the PVC film was totally dissolved but small particles were floating in the other solutions. These may have been portions of reduced material that would not dissolve due to crosslinking which is an expected side reaction in the reduction. All the samples in dichloromethane were greatly swollen after 10 minutes. None had enough integrity to be picked up with forceps without tearing.

The reduced surface layer is at least permeable to these solvents if not soluble. This is due to the presence of polar groups in the surface and a lack of crystallinity, which is a major factor in the solvent resistance of PE.

Oxidation of Reduced PVC, PVC and PE

The surface of PE can be oxidized with chromium (VI) oxide in aqueous sulfuric acid to give a mixture of carboxylic acids and ketones.²⁵ This oxidation was run on samples of reduced PVC (76 4 h), PVC and PE as shown in Scheme 7.2. The contact angle (advancing/receding) and XPS results from these experiments are given in Table 7.8.



Scheme 7.2: Oxidation of PE, PVC and reduced PVC.

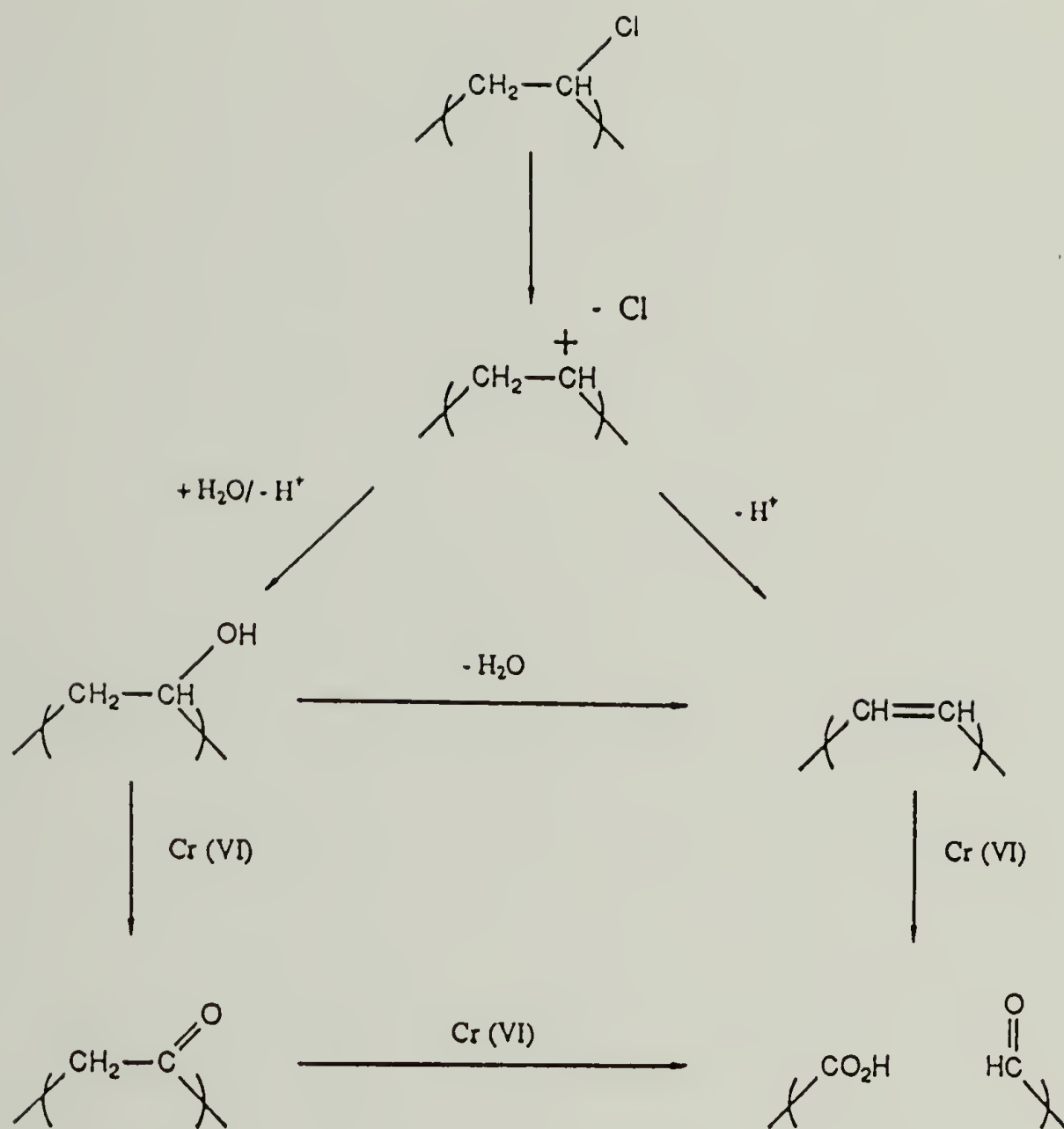
Table 7.8: Contact Angle and XPS Data for Oxidations

<u>Sample</u>	Contact Angles		XPS Cl/C		XPS O/C	
	<u>Before</u>	<u>After</u>	<u>15°</u>	<u>75°</u>	<u>15°</u>	<u>75°</u>
PE	101/75	59/(<15)	--	--	0.17	0.15
PVC	87/53	82/42	0.07	0.22	0.03	0.04
Reduced PVC	85/54	80/42	0.12	0.21	0.13	0.14

The oxidation of PE gave the expected oxidized surface. The contact angles decreased significantly and the XPS spectra indicate the presence of oxygen (the starting material oxygen to carbon ratios are 0.02). A broad absorbance from 1500 - 1800 cm^{-1} was detected in the ATR-IR.

The attempted oxidation of PVC resulted in an eliminated surface. The XPS spectra show a loss of chlorine and of oxygen with reaction. There is no visible change in the ATR-IR spectrum; there is a broad absorbance from 1500 - 1800 cm^{-1} in both the starting material and reacted sample spectra. There is no apparent change in the UV-vis spectra either, an n to π^* carbonyl transition at 276 nm is seen in spectra of both samples. These results are explained by Scheme 7.3.

The polar solvent favors carbocation formation which can lead to elimination or substitution by hydroxide to give alcohol groups. Because elimination leads to allylic structures which are more easily ionized, long stretches of conjugated double bonds can be formed. Under these conditions



Scheme 7.3: Oxidation of PVC surface.

chromic acid cleaves double bonds.²⁶ This results in chain cleavage. Alcohols are rapidly oxidized to ketones which are further oxidized to carboxylic acids resulting in chain cleavage. These oxidations can continue to the formation of carbon dioxide.

The oxidized chain fragments resulting from these processes are lost either during the reaction or the washing procedure. This leaves the eliminated surface seen in the XPS. Evidently the elimination is faster, or perhaps less surface selective, than the subsequent oxidations.

The reduced PVC sample is oxidized by chromic acid. The oxygen to carbon ratios are almost as high as seen in the PE oxidation. This is not a straightforward indication of the oxidation occurring since some of the reduced samples had oxygen to carbon ratios as high as 0.17. The clearest evidence of oxidation is in the UV-vis spectra. The n to π^* carbonyl transition at 276 nm is clearly seen in the oxidized sample spectrum; there is only a slight shoulder there in the reduced sample. There is no change in the ATR-IR spectra; there are broad absorbances from 1500 to 1800 cm^{-1} in both the reduced sample and the reduced sample which had been oxidized with chromic acid.

There is only a very slight drop in the contact angle with the oxidation of the reduced PVC. This is probably due to rearrangement of the surface during drying to lower the surface energy. The contact angle of oxidized PE has been shown to increase with heating, which increases the mobility of the surface chains. The polar functional groups are turned away from the surface, lowering the surface energy.²⁷ Evidently, the chains in the

oxidized reduced layer on PVC are mobile enough to undergo this rearrangement without heating.

Oxidation of PE by this method results in loss of material due to the chain cleavage that results from carboxylic acid formation. An oxygen to carbon ratio of 0.15 in the XPS may be the highest ratio possible for a retainable surface. It is not known how much material is lost in this oxidation of the reduced surface, but apparently the underlying PVC is not exposed since oxidation of the PVC gave a different surface (see above).

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CHAPTER VIII

CONCLUSIONS AND SUGGESTIONS

The surface of PVC can be reduced by HSnBu_3 and a radical initiator in heptane at 60°C . The extent of reduction can be controlled by the concentration of reagents and the reaction time. It is not clear if the reduction occurs randomly or if there is some segregation of more and less reduced portions of the surface. The reduction occurs relatively uniformly throughout the sampling depth of ATR-IR in the carbon hydrogen stretch region of the spectrum, which is approximately 2300 \AA . The lack of change in the portion of the ATR-IR spectrum which samples more deeply and the transmission IR of the film with reduction indicate that the reduction is limited to a depth of thousands of angstroms. The reduction occurs relatively homogeneously through this depth because there is a diffuse interface between the polymer and the reaction solution. Experiments done at 0°C using UV light to dissociate the initiator indicate that the reduction can be done with greater surface selectivity at a lower temperature.

The chemical resistance of PVC is enhanced by surface reduction. An only partially reduced surface prevents elimination of the underlying PVC and of the vinyl chloride units in the reduced layer by hot alcoholic base.

Further modification of the reduced layer while the underlying PVC is protected from the reactants is possible. Oxidation of the reduced surface by chromium (VI) oxide in aqueous sulfuric acid has been done. Roughly the same degree of oxidation is observed as in the oxidation of the surface of PE

by XPS, but the surface is not wetted by water as well as the oxidized PE surface is. This is due to the mobility of the chains in the oxidized reduced surface allowing rearrangement of the surface to lower the surface energy.

No increase in the solvent resistance of PVC was observed. Even a nearly completely reduced surface is permeable to THF and dichloromethane. PVC is still rapidly dissolved by THF and quickly swollen by dichloromethane.

There are some aspects of this research that could be further investigated. Continuing the experiments done at lower temperature to limit the depth of reduction could be fruitful. Conditions may be found in which the XPS sampling depth is thoroughly reduced but the ATR-IR sampling depth is only slightly reduced.

Because of the commercial importance of PVC, surface modification of this polymer could have many practical applications. Determining the extent of the chemical resistance imparted to PVC by the reduced layer by treating PVC and reduced PVC to various environments is one possible practically minded study. The usefulness of this reduction on the surface of plasticized PVC could also be explored. Before studying surface modification for practical purposes, the nature of the surface of commercial PVC should be determined. One commercial sample looked at for use as a starting material in this research was not used because the XPS sampling depth contained almost no chlorine. A large amount of oxygen was found instead. If this is typical of commercial samples the surface modification should take this into account. One approach to take would be to reduce the various

oxygen functionalities to hydroxyl groups. Numerous subsequent modifications are then possible. Using water or alcohol as the solvent for these reactions should limit unwanted reactions in the PVC below the modified layer.

If commercial samples are found with significant chlorine at the surface elimination could be used as an alternate initial modification. The base treatment experiment done in this work indicates that a surface selective elimination is possible. A variety of further modifications of eliminated surfaces have been done.^{1,2}

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